

Focusing of upward fluid migration due to mineral grain size variation

I. WADA^{1*}, M.D. BEHN¹, E.M. PARMENTIER² AND A.M. SHAW¹

¹Woods Hole Oceanographic Institution, Woods Hole, MA, 102543, USA (*correspondence: iwada@whoi.edu, mbehn@whoi.edu, ashaw@whoi.edu)

²Brown University, Providence, RI, 02912, USA (em_parmentier@brown.edu)

In this study, we use numerical models to quantify the effect of mineral grain size on the migration path of aqueous fluids in the mantle wedge. Grain size affects grain-scale permeability of the mantle and fluid migration, which is an important factor that controls the location of hydrous melting in the wedge. By coupling a subduction zone thermal model with a laboratory-derived grain size evolution model, we predict that the spatial variation in grain size in the flowing part of the mantle wedge is large; grain size increases from 10–100 μm in the shallowest part of the region beneath the forearc to a few cm in the hottest part of the mantle beneath the arc. Based on our preliminary modeling results, we find that aqueous fluids that migrate into the shallow fine-grain-size region become trapped in the down-going mantle due to low permeability and dragged downdip until permeability becomes high enough for the fluids to migrate upward. Thus, the grain size distribution can play an important role in controlling the location of hydrous melting by focusing the upward fluid migration. We plan to further develop our model by incorporating the effect of dynamic pressure gradients and accounting for the variation in fluid influx at the wedge base. Our modelling results will then be compared with the locations and degrees of hydrous melting inferred from geophysical and geochemical data for various arcs worldwide.

Metal-silicate partitioning of Mo and W at high pressures and temperatures: Applications to core formation on Earth and Mars

J. WADE¹ AND B. J. WOOD²

¹Dept of Earth Sciences, University of Oxford, South Parks Rd, Oxford, OX1 3AN. (*Jon.Wade@earth.ox.ac.uk)

²Dept of Earth Sciences, University of Oxford, South Parks Rd, Oxford, OX1 3AN. (Bernie.Wood@earth.ox.ac.uk)

In order to place better constraints on the conditions of core formation on Earth and other terrestrial planetary bodies we have performed experiments to determine the partitioning of Mo and W between liquid Fe-rich metal and liquid silicate at pressures of 1.5–24 GPa and temperatures of 1803–2723 K. Experiments performed in MgO capsules at 1.5 GPa/1923 K indicate that Mo is in the +4 oxidation state in the silicate at oxygen fugacities >2 log units below the IW (Fe-FeO) buffer. In contrast W^{6+} is the dominant tungsten oxidation state in the silicate at 1.9–3.2 log units below the IW buffer

Mo metal/silicate partitioning is strongly dependent on pressure and silicate melt composition, but temperature has no detectable effect. In contrast, we find that W partitioning is strongly dependent on silicate melt composition and temperature, but the role of pressure is minor.

Applying these and earlier results to the Earth and Mars indicates that the Mo content of the terrestrial mantle is consistent with core segregation at pressures of 20–40 GPa, in agreement with earlier work on Ni and Co partitioning. The Mo content of silicate Mars is about half that of silicate Earth and is consistent with much lower pressures of core formation (~ 11 GPa) on the smaller planet. In contrast to these results, the W content of silicate Mars (~ 50 ppb) is insensitive to conditions of core formation while that of silicate Earth (~ 12 ppb) is inconsistent with a single stage of core formation at any pressure. Since metal-silicate partitioning of W is strongly influenced by light element (S, Si, O) contents of the metal, we consider it likely that the “light” element in the core is largely responsible for the inconsistency in core-mantle partitioning of this element.

REE and stable isotope constraints on formation of metamorphic quartz veins: A case study from the Rhenish Massif (Germany)

T. WAGNER^{1*}, A.J. BOYCE², J. ERZINGER³

¹Geochemistry and Petrology, ETH Zurich, Switzerland
(*correspondence: thomas.wagner@erdw.ethz.ch)

²Scottish Universities Environmental Research Center,
Glasgow, UK

³GeoForschungsZentrum, Potsdam, Germany

We have investigated fluid-rock reactions during formation of metamorphic quartz veins in the fold-and-thrust belt of the Rhenish Massif (Germany). The veins record two assemblages that were formed in an evolving fluid-rock system, which are (1) massive vein filling (elongate-blocky quartz, chlorite, apatite, albite) and (2) open space filling (euhedral quartz crystals, carbonates, sulfides). We performed a detailed REE and stable isotope study of vein minerals, altered wall rocks and precursor host rock metapelites. The REE and oxygen isotope data of vein quartz and altered wall rocks, combined with mass balance analysis, support that local mobilization of material was dominant during formation of the early massive vein assemblage, but that contributions from advecting fluids were also important. The strong shift in K/Na ratios in altered wall rocks and model fluid temperatures that are higher (350-400 °C) than estimates for the host rocks point to substantial fluid advection. Formation of the veins can be explained by a crack-flow-seal model, with multiple repetition of vein opening, fluid advection and vein sealing events. Each cycle was initiated with vein opening, resulting in enhanced permeability and considerable fluid advection and hydrothermal alteration of wall rocks. Conditions during each cycle evolved towards a decrease in fluid advection, coupled with substantial diffusional leaching of silica and precipitation in the veins. The formation of the later open space filling assemblage records transition from an advection- to a diffusion-dominated regime. This is supported by vein mineral and fluid inclusion textures recording conditions of undisturbed mineral growth, fluid inclusion data that point to a thermally equilibrated state (150-200 °C), and stable isotope data that demonstrate a local source for the vein minerals.

From anoxia to oxic conditions in the aftermath of oceanic anoxic event 2 (Late Cretaceous)

M. WAGREICH

University of Vienna, Center for Earth Sciences, Althanstrasse
14, 1090 Vienna, Austria,
(michael.wagreich@univie.ac.at)

Sections in the Ultrahelvetetic units of the Eastern Alps (Austria) record oceanic anoxic event 2 (OAE 2) at the distal European continental margin of the western Tethys [1, 2]. Upper Cenomanian marl-limestone cycles are overlain by black, organic-rich (5% TOC, kerogen type II) layers, followed by Lower/Middle Turonian light grey to reddish marly limestones. Carbon isotope values display the well documented positive shift. The appearance of red-colored carbonates (CORB - Cretaceous Oceanic Red Beds) indicates a total time span of about 1.5 my for oxic bottom waters to become dominant. Orbital cycles of 400 kyr and 100 kyr frequencies are identified. Benthic foraminifera associations indicate repeated phases of enhanced organic matter flux and less aerated bottom waters during the transitional interval [3]. Sedimentation of red layers was controlled by periods of well oxygenated bottom waters, reduced sedimentation rates and degradation of organic matter in the underlying sediments. Principal component analysis of carbonate chemical data showed that the development of red coloured pelagic sediments is accompanied by a shift towards highly oligotrophic conditions in the surface ocean as well as a decrease in hydrothermal activity [4].

Higher up in the section, red limestone-marl cycles are present. Enhanced input of nutrient- like trace metals during episodes of higher volcanic activity is inferred, terrigenous elements (Al, Li, Rb, Be) decrease upwards. Iron speciation data for marl and limestone layers attest to oxic early diagenesis during marl deposition compared to limestone episodes. Low sediment accumulation rates (2.5 mm/ka) are reconstructed. Geochemistry and stable isotope data indicate a highly oligotrophic environment with efficient recycling of organic matter and nutrients in the upper water column. Nutrient availability varied and resulted in periods of higher primary production. Iron oxides cause the red color in CORBs. The main fraction of iron in CORB sediments is fixed in silicate lattices and immobile.

[1] Neuhuber *et al.* (2007) *PPP* **251**, 222-238. [2] Wagreich *et al.* (2008) *Cret. Res.* **29**, 965-975. [3] Wendler *et al.* (2009) *SEPM Spec. Publ.* **91**, 209-221. Neuhuber & Wagreich (2011) *Sediment. Geol.* **235**, 72-78.

Uniform Os isotopic composition in early-formed planetesimals

R.J. WALKER

Dept. of Geology, University of Maryland, College Park, MD 20742, USA (rjwalker@umd.edu)

The isotopic compositions of some elements, such as W, Ru and Mo, vary among early-formed planetesimals. These variations likely reflect incorporation of different proportions of matter from diverse nucleosynthetic sources, and could be the result of accretion from a poorly mixed nebula, accretionary processes that favored isotopically distinct components, and/or late injection of isotopically diverse matter to the nascent Solar System. Constraints placed on the level of isotopic variability among early-formed planetesimals for additional elements with different chemical characteristics and nucleosynthetic origins may help to elucidate the dominant processes. Osmium is an important element to add to this list as it is one of the most refractory elements, yet is volatile in oxidized forms. Further, separate *s*- and *r*-process enriched components have been shown to exist in low metamorphic grade chondrites. Although, bulk chondrites show no measurable Os isotopic anomalies, early formed iron meteorites are also fertile hunting grounds. Isotopic anomalies for a number of elements are present in irons. For Os, certain irons from groups IAB, IIAB, IIIAB, IVA and IVB also show well resolved anomalies in $\epsilon^{190}\text{Os}$, $\epsilon^{189}\text{Os}$ and $\epsilon^{186}\text{Os}$. These anomalies, however, differ from anomalies observed in components extracted from chondrites, and are attributed to variable exposure of the irons to cosmic rays. Of note, each of the major iron groups contains at least one member with no resolved Os isotopic anomalies. We conclude that Os was homogeneously distributed on the scale of planetesimal accretion within the current level of resolution ($\sim \pm 5$ ppm for $\epsilon^{190}\text{Os}$). This contrasts with heterogeneity in other siderophile elements, such as W, Ru and Mo. Given that W and Os are similarly refractory, this may indicate that anomalies present for other elements in irons resulted from selective incorporation of mineralogic hosts, rather than large scale nebular heterogeneity.

Nuclear forensic analysis of trinitite at high spatial resolution

C.M. WALLACE*, A. SIMONETTI, AND P.C. BURNS

Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, IN 46556, USA (*correspondence: cwallac1@nd.edu)

The world's first atomic bomb, the Trinity "gadget" was detonated on July 16, 1945. The explosion resulted in partial melting of the surrounding desert sand, which subsequently fused into blast-melt glass known as trinitite. Recent investigations of trinitite have been conducted using a variety of analytical techniques, including EMPA, SEM, SIMS, XRF, and light microscopy [1,2]. This study includes preliminary results from optical microscopy, SEM, and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Optical microscopy was used in order to "map" thin sections of trinitite and distinguish remnant crystalline grains and inclusions from the surrounding glassy matrix. SEM was conducted on samples prior to thin sectioning in order to image surface morphology. Quantitative spot analyses were subsequently performed via LA-ICP-MS in order to determine the trace element/radionuclide compositions of different phases. The LA-ICP-MS results to date confirm the "supergrade" nature of the plutonium and the presence of a natural uranium tamper in the Trinity device. In addition, plutonium-rich areas are characterized by higher REE abundances and correlate negatively with the fission product ^{137}Cs . Trace element abundances are extremely variable within individual crystal grains (hundreds of microns). The relationship between Pb isotope ratios and Pu abundances is somewhat ambiguous, i.e. they do not correlate positively in all of the trinitite phases. Future work will include isotopic analysis using a LA-multi-collector-ICP-MS instrument configuration.

[1] Fahey *et al.* (2010) *PNAS* **107**, 20207-20212. [2] Eby *et al.* (2010) *Geology Today* **26**, 180-185.

Incorporation of ^{90}Sr into alkaline altered sediments

S.H. WALLACE¹, S. SHAW¹, K. MORRIS², J.S. SMALL³
AND I.T. BURKE^{1*}

¹School of Earth and Environment, University of Leeds,
Leeds, UK (*correspondence: I.T.Burke@leeds.ac.uk)

²School of Earth, Atmospheric and Environmental Science,
University of Manchester, Manchester, UK

³National Nuclear Laboratory, Risley, Warrington, UK

The use of cementitious materials is ubiquitous at nuclear facilities and in radioactive waste packaging. Water in contact with fresh cement produces a highly alkaline solution dominated by K and Na hydroxides causing localised areas of high pH groundwater at the concrete/soil interface. Silicate minerals within sediments and clay barrier materials are known to alter to zeolite and feldspathoid phases under these conditions. The effect of alkaline pore fluid induced weathering reactions on the mobility of radionuclides is not well understood, especially with respect to potentially highly soluble fission products such as ^{90}Sr (as Sr^{2+}).

Here we used 20 g.L⁻¹ batch experiments containing sediments representative of the UK Sellafield nuclear site in a pH 13.5 high ionic strength cement-based leachate to investigate Sr^{2+} sorption as a function of time. Experiments initially contained 20 ppm Sr^{2+} (spiked with 30 Bq.mL⁻¹ ^{90}Sr tracer) and were sampled from 2 days up to one year (one experiment was aged for one year at 70°C). Change in Sr speciation within sediments was determined using X-ray absorption spectroscopy and sequential extraction techniques.

At 2 days 72.6±8.6% ^{90}Sr was removed from solution, which rose to 93.8±3.3% at 10 days but then decreased to 81.8% after a year. In the 70°C aged sample sorption increased to 98.0±2.5%. This suggests that initial alteration enhances Sr sorption but further recrystallisation releases some sorbed Sr. Sequential extractions show that the majority (65-75%) of ^{90}Sr remains in the MgCl_2 exchangeable fraction even after one year. In the 70°C aged sample, 25.2±5.8% ^{90}Sr was found to be residual. EXAFS analysis revealed two Sr-O-Si(Al) bond distances at 3.69 and 3.84 Å in a 10 day sample and at 3.57 and 3.83 Å in a one year sample, consistent with weak Sr sorption to aluminosilicate phases. EXAFS spectra from a 70°C aged sample contain evidence for a single Sr-O-Si(Al) bond distance at 3.45 Å consistent with Sr incorporation in a neoformed feldspathoid phase such as cancrinite. These results indicate that alkaline altered sediments could be a sink for ^{90}Sr in the environment, however even after alteration ^{90}Sr may remain exchangeable with other ions in solution.

Reactive transport modelling to quantify arsenic mobilization and capture during aquifer storage and recovery of potable water

ILKA WALLIS^{1,2}, HENNING PROMMER^{2,3},
THOMAS PICHLER⁴, VINCENT POST¹
AND CRAIG SIMMONS¹

¹Flinders University / NCGRT, South Australia

²CSIRO Land & Water, Australia

³University of Western Australia

⁴University of Bremen, Germany

Aquifer storage and recovery (ASR) is an artificial recharge technique which is increasingly used as a water management tool to augment depleted groundwater resources. ASR is a critical component of the long-term water supply plan in various regions, including Florida and Australia. However, under particular, site-specific conditions the viability of ASR as a safe and cost-effective water resource may be impacted by elevated arsenic concentrations that are detected during recovery of the injectant. This study describes a conceptual and process-based reactive transport model of the coupled physical and geochemical mechanisms controlling the fate of arsenic during ASR. The conceptual/numerical model assumes that (i) arsenic is initially released following pyrite oxidation triggered by the injection of oxygenated water (ii) then largely complexed to neo-formed hydrous ferric oxides before (iii) being released again during recovery as a result of both dissolution of hydrous ferric oxides and displacement from sorption sites by competing anions. Multi-cycle hydrochemical data from an affected site where oxidic, potable water was injected into a reducing pyrite-containing storage zone were used to evaluate the model. For this site a detailed assessment of the partitioning of arsenic among mineral phases, surface complexes and aqueous phases during injection, storage and recovery is given, together with an evaluation of temporal and areal extent of arsenic mobilization and capture.

Physico-chemical and mineralogical transformations of fluid fine tailings (FFT) associated with the Alberta oil sands end pit lakes

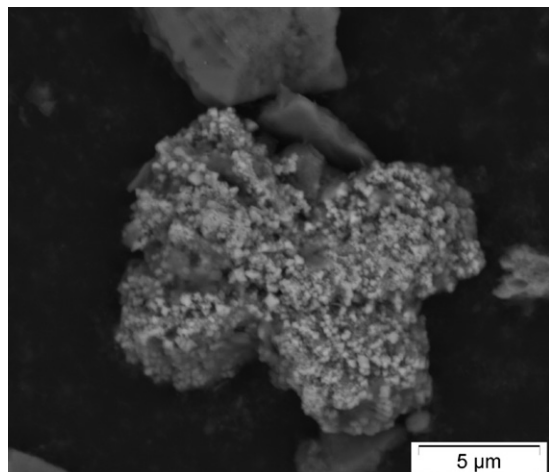
G.E. WALSH^{*}, M. CHEN, E. CHI FRU AND C.G. WEISNER

GLIER, University of Windsor, Windsor, Ontario, Canada
(gwalshe@uwindsor.ca; chen112h@uwindsor.ca; echifru@uwindsor.ca; weisener@uwindsor.ca)

Traditional methods used to extract bitumen involve caustic hot water digestion and flotation, which produce a fine tailing slurry consisting of water, sand, fines residual bitumen and naphtha products [1]. The current practice is to store the tailings in large settling basin to allow the solids to settle out by gravity forming a denser unconsolidated mass termed fluid fine tailings (FFT). To date little information exists on the biogeochemical nature of the newly processed FFT product prior to deposition and the evolution of the material during long term storage in settling basins.

Discussion and Results

During the development of the material significant changes in pore water geochemistry and the associated *in situ* development of AVS are observed, giving rise to the deposition of proto-iron sulfides (Fig. 1). The chemical evolution of porewater and head water was tracked over a period of 6 months. The significance of changes observed will be discussed in terms of the biotic versus physico-chemical processes.



[1] Chalaturnyk et al. (2002) *Petroleum Science and Technology*, **20**, 1025-1046

Highly oxidized species in TSR-altered oils

C.C. WALTERS^{1*}, K. QIAN¹, C. WU¹, A.S. MENNITO¹, AND Z. WEI²

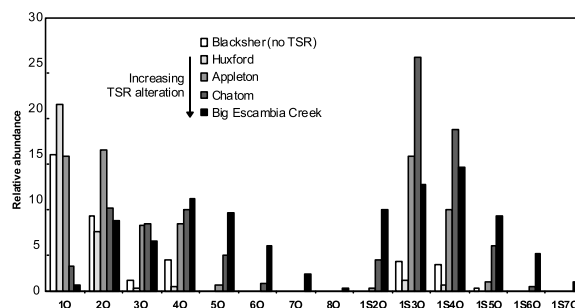
¹Exxonmobil Research & Engineering, 1544 Route 22 East, Annandale, NJ 08801

(*correspondence: clifford.c.walters@exxonmobil.com)

²Exxonmobil Exploration Co., 233 Benmar, Houston TX 77060

Thermochemical sulfate reduction (TSR) involves a complex series of redox reaction that occur typically in hot (>120°C) carbonate reservoirs whereby petroleum is oxidized by sulfate forming H₂S, CO₂, and a sulfur-rich insoluble solid. It is well documented that oils altered by TSR are enriched in organosulfur species, primarily thiophenic, that form as a consequence of the primary sulfate reduction reaction and back reactions with produced H₂S or other low valence state sulfur species. In contrast, enrichment in partially oxidized hydrocarbons has not been reported in TSR-altered oils, which typically have low Total Acid Numbers (TAN < 0.2).

Oils from onshore Alabama were analyzed by negative ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (NESI-FTICR-MS). The suite includes oils at varying extent of TSR-alteration as well as oils of equivalent thermal maturity that have not subjected to TSR-alteration. Although the total amount of oxygen species is low in all samples, their relative distribution varies in a systematic manner. With increasing extent of TSR, 1O and 2O species, which dominate unaltered oils, are replaced with species containing additional oxygen atoms. Hydrocarbons and organosulfur species with 5 to 8 oxygen atoms are detected only in the most TSR-altered oils.



The distributions of the Ox and SOx species appears to accurately reflect the extent of TSR and are particularly useful in deciphering the geohistory of reservoirs where H₂S and light hydrocarbons have migrated in from off-structure.

The evolution dynamics of chemical mantle reservoirs – 3D numerical results

U. WALZER^{1*} AND R. HENDEL²

¹Institut für Geowissenschaften, Friedrich-Schiller-Universität Jena, Humboldtstr. 11, 07743 Jena, Germany (*correspondence: u.walzer@uni-jena.de)

²Institut für Geowissenschaften, Friedrich-Schiller-Universität Jena, Humboldtstr. 11, 07743 Jena, Germany (roland.hendel@uni-jena.de)

A dynamic 3-D spherical-shell model for the chemical evolution of the Earth's mantle is presented. Chemical differentiation, convection, stirring, and thermal evolution constitute an inseparable dynamic system. Our model is based on the solution of the balance equations of mass, momentum, energy, angular momentum, and four sums of the number of atoms of the pairs ^{238}U - ^{206}Pb , ^{235}U - ^{207}Pb , ^{232}Th - ^{208}Pb , and ^{40}K - ^{40}Ar . Similar to the present model, the continental crust of the real Earth was not produced entirely at the start of the evolution but developed episodically in batches. The details of the continental distribution of the model are largely stochastic, but the spectral properties are quite similar to the present real Earth. Some preliminary results have been published in [1]. The modeled present-day mantle has no chemical stratification but we find a marble-cake structure. If we compare the observational results of the present-day proportion of depleted MORB mantle with the model then we find a similar order of magnitude. The MORB source dominates under the lithosphere. In our model, there are nowhere pure unblended reservoirs in the mantle. It is, however, remarkable that, in spite of 4500 Ma of solid-state mantle convection, certain strong concentrations of distributed chemical reservoirs continue to persist in certain volumes, although without sharp abundance boundaries. It is interesting to compare these results with the survival of primitive blobs in the lower mantle proposed by Becker *et al.* [2]. Finally we present results regarding the numerical method, implementation, scalability and performance.

[1] U. Walzer and R. Hendel. Mantle convection and evolution with growing continents. *J. Geophys. Res.* **113**:B09405, doi:10.1029/2007JB005459, 2008. [2] T. W. Becker, J. B. Kellogg, and R. J. O'Connell. Thermal constraints on the survival of primitive blobs in the lower mantle. *Earth Planet. Sci. Lett.* **171**:351–365, 1999

Wettability alteration upon reaction with scCO₂: Pore scale visualization and contact angle measurements

JIAMIN WAN*, YONGMAN KIM AND JONGWON JUNG

Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720 USA (jwan@lbl.gov, ymkim@lbl.gov, jjung@lbl.gov)

The interfacial forces among reservoir mineral substrates, brine and supercritical (sc) CO₂ can greatly affect the distribution of scCO₂ injected in geological formations for its sequestration. When brine and scCO₂ contact with a substrate, the equilibrium configuration among the three interfacial tensions determines the wetting property (contact angle) of the substrate. The contact angle together with the pore size distribution determines the distribution of capillary entry pressures for porous media. Therefore, contact angles in the mineral-brine-scCO₂ system control the pore-scale advance of the scCO₂-brine interface during injection, structure trapping of CO₂ at reservoir-caprock boundaries, and residual trapping of scCO₂ at later stages of geologic sequestration. The wetting behavior of scCO₂ in contact with caprocks is especially important because it is a primary factor controlling CO₂ leakage from reservoirs to the land surface and atmosphere. Although CO₂ is commonly assumed to be the non-wetting phase in the current predictive models for CO₂ storage capacity, recent studies have begun to show that the wettability of caprock minerals can be altered in the presence of scCO₂ under pressures and temperatures representative of geological storage conditions. Understanding is critically needed on how and to what degrees chemical reactions and physical processes in the deep reservoirs affect the wetting properties of rock surface. Such understanding will enable more reliable estimates of CO₂ residual saturations and capillary threshold pressures needed for predicting larger scale system behavior.

We studied silica wettability alteration within single pores containing brine and scCO₂ under flow conditions, using engineered transparent micromodels. The process of scCO₂ injection into an initially brine saturated silica porous network (pore throat and body sizes are 30 and 120 μm, respectively) was conducted under controlled P and T. We observed (1) the CO₂ phase entering pores, displacing brine, and leaving initially smooth brine films coating silica pore walls with the contact angle θ close to zero, and (2) over longer times (CO₂ diffused into brine films), the brine films contracted into small brine-droplets as a result of decreased wettability (increased θ). At steady state, the θ values of these brine-droplets are $49^\circ \pm 10^\circ$ for the 1.0 M, and $70^\circ \pm 7^\circ$ for 5.0 M NaCl. We hypothesize that neutralization of the silica surfaces resulting from brine film acidification by CO₂ is responsible for the observed wettability alteration.

Quantifying electron flow in the sulfidation of lepidocrocite

M. WAN¹, C. SCHRÖDER^{1,2} AND S. PEIFFER^{1,*}

¹Department of Hydrology, University of Bayreuth, Bayreuth Germany (moli.wan@uni-bayreuth.de;

*correspondence: s.peiffer@uni-bayreuth.de)

²Center for Applied Geoscience, Eberhard Karls University, Tübingen, Germany

The interaction between sulfide and ferric (oxyhydr)oxides exerts control on electron flow and ultimately the sulfur cycle in many anoxic groundwater, soil and marine systems. In most situations it leads to pyrite formation, the pathway still being researched [e.g. 1]. To identify the intermediate products and to quantify the electron flow during the reaction we used Mössbauer spectroscopy, TEM, wet chemistry analyses and a novel technique to determine polysulfides.

We reacted synthetic lepidocrocite enriched in the Mössbauer-sensitive isotope ⁵⁷Fe and dissolved sulfide at neutral pH in an anoxic glove box. The solid fraction was extracted at different time steps (15 min, 2hrs, 48 hrs, 72 hrs and one week), frozen and analyzed with Mössbauer spectroscopy. Both iron and sulfur species were measured with wet chemistry analysis methods in parallel runs. Polysulfides were derived with Trifluoromethanesulfonate and measured by HPLC with UV-Detector.

Mössbauer spectra showed the formation of pyrite after 48 hrs. Mackinawite and magnetite were identified as intermediate products and confirmed TEM observations by Hellige *et al.* [1]. The spectra also provided evidence for Fe-deficient FeS phases such as pyrrhotite. Wet chemistry analysis shows polysulfides form in the first few minutes, accompanying with the formation of elemental sulfur. Most of them are surface associated. With the knowledge on the distribution of Fe between its oxidation states, mineral phases and dissolved species and the determination of polysulfides we can quantify the electron flow along the reaction path to pyrite formation.

[1] Hellige *et al.* (2011) *Geochim. Cosmochim. Acta* in review.

A thermogravimetric study of thermally treated silica nanoparticles

QUAN WAN^{1,*}, YI XIAO¹ AND GEORGE BARAN^{2,*}

¹Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, Guizhou, 550002, P.R. China

(*correspondence: wanquan@vip.gyig.ac.cn, grbaran@temple.edu)

²College of Engineering, Temple University, Philadelphia, Pennsylvania 19122, USA

Silica is the most abundant mineral in the earth's crust. The surface chemistry of silica often plays a critical role in many earth processes, for example weathering of rocks. When the size of silica particles approaches the nanoscale or when they contain nanoscale pores, the surface area of the silica particles increases dramatically and this can fundamentally affect several properties of interest. Using a combination of dehydration (heating 2hrs at 200°C), dehydroxylation (heating 2hrs at 400, 600 or 800°C) and rehydroxylation (boiling overnight in water), we thermally treated three different types of silica particles, *i.e.* AA-05 (spherical, diameter ~ 500 nm) synthesized via the Stöber process, N-2329 (spherical, diameter ~ 75 nm) synthesized through water glass route, and V-258 (irregular, median size ~700 nm) ground glass [1]. Samples were characterized by thermogravimetric analysis (TGA), pycnometry, elemental analysis and scanning electron microscopy (SEM). We found that heating 2hrs at 200°C removed physically absorbed water, while heating at higher temperature incrementally removed surface silanol groups. Boiling overnight in water resulted in partial recovery of silanol groups. However dehydroxylation became irreversible for samples treated at over 400°C inconsistent with the Zhuravlev model [2]. Our results also indicated that AA-05 Stöber silica was nanoporous with a lower density (1.9 g/cm³) than that (2.2 g/cm³) of the fully condensed N-2329 which was obtained through the water glass route. The considerable carbon content (~ 2wt%) in AA-05 was also consistent with incomplete condensation during Stöber synthesis. Both AA-05 and N-2329 showed better thermal stability than did V-258, which melted at 800°C. The increased density of AA-05 after treatment at 600 and 800°C suggested that the nanopores in Stöber silica begin to collapse at 600°C.

[1] Wan *et al.* (2010) *J Therm Anal Calorim* **99**, 237-243. [2] Zhuravlev (2000) *Colloid Surface A* **173**, 1-38.

Carbon biogeochemical cycle in the impounded Wujiang River, China

B. WANG¹, C. Q. LIU¹ AND F. WANG²

¹Chinese Acad Sci, Inst Geochem, State Key Lab Environm Geochem, Guiyang 550002, Peoples R China
(*correspondence: baoliwang@163.com)
(liucongqiang@vip.skleg.cn)

²Shanghai Univ, Sch Environm & Chem Engn, Inst Appl Radiat, Shanghai 201800, Peoples R China
(fswang@shu.edu.cn)

Wujiang River is a major hydropower source for China's massive West-to-East Power Transmission Project. A series of reservoirs were constructed along it and now it becomes a typical impounded river. We have seasonally determined the $\delta^{13}\text{C}$ values of dissolved inorganic carbon (DIC), particulate organic carbon (POC), and phytoplanktonic carbon (PPC), and related hydro-chemical parameters to understand the carbon biogeochemical cycle in the impounded Wujiang River.

Soil organic matter and aquatic phytoplankton are the possible contributors of riverine POC. $\delta^{13}\text{C}_{\text{PPC}}$ showed a perfect linear relationship with $\delta^{13}\text{C}_{\text{POC}}$, suggesting that POC was mainly derived from phytoplankton. With the development of reservoir after damming, riverine heterotrophic ecosystem is transformed to autotrophic one, and phytoplankton becomes the dominant contributor of POC. pH values in the reservoir waters were generally larger than 8, indicating a predominance of bicarbonate in DIC. HCO_3^- concentrations decreased while the $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{POC}}$ increased in the surface water of the reservoirs. And with the increase of phytoplanktonic biomass, algae assimilate more inorganic carbon and thereby exhibit more positive $\delta^{13}\text{C}$ value. So, photosynthesis is one of the main processes that affect $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{POC}}$ in the surface water. Compared to the surface water before dam, DIC in release water showed the deficit in ^{13}C when thermal stratification developed. Release water is from deep water of reservoir and $\delta^{13}\text{C}_{\text{DIC}}$ values decrease with water depth as photosynthesis declines and respiration increase. Thus, respiration, which makes the DIC pool enriched in ^{12}C , is the other main process affecting $\delta^{13}\text{C}_{\text{DIC}}$ in the reservoirs. Compared to DIC, POC showed larger fluctuations in $\delta^{13}\text{C}$ values because phytoplankton had more influences on $\delta^{13}\text{C}_{\text{POC}}$ than that on $\delta^{13}\text{C}_{\text{DIC}}$ during the transformation of inorganic carbon into organic carbon. Our results demonstrated that river damming has important impacts on riverine carbon biogeochemical cycling.

Multiple generations of granitic magma in the West Kunlun, NW China: Implications for crustal melting and mantle-crust interaction at an active continental margin

C. WANG^{1,2*}, L. LIU², W.Q. YANG², Y.T. CAO², R.S. LI¹ AND S.P. HE¹

¹Xi'an Center of Geological Survey, China Geological Survey, Xi'an 710054, P R China
(*correspondence: wang-mail@163.com)

²State Key Laboratory of Continental Dynamics, Department of Geology, Northwest University, Xi'an 710069, P R China

Active margins along accretionary orogens are considered to be major sites of the formation of juvenile continental crust [1], but subduction processes also produce crustal recycling and differentiation rather than growth [2]. West Kunlun is a large accretionary orogen formed by long-standing subduction, arc-continent collision and closure of Paleo-Tethys between the south margin of the Tarim Block and western portion of the Himalayan-Tibetan orogen from the early Paleozoic to the early Mesozoic. Two major granitoid belts based on geochronology data were identified, the early Paleozoic suite and the early Mesozoic suite. Mafic magmatic enclaves are abundant in most of these granitoids. There is a strong mantle component to these rocks, and imply production of the rock series has involved mixing between mantle and crustal magma components. The source characteristics of granites and zircon Hf isotope characteristics indicated that the West Kunlun granitic magma was formed on the base of continental crust. Recycling of older continental crust, and of Mesoproterozoic crust in particular, appears to be an important process in the evolution of the orogenic continental crust of West Kunlun between early Paleozoic and Mesozoic. There is not of pronounced new crust formed and formation of the West Kunlun orogen in the outboard of the ancient Tarim margin related with Paleo-Tethys subduction. Such processes may represent an advancing orogen.

This work is supported by the National Science Foundation of China (Grant No.40902022, 40972128) and Natural Science Foundation of Shanxi Province, China (Grant No. 2010JM5007)

[1] Condie (2007). *GSAM* 200, 145-158. [2] Plank (2005). *J. Petrol.* 46, 921-944.

13 α (*n*-alkyl)-tricyclic terpanes: A series of biomarkers for the unique microbial mat ecosystem in the middle Mesoproterozoic (1.45~1.30Gyr) North China Sea

C. WANG*, M. WANG, J. XU, Y. LI, Y. YU, J. BAI,
T. DONG, X. ZHANG, X. XIONG AND H. GAI

State Key Laboratory of Oil Science and Prospecting, China
Univ. of Petroleum, Beijing, 102249, China
(*correspondence: wchj333@126.com)

Anoxygenic photosynthesis may have modulated Proterozoic oxygen production and sustained an intermediate redox state in the oceans for the Earth's middle age [1, 2]. A special biomarker assembly indicates that a unique prokaryotic microbial mat ecosystem may have contributed to the major primary production in the middle Mesoproterozoic (1.45~1.30Gyr) North China sea [3]. However, we know little about the microbial structures of the Mesoproterozoic microbial mats. Here, we report for the first time that the series of 13 α (*n*-alkyl)-tricyclic terpanes (C₁₈~C₃₃) (13 α NATTs) occurs in the organic-rich shales from this middle Mesoproterozoic sequence, including Hongshuizhuang Fm, Tieling Fm and Xiamaling Fm. We infer the long straight-chain substitution (up to C₁₅) in 13 α NATTs to be originally of *n*-alkyl-substituted chain, while not of demethylated isoprenoid chain [4]. This scenario is probably just like that of hopanes. Thus, 13 α NATTs may have originated from prokaryotes, given the robust evidence of steranes being undetectable in the shales [3].

The fact that 13 α NATTs have not been detected from the post-Mesoproterozoic sedimentary sequences in China, may suggest that 13 α NATTs could be a unique series of biomarkers for some special Mesoproterozoic prokaryotes, which probably disappeared from the late geological record. The remaining key question is to reveal what kinds of prokaryotes may have contributed to 13 α NATTs?

[1] Johnston *et al.* (2009) *PNAS* **106**, 16925–16929. [2] Lyons *et al.* (2009) *PNAS* **106**, 18045–18046. [3] Wang (2010) *GCA* **74**, A1099-A1099. [4] Wang and Simoneit (1995) *Chem. Geol.* **120**, 155–170.

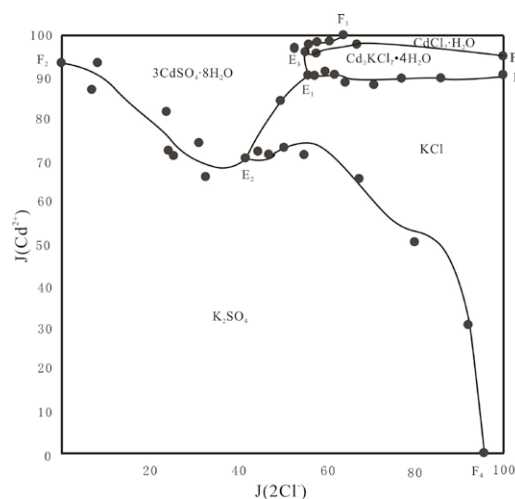
Phase equilibrium of the Cd-bearing quaternary reciprocal system at 298 K

WANG CHUNLEI¹, HUANG YI^{1,2*}, ZOU FANG¹ AND
NI SHIJUN^{1,2}

¹Department of Geochemistry, Chengdu University of
Technology, Sichuan, PRC
(*correspondence: huangyi@cudt.cn)

²Applied Nuclear techniques in Groscience Key Laboratory of
Sichuan Province, PRC

Solid-Liquid Equilibrium of reciprocal quaternary system K⁺, Cd²⁺//Cl⁻, SO₄²⁻-H₂O at 298 K were studied by an isothermal solution saturation method. Experimental results indicate that there are seven univariant curves F₂E₂, F₄E₂, E₂E₁, F₃E₁, E₁E₃, F₃E₃, F₁E₃, three invariant point: E₁, E₂ and E₃ and five crystallization fields in the reciprocal quaternary system. There is double salt Cd₃KCl₇·4H₂O existing in the reciprocal quaternary system. The crystallization zones of equilibrium solid phases are K₂SO₄ (F₂E₂F₄), KCl (F₄E₂E₁F₃), CdCl₂·H₂O (F₃E₃F₁), Cd₃KCl₇·4H₂O (F₃E₁E₃F₃), 3CdSO₄·8H₂O (F₁E₃E₁E₂F₂), respectively. The point E₁ represents the equilibrium of three solid phase KCl, Cd₃KCl₇·4H₂O, and 3CdSO₄·8H₂O. The eutectic point E₂ represents the equilibrium of three solid phase K₂SO₄, KCl and 3CdSO₄·8H₂O. The other eutectic point E₃ represents the equilibrium of three solid phase Cd₃KCl₇·4H₂O, CdCl₂·H₂O and 3CdSO₄·8H₂O. Potassium Sulfate has the biggest crystallization field while Cadmium Chlorine has a smaller crystallization region than others.



Integrated development and management of water resources: A typical area in China

DONG WANG^{1*}, JICHUN WU¹, LACHUN WANG² AND YUN LIANG SHI

¹Department of Hydrosociences, School of Earth Sciences and Engineering, State Key Laboratory of Pollution Control and Resource Reuse, Nanjing University, Nanjing 210093, China (*correspondence: wangdong@nju.edu.cn)

²School of Geographic and Oceanographic Sciences, Nanjing University, Nanjing 210093, China

It is unfortunate that problems with water are considered to grow worse in the coming decades. Water Scarcity is one of the most pervasive problems afflicting people throughout the world. According to the World Water Council, human beings have access to less than eight-tenths of one percent of the total water on our blue planet. Although freshwater is a renewable natural resource, its circulation rate is determined by climate system, human activities, etc., and there is an upper limit to the volume of freshwater natural resource.

More intense droughts in the past decade, affecting an increasing number of people, have been linked to higher temperatures and decreased precipitation, but are also frequently a consequence of the misunderstanding of water resources. The increased exposure to potential hazards has led to more awareness of intergraded groundwater and surfacewater development and management, especially in Karst area, which have complicated hydrologic and hydrogeologic conditions.

Houzhai Catchment is a typical Karst area in Guizhou Province in the southwest of China. A conceptual Karst streamflow model is established, whose parameters are calibrated and determined by Genetic Algorithm. According to three indexes (Relative Error, Cross-correlation Coefficient and Deterministic Coefficient), the results show that the proposed model can simulate and forecast the special runoff yield and flow concentration process of this typical Karst area, which is useful to improve the evaluation method and promote growing awareness of the need for properly integrated development and management of water resources.

This study was supported by the National Natural Science Fund of China (No. 41071018, 41030746, 40725010, and 40730635), the Skeleton Young Teachers Program and Excellent Disciplines Leaders in Midlife-Youth Program of Nanjing University.

Effects of soil environment on activity of rare earth elements: Implications for land utilization

D.Y. WANG¹, Y.F. LI¹, Y. Y. YANG¹, Y. SHANG² AND M. WANG¹

¹College of Earth Sciences, Jilin University, Changchun 130061, China (wang_dy@jlu.edu.cn, yfli@jlu.edu.cn, yyyang10@mails.jlu.edu.cn, wangmeng880716@163.com)

²Land Surveying and Mapping Institute of Shandong Province, Jinan 250013, China (rulyshang@yahoo.com.cn)

Rare earth elements (REEs), as an agent for increasing products, have been widely used in agricultural processes. However, how do the soil environments affect the activity of REEs in the soil? It is one of the hotly-discussed issues in the land utilization. This paper reports the total REE contents of 40 surface soil samples and available REE contents of 20 samples from the Yanbian region in the eastern Jilin Province, NE China analyzed using ICP-MS. The total REE contents range from 95.7 to 266 ppm, yielding a weighted mean value of 150 ppm, which is lower than the average REE content (187 ppm) of soil in China. The available REE contents for 20 samples vary from 18.5 to 118 ppm, yielding a weighted average value of 56.8 ppm. The average REE activity indexes in the soil, i.e., available REE contents/total REE contents, are between 23.2% and 46.5% (average 37.9%). Correlation analyses done by SPSS software indicate that the total and available contents of Yb and Lu exhibit evidently positive correlations while these of other REE have extremely remarkable positive correlations. The activity indexes of Y, Sm, Gd, Er, Tm, Yb, and Lu show evidently positive correlations with pH values in soil. Additionally, the difference of REE activity indexes between different types of soils also occurs. Compared with the similar studies of Hainan province, southern China where the climate, soil type and soil physical and chemical properties are different from the Yanbian area, REE activity index in the soils from NE China is evidently low, suggesting that the climate, soil type, and soil physical and chemical properties have important affects on REE activity in soil. Therefore, it is of important implications for scientifically using land, protecting soil environment, and maintaining agro-ecosystems to understand and utilize relationship between soil environment and REE activation in them.

Late Triassic bimodal magmatism in the Lesser Xing'an-Zhangguangcai Range, NE China: Constraints on the timing of transformation of Paleo-Asian ocean into circum-Pacific ocean tectonic systems

F. WANG, W.L. XU *, E. MENG, F.H. GAO AND H.H. CAO

College of Earth Sciences, Jilin University, Changchun 130061, China (jlu-wangfeng@sohu.com; *correspondence: xuwl@jlu.edu.cn)

The Lesser Xing'an-Zhangguangcai Range, NE China, is located in the eastern section of Central Asian Orogenic Belt (CAOB) [1]. Geochronological and geochemical data of Triassic igneous rocks from the region provide constraints on the timing of the transformation of the Paleo-Asian tectonic system into the circum-Pacific system. LA-ICP-MS and SIMS zircon U-Pb dating results for two basalts, one gabbro, two rhyolites, and one dacite indicate that they formed during the Late Triassic (208-228 Ma). The mafic rocks have $\text{SiO}_2 = 48.97\text{-}51.89$ wt.%, $\text{TFe}_2\text{O}_3 = 7.86\text{-}10.13$ wt.%, $\text{K}_2\text{O} = 1.05\text{-}1.72$ wt.%, $\text{Mg\#} [\text{Mg}/(\text{Mg}+\text{Fe}^{2+})] = 0.54\text{-}0.63$, $\text{Cr}=107\text{-}405$ ppm, $\text{Ni}=44\text{-}102$ ppm, whereas felsic rocks have $\text{SiO}_2 = 73.60\text{-}75.69$ wt.%, $\text{TFe}_2\text{O}_3 = 0.69\text{-}1.19$ wt.%, $\text{K}_2\text{O} = 4.10\text{-}4.36$ wt.%, $\text{Mg\#} = 0.05\text{-}0.23$, suggesting a typical bimodal igneous association. In addition, these mafic rocks are characterized by enrichment in LREEs and LILEs, depletion in HREEs and HFSEs (such as Nb, Ta, Ti), and weak Eu anomalies (0.87-1.05), whereas felsic rocks exhibit strongly depletion in Sr, P, Ti, enrichment in Th, U, K, and relatively obvious negative Eu anomalies (0.61-0.65). The above findings, combined with the coeval A-type rhyolites in eastern Heilongjiang and Jilin provinces [2], imply that they formed under a post-collisional extensional environment related to the final collision between the North China Craton and the Siberia Craton in the Late Permian and/or Early Triassic. Meanwhile, this finding also suggests that the subduction of the Paleo-Pacific plate beneath the Eurasian continent could take place after the Late Triassic.

This research was financially supported by research grants from the Natural Science Foundation of China (Grant 41072038) and the Geological Survey of China (Grants 1212010070301 and 1212010611806).

[1] Sengör *et al.* (1993) *Nature* **364**, 299–307. [2] Xu *et al.* (2009) *J. Asian Earth Sci.* **34**, 392–402.

Genetic and functional properties of uncultivated Miscellaneous Crenarchaeota Group (MCG): Implication from the metagenome analysis

FENGPING WANG^{1*}, JUN MENG², YANPING ZHENG^{1,2}, DAN QIN², JUN XU¹ AND XIANG XIAO¹,

¹State Key Laboratory of Microbial Metabolism and State Key Laboratory of Ocean Engineering, Shanghai JiaoTong University, Shanghai, 200240, People's Republic of China (*correspondence: fengpingw@sjtu.edu.cn)

²The School of life science, Xiamen University, 361005, People's Republic of China

The MCG Archaea is one of the most predominant Archaeal groups in various environments. Till present, no member of MCG has been cultivated or characterized, and its ecological roles and evolutionary position remain obscure. Within this study, the genetic potential and physiology of MCG and its evolutionary relationship with other archaeal members were analyzed and inferred based on metagenomic analysis. Comparisons of gene organizations and similarities around the 16S rRNA genes of available MCG Fosmid and Cosmid clones found completely no synteny, demonstrated big genetic variations within groups of MCG. A topoisomerase IB gene (TopIB) was found in a MCG Fosmid genome fragment, TopIB phylogenetic analysis placed MCG within the newly postulated archaeal Phylum-Thaumarchaeota. Functions of some genes on the genome fragment were tested by in-vitro expression. Gene involved in protocatechuate degradation and chemotaxis were found in a genome fragment, suggesting a role of this group of archaea in protocatechuate degradation. The up-expression of 4-carboxymuconolactone decarboxylases was observed when the sediment was amended with protocatechuate, further supporting the idea of MCG group as protocatechuate degrader.

Study on diagenetic environments of calcite veins hosted in marine carbonate rock in middle Yangtze region of Southern China

WANG FURONG^{1,2}, HE SHENG^{1,2} AND YANG XINGYE²

¹Key Laboratory of Tectonics and Petroleum Resources
Ministry of Education, China University of Geosciences,
Wuhan 430074, China

²Faculty of Earth Resources, China University of Geosciences,
Wuhan 430074, China

Thin slices suggest that calcite veins hosted in marine carbonate rock of appearing locating in middle Yangtze region of southern China develop two crystal forms including radial calcite and isometric structure calcite in Triassic, and isometric structure calcite can be identified of calcite veins in Permian and Ordovician. And some calcite veins develop double-crystal pattern.

Cathodoluminescence document that different structure calcite veins show different luminous intensity in Triassic which can identified three periods of calcite veins, and luminous intensity has no different between calcite veins and surrounding rocks in Permian and Ordovician with medium orange to dark light.

Carbon-oxygen isotopes of calcite veins show that The range of $\delta^{13}C$ is $-6.76\text{‰} \sim 4.01\text{‰}$ (PDB), $\delta^{18}O$ is $-17.95\text{‰} \sim -5.67\text{‰}$ (PDB) in calcite veins, which indicates that calcite veins deposit in marine phreatic environment and mixing phreatic environment. Calcite veins in Triassic are sedimentary origin, and part of calcite veins in Permian and Ordovician suffer latter diagenetic fluid dissolution. Fluid generating from organic-matter maturation effect the information of calcite veins in Permian to some degree.

Tectonothermal evolution of the Triassic flysch in the Songpan-Garzê orogen, Eastern Tibetan plateau

H. WANG¹, M. RAHN², J. ZHOU³, X. TAO⁴

¹School of Earth and Space Sciences, Peking University,
China (*correspondence: hjwang@pku.edu.cn)

²Swiss Federal Nuclear Safety Inspectorate (ENSI), 5200
Brugg, Switzerland

³Chinese Academy of Geological Sciences, China

⁴College of Earth Sciences, Chengdu University of
Technology, China

Low temperature metamorphic indicators give an insight into the tectonothermal evolution of the Triassic flysches in the Songpan-Garzê orogen, eastern Tibetan plateau. The Triassic flysches experienced large-scale folding, faulting and a thermal overprint from diagenesis to lower greenschist facies. Maximum metamorphic conditions were $380 \pm 25^\circ\text{C}$ and low to intermediate pressures. Iso-thermal zones mapped with illite crystallinity (IC) describe following relationships between thermal zones and fold axes, faults and strata boundaries: i) anchizonal boundaries run across strata boundaries and fold axes indicating the main folding of the flysches occurred prior to metamorphism; ii) large-scale faults make boundary offsets in thermal zones suggesting the structural movement along the Longmenshan (LMS) and the Xianshuihe faults took place after low grade metamorphism.

From NW to SE, the Triassic flysches in the Songpan-Garzê orogen show a complex pattern. From this pattern a general increase in grade towards the LMS fault belt and across the LMS fault belt, greenschist facies rocks on its NW side are juxtaposed to diagenetic rocks in the Sichuan basin on its SE side. This juxtaposition is marked by IC jumps of $0.23^\circ\Delta 2\theta$ in SW of LMS, $0.40^\circ\Delta 2\theta$ in the Middle and $0.66^\circ\Delta 2\theta$ in NE of LMS. Across the Xianshuihe fault, the truncated IC zones within the flysches suggest a total offset of roughly 60 km due to post-metamorphic sinistral strike-slip.

Compression at the end of the Triassic induced by the interaction of the South China, North China and the North Tibetan blocks caused the closure of the Paleotethys ocean and led to folding of the flysches within the Songpan-Garzê basin. Very low to low grade metamorphism may have been caused by the increase in thermal gradient due to large-scale magmatic activity in the Jurassic. FT ages reveal Early to mid-Cretaceous exhumation. Finally the India-Asia collision caused the formation of the Longmenshan fault and the Xianshuihe strike-slip fault in the early Tertiary and disturbed the distribution of metamorphic zones.

3.84 Ga crustal material in Dunhuang Block, Gansu Province, China

HONG-LIANG WANG, XUE-YI XU, TAO ZHU, TING LI
AND ZHI-PEI LI

Xi'an Center of Geological Survey (Xi'an Institute of Geology and Mineral Resource), CGS, Xi'an, Shaanxi 710054, China

Crustal materials formed in the early period of solid earth (≥ 3.8 Ga) are few reserved in the world. We get magma crystallization age 3841 ± 16 Ma from metamorphic amphibolite of Dunhuang block rock recently (Fig. 1, Table.1), which is the oldest crustal material had been detected in Dunhuang block, and early earth material found in metamorphic basic volcanics is also rare in the world yet. This metamorphic basic volcanics belong to sub-alkaline volcanics and tholeiite series with $\text{SiO}_2 = 47.94 \times 10^{-2} \sim 49.32 \times 10^{-2}$. We also get metamorphic zircon ages of ~ 3.5 Ga and 3.3 Ga, consistent with previous Sm-Nd age 3487 Ma. It indicates that Archean basement exist in Dunhuang block. This new result has important significance for exploring and studying the age, properties and growth characteristic, and developing comparison study between Dunhuang block and Huabei craton.



Figure 1: CL images and ages of zircons for amphibolite of Dunhuang rock group

Samp.	$^{207}\text{Pb}/^{206}\text{Pb}$	1σ	$^{207}\text{Pb}/^{235}\text{U}$	1σ	$^{206}\text{Pb}/^{238}\text{U}$	1σ
23	3841	16	3842	6	3845	17
24	3820	15	3608	65	3240	14
16	3496	16	3311	6	3015	13
34	3332	17	3332	7	3331	16

Table 1: older zircon U-Pb data for amphibolite from Dunhuang rock group (Ma)

This study was supported by China territorial resources survey project (No.1212010610319) and the National Natural Science Foundation of China (No.40773044).

Implications of fault spilling gases in searching active ruptures

HUALIN WANG¹, GUODONG ZHENG², JIQIANG WANG¹,
CHAO HU¹ AND XIA LIU¹

¹Shandong Institute of Seismic Engineering, Jinan 250021, China

²Key Laboratory of Petroleum Resources Research, Institute of Geology and Geophysics, CAS, Lanzhou 730000, China

The seeped gases as called as fault spilling gases may contain abundant information about the geological processes in the deep Earth, and also be significant in searching and studying on the spatial distribution and activity of faults. In this paper, a systematic study was performed on the Yishu tectonic zone, the Haiyuan tectonic zone for an Ms8.5 earthquake in 1920, the Tancheng tectonic zone for an Ms8.5 earthquake in 1668, the Xanshuihe tectonic zone, and several active faults in the Shandong flatlands and some major results were summarized as the followings.

1, the concentration of Rn and Hg and their variation degree of fault spilled gas could be used as sensitive index to evaluate the activity of faults connection. Higher concentration of Rn and lower Hg may indicated stronger stress accumulation and poorer connection of faults, lower concentration of Rn and higher Hg may indicated lower stress accumulation and better connection of faults, and lower concentrations of both Rn and Hg may indicate poorer stress accumulation and poorer connection of faults.

2, the measurement of fault spilled gas has been implied well in searching active faults in the flatlands area. The Rn measurement of fault spilled gas combined with engineering drilling profiles to the Yidu fault zone, the Shuangshan-Lijiazhuang fault zone, and the Heze fault zone for the Ms7.0 earthquake in 1937 was successful to identify all the locations and displacement of faults, and their activity times.

3, the measurement of fault spilled gas can be also used well in the geometric and kinetic studies of faults. The structural pivot area, the pull-apart area and the compression area of strike-slip faults could be located according to the distribution pattern of geochemical surroundings from the measurement of fault spilled gas, which may supply a fast and simple method to study on the geometric and kinetic properties of faults and used successfully to the Haiyuan seismic fault zone and the Xianshuihe fault zone.

Assessment of heavy metal pollutions from lead-zinc mining activities in the North River Basin, China

J. WANG¹, J. LIU¹, Y.H. CHEN^{1*}, T.F. XIAO²,
C.L. WANG³, X.P. LI¹ AND J.Y. QI⁴

¹School of Environmental Science and Engineering,
Guangzhou University, Guangzhou 510006, China
(*correspondence: chenyheng@eyou.com)

²Institute of Geochemistry, Chinese Academy of Sciences,
Guiyang 550002, China (xiaotangfu@vip.gyig.ac.cn)

³Guangdong Provincial Academy of Environmental Science,
Guangzhou 510045 (wangchunlin1982@163.com)

⁴South China Institute of Environmental Sciences, MEP,
Guangzhou 516005, China (qjyyjq78@163.com)

Chemical analysis of 120 samples of surface sediments and 82 samples of surface water around the lead-zinc ore mining area in the North River Basin (upper part of the Pearl River Delta), South China was performed in order to (i) determine the contamination levels of heavy metals (Tl, As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) by means of Inductively Coupled Plasma Mass Spectrometry (ICP - MS); (ii) identify potential sources of the heavy metals; and (iii) to identify those processes that determine the spatial variability of the heavy metals between the source areas and some distant locations in downstream direction. Among the examined elements, high contents of Tl, As, Cd, Cu, Pb and Zn were found in the sediments from the mainstream and feeders of the North River close to the mining area. We interpret the most likely sources of the heavy metal contamination in the sediments are wastewater discharges, mineral tailing materials and dust depositions resulting from the excessive mining activities, since the heavy metal distribution in the basin generally shows a decreasing trend from the location closest to the mining sites towards the downstream directions, and most importantly because the heavy metal contents are mostly related to the Tl contents. Thallium, as a rare element is seldom found in the normal environmental settings but is highly concentrated in the lead-zinc ore minerals in this area. Thus, the good relationships between the Tl contents and the contents of other heavy metals signify that Tl could be used as a special environmental tracer to track, and eventually to quantify the heavy metal contaminations from mining activities of ore specifically bearing Tl. This work enhances our understanding of heavy metal contaminations around a mining site. The local environmental protection and future mineral resources exploitation activities might also benefit.

This work is supported by NSFC (No. 40930743).

The characteristics of generation and distribution of CO₂ gas pools in Songliao Basin, China

J.H WANG¹, X. LUO², L.H HOU³ AND Y.WANG⁴

¹Research Institute of Petroleum Exploration and
Development, Beijing, China (284174762@qq.com)

²Research Institute of Petroleum Exploration and
Development, Beijing, China

³Research Institute of Petroleum Exploration and
Development, Beijing, China (lhhou@petrochina.com.cn)

⁴Research Institute of Petroleum Exploration and
Development, Jilin Oil Company, songyuan, China
(wangyl@petrochina.com.cn)

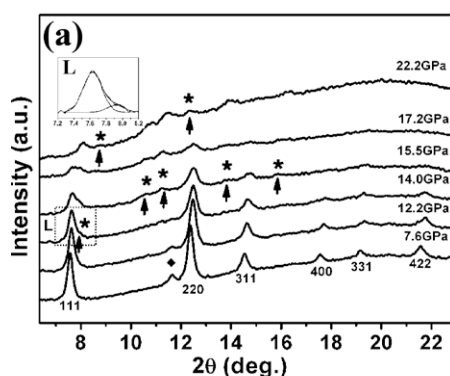
There are so many gas pools with high CO₂ component are distributed in volcanic reservoir. It also indicates that the CO₂ in CO₂ gas pools are mainly of magma origin by the analysis of the characteristics of gas components, carbon isotope composition of CO₂ and helium isotope composition of He in 10 of CO₂ gas pools in Songliao Basin. The main characters of CO₂ gas pools are $\delta^{13}\text{C}_{\text{CO}_2} > -8\text{‰}$ and R/Ra=1.9~7.2. Geological background and analysis of fluid inclusion indicate that the CO₂ in Changling, De hui and Gu long etc fault depression are mainly forming lately. The reasons are following. The first is that the fluid inclusions of CO₂ are late period fluid inclusions which are banded occurrence in cracks of transecting quartz grain or transecting widen quartz. Their homogenization temperatures are 120~140°C. So, the forming stage of CO₂ may be mainly between 72Ma and 48 Ma. The formation and distribution of CO₂ are relatives with many kinds of faults including lithosphere faults, crust fractures, basement rifts and overburden faults especially relatives with NE-NNE deep faults which have strike slip motion in late stage. These kinds of faults mainly controlled depression formation in early stage and had NE-NNE left-lateral strike slip motion in late stage. Also, volcanic erupted with amazing amount of CO₂ in this stage and the faults became the channel of the CO₂ migration and then prompted the formation of CO₂.

High-pressure behavior of CaF₂ nanocrystals

J.S. WANG, C.L. MA, J. HAO, D. ZHOU AND Q.L. CUI*

State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, PR China
(*correspondence: cq1@jlu.edu.cn)

The alkaline-earth fluoride CaF₂ is a well-known face-centered-cubic ionic minerals, and has long been used as mineralogical models for the behavior of ionically bonded minerals in the Earth's mantle [1]. It is widely accepted that the actualization of nanosized materials have opened doors for finding new properties with respect to their macroscopic counterparts. Although there are many high-pressure studies on bulk CaF₂, pressure induced structural phase transitions in nanoscale system has rarely been reported [2, 3].



High-pressure behavior of nanocrystalline CaF₂ samples with an average grain size of 8 nm have been studied by *in situ* synchrotron radiation x-ray diffraction. A pressure-induced fluorite structure to orthorhombic PbCl₂-type structure transition starts at 14.0 GPa, and phase transition is sluggish. The orthorhombic phase of nanocrystalline CaF₂ is stable up to 46.5 GPa. The enhancement of transition pressure in CaF₂ nanocrystals as compared with the corresponding bulk material is mainly caused by the surface energy difference between the phases involved.

[1] Abby Kavner (2008) *Phys. Rev. B* **77**, 224102. [2] X. Wu, S. Qin & Z. Y. Wu (2006) *Phys. Rev. B* **73**, 134103. [3] E Morris, T Groy & K Leinenweber (2001) *J. Phys. Chem. Solids* **62**, 1117.

Elastic properties of hydrous and anhydrous mantle minerals at high pressure

J. WANG AND J.D. BASS*

Geology Department, University of Illinois, 1301 W Green Street, Urbana, IL 61801 USA
(*correspondence: jaybass@uiuc.edu)

Anhydrous and hydrous forms of wadsleyite and ringwoodite, high-pressure phases of (Mg,Fe)₂SiO₄ + H₂O, are major constituents of the transition zone of Earth's mantle, and are likely abundant in many subducting slabs. Therefore, the seismic properties of these phases are essential to understand the chemical and thermal state of these regions, as well as the seismic signature of water in the mantle to 660 km depth. We have measured the acoustic wave velocities of several key anhydrous and hydrous forms of these minerals up to transition zone pressures by Brillouin spectroscopy on samples compressed in a diamond anvil cell. Hydrous samples contained roughly 2% by weight of H₂O. These experiments allow us to assess the effects of pressure, Fe and H₂O on the elastic properties of these phases. These measurements should provide insight on key questions such as the olivine content and hydration state of the transition zone. It appears that one of the critical issues in addressing the effects of hydration on these phases is the accurate measurement of water content. Our results indicate that determinations of the structurally-bound hydrogen content by SIMS and IR spectroscopy on these samples can vary greatly.

Primordial ages of lithospheric mantle vs ancient relicts in the asthenospheric mantle: *In situ* Os perspective

KUO-LUNG WANG^{1*}, S.Y. O'REILLY², W.L. GRIFFIN², N.J. PEARSON², V. KOVACH³ AND V. YARMOLYUK⁴

¹Institute of Earth Sciences, Academia Sinica, Taipei, Taiwan (*correspondence: kwang@earth.sinica.edu.tw)

²GEMOC, Macquarie University, Sydney, Australia

³IPGG, Russian Academy of Sciences, St. Petersburg, Russia

⁴IGEM, Russian Academy of Sciences, Moscow, Russia

Recent studies have shown that volumes of ancient depleted material can survive in the convecting asthenospheric mantle for long periods so that the use of Os model ages of mantle xenoliths to constrain the age of lithospheric mantle events should be approached with caution. In this study, we use *in situ* Os-isotope dating on sulfides in peridotitic xenoliths from cratonic (Tok, Russia) and off-craton (Tariat and Dariganga, Mongolia) settings of the Neoproterozoic-Phanerozoic Central Asia Orogenic Belt (CAOB) to examine lithosphere formation. A few Tok sulfides yield an apparent isochron indicating an age of 3.2 Ga. The high initial ¹⁸⁷Os/¹⁸⁸Os (0.117) of the apparent isochron suggests that it represents a mixing line, possibly involving an Archean component. In Tariat, both T_{MA} ages from the least-disturbed sulfides (¹⁸⁷Re/¹⁸⁸Os < 0.07) and T_{RD} ages from higher-Re/Os sulfides yield model ages ranging from 0.5 to 3.0 Ga, with peaks around 1.7-1.5, 1.2 and 0.7-0.5 Ga. These ages suggest that SCLM beneath the Tariat region existed at least by Proterozoic time, and that some domains are Archean. The Os model ages are well-correlated with crustal events recorded in the overlying Precambrian Tarvagatay Terrane. It would be a remarkable coincidence if sulfides derived from randomly selected fragments of refractory materials in the convecting asthenospheric mantle would combine to give such a systematic correlation. We therefore prefer the simplest interpretation: the sulfide Os ages in the Tok and Tariat peridotites record major events that affected the crust+SCLM. The oldest of these events may record major melt extraction, and the later ones metasomatic events. Sulfides in Dariganga peridotites also have Mesoproterozoic Os model ages. Although Proterozoic crustal events have not been reported in this region so far, Proterozoic Nd model ages for basement rocks around the Xilinhot region in the vicinity of the Dariganga Plateau (B. Chen, pers. comm.) suggest that a Precambrian crustal terrain should be expected and might be found by studies of deep-crustal xenoliths in the Dariganga region.

The geochemistry of fluid inclusions in Yimen Sanjiachang copper deposits

LEI WANG¹, RUN-SHENG HAN¹, GUO TANG¹, YI-DUO HU² AND JIAN-GUO HANG¹

¹Kunming University of Science and Technology; Southwest Institute of Geological Survey, Geological Survey Center for Non-ferrous Mineral Resources, Kunming, China, 650093 (*correspondence: cumtwl1983@yahoo.com.cn)

²Kunming Vocational and Technical College of Industry, Kunming, China, 650302

Sanjiachang copper deposits including three copper deposits of Shishan copper deposit, Caiyuanhe copper deposit and Fengshan copper deposit [1]. Shishan Copper deposit is a diagenesis - weak reworked deposit Fengshan copper deposit is a strongly reworked deposit which controlled by diapir structure [2], Caiyuanhe copper deposit is a transitional type of the first two deposits, The fluid inclusions have significant differences of the three copper deposits with the following characteristics: From Shishan copper Caiyuanhe copper deposit Fengshan copper deposit Inclusions size are increase (1.5 μm-2.15 μm), and number are increase, pure liquid inclusions in order to reduce and liquid inclusions in order to increase, Fengshan copper found gas inclusions (about 15%) and a small amount of NaCl sub-inclusions. From Shishan copper Caiyuanhe copper deposit Fengshan copper deposit gangue mineral homogenization temperatures are gradually increasing there are two homogenization temperature range of 113.4 ~ 194.3 °C (95% of this range) and 220 ~ 320 °C in Fengshan copper deposit-hishan copper deposit salinity inclusions have the feature of high K⁺ content, low Na⁺ content, Caiyuanhe copper deposit and Fengshan copper deposit have the feature of high Na⁺ content, low K⁺ content [2], Fengshan copper has two salinity content range of 4-10% and 12-18%.

The results show that from Shishan copper deposit - Caiyuanhe copper deposit - Fengshan copper deposit is gradually enhanced the role of structural transformation, Fengshan copper mineralization has the characteristics of two and the main ore mineralization in the low temperature of 113.4 ~ 194.3 °C.

Granted by the project of the State Crisis Mine (20089 943) and the Distinguishing Discipline of KUST (2008).

[1] Tian Yulong *et al* (2000). *Acta Mineralogica Sinica* **20**, 73-79. [2] Lei Wang *et al* (2010). *Geochimica Et Cosmochimica Acta* **74**, A1104-A1104.

Microecology perspective and environmental impact of coal mine sulfur-bearing waste dump

L.L. WANG^{1*}, M. YUE² AND L.L. WANG¹

¹School of Resources and Environmental Engineering, Hefei University of Technology, Hefei 230009, China (wangllhfut@gmail.com)

²Hefei University, Hefei 230022, China

Coal mines in Chian are mostly located in the north. Below the coal layer, there is a fracture-karst aquifer with strong anisotropy often used as drinking water source for local inhabitants[1-2]. Mining has caused environmental pollution. Some studies involve flow and solute transportant in fractured media[3-7]. Others pay attentions to the pollution control from sources [8]. In this study, by hydrogeological survey, sampling and testing in the sulfur-containing waste dump of the mining area in Sitai mine, Shanxi Province, the content of the material and its environmental characteristics were analyzed. The advantage of microbial flora in the sulfur-containing waste dump and its colony structure were discussed. The 16S rDNA of the special microorganisms was determined; The role of microorganisms and kinetic parameters in the weathering process of sulphide were studied.

The pH values of leaching water in the yard of sulfur containing waste dump were around 2.5, the color of leaching filtrate were almost reddish-brown.

The 9 strains which isolated from the acid water belonged to two species: *Acidiphilium sp.* and *Acidithiobacillus ferrooxidans*, they were the advantage microbial flora in this environment.

The initial pH of liquid phase, temperature, solid-liquid ratio and particle sizes of mining rocks would affect the behavior of microorganisms in the process of pyrite weathering.

When microorganisms and culture medium were coexist, the pyrite oxidation rate reached 3.14 mmol.d-1.L-1, it was 28.55 times of the control group. the release regularities of As, Cu, Zn, Ni, Pb influenced obviously by microorganisms.

[1] Qian *et al.* (2006) *Hydrogeol. J.* **14**: 1192-1205. [2] Qian *et al.* (2009) *Hydrogeol. J.* **17**: 1749-1760. [3] Zhou *et al.* (2004) *Int. J. Rock Mech. Min. Sci.* **41**:402. [4] Qian *et al.* (2005) *J. Hydrol.* **311**: 134-142. [5] Qian *et al.*(2007) *J. Hydrol.* **339**: 206-219. [6] Qian *et al.* (2011) *Hydrol. Process.* **25**: 614-622. [7] Qian *et al.* (2011) *J. Hydrol.* **399**: 246-254. [8] Qian *et al.*(2010) *Geochim.Cosmochim. Acta* **74**: 837-837.

Precious metal (Pt, Pd, and Au) in Fengshan porphyry Cu-Mo deposit, China

MINFANG WANG^{1,2}

¹Faculty of Earth Resources, China University of Geosciences, Wuhan, Hubei, 430074, China (wang_minfang@163.com)

²State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan, Hubei, 430074, China

Nine hand specimen and four flotation concentrates have been analyzed (Table 1).

Sample	Type	Au ppb	Pt ppb	Pd ppb
FS50	intrusive rock	11	0.137	0.165
FS94	altered rock	4	0.234	0.288
FS57	altered rock	10	0.389	3.907
FS4	ore, skarn	1480	0.037	3.095
FS9	ore, skarn	531	0.204	17.979
FS45	ore, skarn	310	0.099	0.403
FS64	ore, skarn	402	0.07	1.314
FS8	ore, porphyry	28	1.765	13.888
FS36	ore, porphyry	220	0.175	6.877
SC	sulfide concentrate	897	15.9	13
CFC	copper flotation concentrate	6070	21.8	32
MFC	molybdenum flotation concentrate	2360	81.4	32
CMFC	copper-molybdenum flotation concentrate	12	1.3	1

The results show that concentrate samples have the highest content of precious metal and almost are 1-2 orders of the magnitude higher than ore samples, while the rock samples are the poorest. Meanwhile, the porphyry ore samples have the higher content of Pd, Pt and Au than in the skarn ore samples. PGE enrichment in porphyry deposits probably requires a mantle source region, liberation of mantle sulfides during partial melting in the source region, and an oxidized melt that effectively prohibits the formation of magmatic sulfides during fractionation. This study clearly demonstrates the potential for further research.

Contrasting microbial communities and geochemical patterns reflect different styles of methane oxidation and methanogenesis in terrestrial mud volcanoes

PEI-LING WANG¹, LI-HUNG LIN², TING-WEN CHENG², YUNG-HSIN CHANG², WEN-JING LAI¹, JING-YI TSENG¹, WEN-YU TSAI² AND CHIH-HSIEN SUN³

¹Institute of Oceanography, National Taiwan University

²Department of Geosciences, National Taiwan University

³Exploration and Development Research Institute, CPC Corporation Taiwan

Hydrocarbon seeps and mud volcanoes are ubiquitous in marine and terrestrial environments where gaseous fluids with unconsolidated sediments ascend along fractures tapping into potential gas or petroleum reservoirs in deep subsurface. Although extensive geochemical and microbiological studies have been conducted on marine settings, terrestrial counterparts remain poorly constrained.

This study combined molecular screening of 16S rRNA and functional genes, and geochemical analyses of porewater, sediment and gas collected from mud volcanoes distributed in eastern and southwestern Taiwan to determine how microbial communities respond to various methane fluxes and geological contexts. Our findings indicated that mud volcano systems in both regions were characterized by stratified geochemical characteristics and community assemblages resembling or contrasting those in marine settings in several aspects. In particular, anaerobic methanotrophy was linked to different electron accepting processes (sulfate versus iron reduction) in different regions, suggesting various affinities of functional expression on the presence of specific minerals. The proliferation of anaerobic methanotrophy is apparently decoupled from the supply of deeply-sourced methane but strongly dependent on the in-situ methanogenesis controlled by the fermentative production of specific methanogenic precursors. Microbial communities compartmentalized into different depth intervals collectively enable less than 40% of methane inventory emitted to atmosphere. Contrasting patterns of metabolic and geochemical stratification reflect microbial communities thriving on inherited minerals and geochemical disequilibria induced by the interaction between the upward transport of gaseous, reducing, diluted fluids and the downward infiltration of oxidizing, solute-enriched fluids subjected to surface evaporation.

Potential-pH diagram for the V-Cl-H₂O system at high chlorine concentration

R. L. WANG¹, Y. ZENG^{1,2*} AND S. H. ZHANG¹

¹Department of Geochemistry, Chengdu University of Technology, Chengdu, 610059 China;

²Mineral Resources Chemistry Key Laboratory of Sichuan Higher Education Institutions, Chengdu 610059, China (*correspondence: zengyster@gmail.com)

Vanadium, widely distributed in the nature, is essential to human and closely related to human health. While the total amount of vanadium in human body gathers to a certain degree, it shows middle-high toxicity. The toxicity of vanadium depends on its species and valence, which are mainly due to pH value, potentials, the total concentration of vanadium, and the kinds of coexistent ions in the solution. Moreover, the toxicity of vanadium increases with increasing oxidation state.

Under natural environmental conditions in soil and water, vanadium dominantly exists in either +4 or +5 oxidation state as aquatic species of vanadyl(VO₃²⁻) or vanadate(VO₄³⁻), respectively. Under weak reducing conditions, vanadyl(V^{IV}) species is stable, while in oxidizing conditions, vanadate(V^V) is stable across almost the entire pH range. VO₃²⁻ and VO₄³⁻ can coexist depending on the redox potential and pH value of the solution and concentration.

In this paper, the potential and pH value of the V-Cl-H₂O system at C_{T(Cl)} = 1.0 mol·L⁻¹ are determined by using a concentration comparison method. Based on the measured data, the preliminary predominance diagrams were constructed. A Comparison between the predominance diagrams for the V-Cl-H₂O system with C_{T(Cl)} = 1.0 mol·L⁻¹ at different vanadium concentrations (C_{T(V)} = 1.0×10⁻³ mol·L⁻¹ and C_{T(V)} = 1.0×10⁻⁵ mol·L⁻¹) [1],[2] has been done. It is shown that the location and size of the advantage regional of vanadium ion VO₂⁺, H₂VO₄⁻, VO₄³⁻ are similar. Under the conditions with pH 0.00-5.68, and Eh 0.5-0.9 V, the area of VO₂⁺ advantage region is decreased at C_{T(V)} = 1.0×10⁻⁵ mol·L⁻¹. At Eh value of 0.0-0.5 V, the HV₂O₅⁻ advantage region is replaced by VO⁺ with pH 3.68-14.00.

The authors acknowledge the support of the Program for New Century Excellent Talents in University (NCET-08-0900)

[1] Zeng, Y.; Ma, M. R. (2009) *Acta Phys.-Chim.Sin.*, , **25**: 955. [2] Wu, J.M.; Zeng, Y. (2007) *Acta Phys.-Chim.Sin.*, , **23**: 1141.

The temporal and spatial variations of N₂O saturations in a eutrophic lake

SHILU WANG

Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences
(wangshilu@mails.gyig.ac.cn)

Much of the N₂O emitted from aquatic ecosystems is anthropogenically derived [1]. However, there remains considerable uncertainty in the magnitude of anthropogenic N₂O emitted from aquatic environments and how N₂O emissions respond to increasing loads of anthropogenic N and eutrophication in general. In this study, N₂O saturations were examined in the ecologically heterogeneous, eutrophic lake, Lake Taihu, in eastern China. I found that anthropogenically-enhanced inorganic nitrogen N inputs act as a limited primary control on the spatial distribution of N₂O saturations in heavily eutrophied parts of the lake only and that overall, lake N₂O production and emission are not raised as significantly as expected due to high N input [2]. A distinct diurnal pattern of N₂O saturations is displayed in July, which is controlled by biogeochemical processes [3]. While large-scale changes (~25-fold) in N₂O fluxes in Lake Taihu are a function of variable N loading, biogeochemical processes concerning O₂ and N transformation at the sediment-water interface have significant (~twofold) impacts on the regulation of N₂O production over very short time scales.

This work was supported by the major projects on control and rectification of water body pollution (2009ZX07101-013).

[1] Seitzinger (2000) *Chemosphere, Glob. Chang. Sci.* **2**, 267-279. [2] Wang S (2009) *Sci. Total Envir.* **407**, 3330-3337. [3] Wang S (2010) *J. Environ. Qual.* **39**, 1858-1863.

The dissolving and driving process in Qarhan salt lake, China

WANG WENXIANG^{1*}, LI WENPENG² AND HAO AIBING³

¹China University of Geoscience, Beijing, 100083, China
(*correspondence: hiwangwenxiang@126.com)

²China Institute of Geo-Environment Monitoring, Beijing, 100081, China

³China Geological Survey, Beijing, 100037, China

Qarhan salt lake is located in Qaidam Basin, Qinghai Province, China. There are about 3 million tons of solid potassium resources in Qarhan salt lake^[1]. About half of the solid resources are of low grade. We can't exploit the low grade resource directly.

The solid potassium can be dissolved and transferred to liquid state by mixed with solution in low potassium concentration. We use water from Seniehu lake as the solution to carry on the research. The experiment area is 1 km². 35 monitoring wells are set up in order to obtain data of the saline water level and composition. There is a recharge trench on one side of the experiment area and a drainage trench on the other side. The low potassium solution comes into the experiment area from the recharge trench. During the flowing process, the concentration of potassium resolution becomes high. In the end, the high potassium solution flows out of the experiment area through the drainage trench.

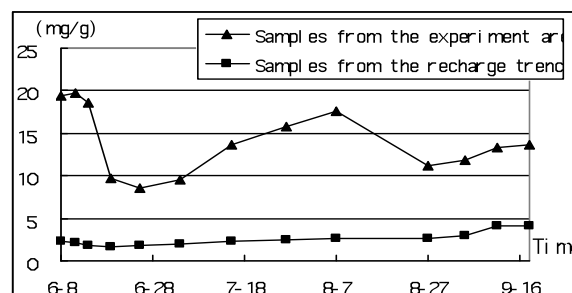


Figure 1: Potassium concentration duration curve

The result shows that solution with low potassium concentration can easily dissolve the solid potassium. However, the concentration of sodium must not be too high.^[2]

[1] Li Wenpeng (1993) *Journal of Hebei College of Geology* **16**, 254-263. [2] Wang Wenxiang (2010) *Mineral Deposits* **29**, 697-703.

U–Pb zircon, geochemical and isotopic constraints on age and origin of Cretaceous granites from the North Qinling, central China and implications for interaction between crust and mantle

XIAOXIA WANG^{1*}, TAO WANG², QIUJU QI³ AND SHAN LI²

¹Institute of Mineral and Resource, Chinese Academy of Geological Science, Beijing 100037, China
(*xiaoxiawang@hotmail.com)

²Institute of Geology, Chinese Academy of Geological Science, Beijing 100037, China

³China University of Geosciences, Beijing 100083, China

Zircon U-Pb dating, geochemical and isotopic (Nd, Sr, Hf) analyses for two granitoid plutons have been carried out in the different blocks of the North Qinling. Zircon dating by LA-ICP-MS for the Liantian granite in the southern margin of the North China Block and Muhuguan granite in the North Qinling orogen yields ages of 133 ± 1 Ma and 150 ± 1 Ma, respectively. The samples studied from the Liantian granite contain zircons mostly having xenocrystic cores. The inherited zircons have Paleoproterozoic ages. Both granites exhibit similar mineralogical, chemical and isotopic characteristics. They have metaluminous to peraluminous compositions (A/CNK ratios 0.9 to 1.05) and display K_2O/Na_2O ratios of 0.9 to 1.5. In terms of trace elements, they show an enrichment of LREE and medium fractionation between LREE and HREE (La_N/Yb_N ratios 16 to 33). Compared with the primordial mantle, distinct negative anomalies of P and Ti, and slight negative anomalies of Ba and Nb are observed in both granite plutons. They are further characterized by low $\epsilon_{Nd}(t)$ of -11.8 to -18.3 and $\epsilon_{Hf}(t)$ of -23.4 to -5.7 for the Liantian granite and low $\epsilon_{Nd}(t)$ of -7.6 to -11.4 and $\epsilon_{Hf}(t)$ of -17.4 to -7.3 for the Muhuguan granite. We interpret these Cretaceous granites as partial melting of old crust, mixed with juvenile mantle component and suggest the basement of the North Qinling with more juvenile composition from the southern margin of North China block to Shangdan suture.

Particle size effects in bioleaching of uranium waste ore

WANG XUEGANG^{1,2,3*}, SUN ZHANXUE³ AND LIU JINHUI³

¹State Key Laboratory Breeding Base of Nuclear Resources and Environment, East China Institute of Technology, Nanchang, JX 330013, P. R. China

(*correspondence:xuegangwang@yahoo.com.cn)

²Key Laboratory of Radioactive Geology and Exploration Technology Fundamental Science for National Defense, East China Institute of Technology, Fuzhou, JX 344000, P. R. China

³Department of Civil and Environmental Engineering, East China Institute of Technology, Fuzhou, JX 344000, P. R. China (zhxsun@ecit.cn, liujh@ecit.cn)

The effect of mineral particle size on the bioleaching of uranium from the 721 Uranium Mine Shan-nan deposit waste ore, located in the Jiangxi Province, south of China, was investigated. A mixed bacteria, which isolated from the uranium mine ores and the predominant bacteria were *Acidithiobacillus ferrooxidans* and *Leptospirillum ferriphilum*, was applied into the column bioleaching test. The uranium leaching effect in different particle size uranium ore were shown in table 1.

particle size (mm)	U content (%)	Slag U content (%)	Leaching rate(%)
>25	0.0289	0.00258	10.73
20-25	0.0141	0.00098	30.49
15-20	0.0161	0.00089	44.72
10-15	0.0330	0.00093	71.81
5-10	0.0332	0.00069	79.21
2-5	0.0403	0.00068	83.13
1-2	0.0434	0.00058	86.63
<1	0.0479	0.00057	88.10

Table 1: The leaching rate of different particle size

As can be seen from table 1, with the waste uranium ore particle size decreasing, the leaching rate was increasing. Decreasing the particle size from 25mm to 1mm the uranium leaching rate enhanced from 10.73% to 88.1%. While the particle size less than 15mm fraction leaching rate was over 71.81%, also the particle size greater than 15mm fraction leaching rate less than 44.72%, which adverse to uranium bioleaching. Consider the actual process, recommended crushed ore to <15mm can be obtained better effect.

Project supported by the National High-tech R&D Program of China (863 Program) (No.2007AA06Z120) and International Cooperation Projects of China (No. 2008DFA71760).

From solids to liquids: A coordinated approach for studying dynamic processes in the deep Earth using large-volume apparatus and synchrotron radiation

YANBIN WANG

Center for Advanced Radiation Sources, The University of Chicago, 5640 S. Ellis Ave., Chicago, IL 60637, USA (wang@cars.uchicago.edu)

For the past fifteen years, we have been developing synchrotron-based large-volume high pressure (LVP) techniques at the GeoSoilEnviroCARS (GSECARS) sector of the Advanced Photon Source (APS) for a better understanding of the thermodynamic state, the dynamic processes, and the evolution of the Earth and other planets. The technical and scientific developments have enabled us to conduct coordinated studies on materials in both the solid and liquid states under simultaneously high pressure and high temperature conditions. In this presentation I will discuss the following dynamic aspects of recent scientific studies: (1) rheological properties of earth materials at high pressure and temperature, using the deformation DIA (D-DIA) – recent results on olivine deformation will be used as an example, (2) textural evolution in multi-phased materials under large shear deformation using the high-pressure x-ray tomographic microscope (HPXTM) – applications of such studies on mantle dynamics will be discussed, (3) in-situ high-pressure tomographic studies on Fe-S melt segregation from silicate using HPXTM and new constraints on the timing of formation of the Earth's core, and (4) new development for melt studies, including fusion curve, structure, density, and elasticity, aiming at a “complete suite” of physical properties for a better understanding of melt physics. A brief discussion on future prospect will also be presented.

Quantitative ^2H NMR as site-specific $^2\text{H}/^1\text{H}$ probe to study organic matter

Y. WANG¹, G.D. CODY¹, C.M.O'D. ALEXANDER² AND M.L. FOGEL¹

¹Geophysical Laboratory, Carnegie Institution of Washington (ywang1@ciw.edu, gcody@ciw.edu, mfofel@ciw.edu)

²Department of Terrestrial Magnetism, Carnegie Institution of Washington (alexander@dtm.ciw.edu)

Recent studies show that the biosynthetic fractionation between fatty acids and water can vary by up to 500‰, depending on biological and environmental factors that include: species, metabolic pathways, aridity, and salinity. These variations are poorly understood, which has restricted the specificity of biomarker $\delta^2\text{H}$ records and thus their use as paleoenvironmental and geobiological proxies. Direct detection of the site-specific ^2H distribution via ^2H NMR provides a powerful means for investigating these variations and the underlying mechanisms. Unlike approaches that employ chemical/thermal fragmentation and IRMS measurements, ^2H NMR is non-destructive, applicable to almost all types of organic molecules, and free of isotopic fractionation. Similar to the advent of compound-specific isotope analyses, it has the potential to open a new door to the study of organic materials that will benefit a broad range of biogeochemical and low-temperature geochemical studies.

Historically, ^2H NMR experiments on natural samples have been difficult due to the scarcity of the ^2H nucleus and its low receptivity to radio frequency radiation which together lower the sensitivity by $\sim 7 \times 10^5$ times compared to ^1H NMR. Furthermore, the ^2H NMR spectra is complicated by the quadrupolar interaction of the ^2H nuclei. We have successfully developed a solid state ^2H NMR experimental protocol to significantly amplify the signal-to-noise ratio and yield simplified, purely isotropic spectra.

With this method, we studied the site-specific ^2H distribution in residual organic matter from two carbonaceous chondrite meteorites and a bituminous coal. Combined with ^1H NMR spectra and bulk $^2\text{H}/^1\text{H}$ analyses, we derived the $\delta^2\text{H}$ values for aliphatic and aromatic sites and the $^2\text{H}/^1\text{H}$ fractionation factor between these groups, which provide a unique basis for coupling the $^2\text{H}/^1\text{H}$ distribution to the chemical history of chondrites. In an on-going study, we investigated H isotope exchange rates by incubating pristane, cumene, and anthracene, separately, with clay minerals soaked in ^2H -enriched water. Liquid state ^2H NMR was used to study the efficiency of ^2H substitution at methyl, methylene, methine, and aromatic sites. The results will improve our understanding of the influences on H isotopic composition of sedimentary organic matter and petroleum.

Nd-Sr-Pb isotopic and elemental geochemistry of silicalites from the sulphide ore deposit in the Guangdong region, China

WANG YINXI¹, LI HUIMING¹, WANG YUANYUAN², CHEN YIJUN¹, ZHANG MENGQUN¹ AND WANG HENIAN²

¹Center of Modern Analysis, Nanjing University, Nanjing 210093, China

²Nanjing Institute of Geology and Paleontology, Academy of Sciences, Nanjing 210008, China.

³Dept.of Earth Science, Nanjing University, 210093, China

Silicalite is well developed and is present as layers, thin layer or siliceous band in the banded ores. The Dajiangping pyrite deposits lie on the Yunfu County of Guangdong region, China. is a super-large pyrite ore deposit.

The silicalite is mainly composed of microlitic and cryptocrystalline quartz. SiO₂ is the essential chemical composed of the silicalite, ranging from 81.50% to 94.32%, together with Al₂O₃ content between 0.45% and 9.44%, CaO < 0.12% and MgO < 0.36%. The contents of FeO, MnO, K₂O and Na₂O are commonly low. The isotopic characters of the Dajiang pyrite orebody are: $\epsilon_{\text{Nd}}(t) = -12 \sim -13$, $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{I}} = 0.73085 \sim 0.73104$, $(^{206}\text{Pb}/^{204}\text{Pb})_{\text{I}} = 18.467 \sim 18.485$, $(^{207}\text{Pb}/^{204}\text{Pb})_{\text{I}} = 16.239 \sim 16.384$ and $(^{208}\text{Pb}/^{204}\text{Pb})_{\text{I}} = 39.805 \sim 39.873$. Because of the isotopic characteristic of Sr-Nd-Pb in the whole rock, these evidences reflect the character of crust source but not that of magmatic source region.

The determination of Dajiangping pyrite deposit indicates that the Precambrian continental rift massive sulphide ore deposit is also an important kind of deposit in South China basins. Evidently, the above-mentioned Sr-Nd-Pb isotopic geochemistry reflects the crust source of the Dajiang pyrite deposits.

This work is granted by the National Natural Science Foundation of China (No. 40872028) and by the Analysis Testing Foundation of Nanjing University

[1] Wang Henian et al. (1997). *Chinese Science Bulletin*, Vol. 42, 23:1983-1985

Rb-Sr and Sm-Nd isotopic ages of Sulphide deposits in the Guangdong region, China

WANG YINXI¹, LI HUIMING¹, WANG YUANYUAN², HU XIN¹, LIU DI¹, TAO XIANCONG¹ AND WANG HENIAN³

¹Center of Modern Analysis, Nanjing University, Nanjing 210093, China (*correspondence: yxwang@nju.edu.cn)

²Nanjing Institute of Geology and Paleontology, Academy of Sciences, Nanjing 210008, China.

³Dept.of Earth Science, Nanjing University, 210093, China

The Dajiangping pyrite deposits lie on the Yunfu County of Guangdong region, China. is a super-large pyrite ore deposit.

Rb-Sr and Sm-Nd isotope ages were measured by using VG354 mass spectrometer at Modern Analysis Centre, Nanjing University and the analytical procedures were discussed and given in detail by Wang⁽¹⁾

The Rb-Sr and Sm-Nd dating of the orebody give the ages of 630.1±7.3Ma and 637.5±6.9Ma, respectively. The ages slightly approximate the age inferred from the occurrence of the later Proterozoic algae. This may be related to the subsequent geological effect on the Rb-Sr and Sm-Nd isotope system of the Dajiangping pyrite orebody. Because of the good linearity of Rb-Sr and Sm-Nd internal isochron between the whole rock, these evidences reflect the character of well-distributed source. Evidently, the above-mentioned Rb-Sr and Sm-Nd isotopic ages reflect the ages of the Dajiang pyrite deposits.

The silicalite ages of deposits in this are 630.1±7.3Ma and 637.5±6.9Ma, belonging to the later Proterozoic epoch. The determination of Dajiangping pyrite deposit indicates that the Precambrian continental rift massive sulphide ore deposit is also an important kind of deposit in South China basins. The Dajiangping pyrite deposit is similar to the famous Proterozoic super-large deposits in the world. The age determination of Dajiangping pyrite deposit bed plays an important role in confirming the ages of the Yunkai Group.

This work is granted by the National Natural Science Foundation of China (No. 40872028) and by the Analysis Testing Foundation of Nanjing University

[1] Wang Yinxi et al. (1992). *Chinese Science Bulletin* 37, 36-39

Nd-Sr isotopic geochemistry of fossils from the bottom of Cambrian in the Yunnan, Sichuan and Xinjiang region, China

YINXI WANG^{*1}, YUANYUAN WANG, JIEDONG YANG¹
AND HUIMING LI¹

¹Center of Modern Analysis, Nanjing University, Nanjing 210093, China (*correspondence: yxwang@nju.edu.cn)

²Nanjing Institute of Geology and Palaeontology, Academy of Sciences, Nanjing 210008, China.

This paper the results of Rb-Sr and Smi-Nd isotopic date from phosphatic fossils and collophanites collected from three important Precambrian-Cambrian boundary section in China. The samples under study were collected from three important sections in China, namely, the Meishucun section at Yunnan Province, the Maidiping section at Sichuan province and the Wushi section at Xinjiang Uygur Autonomous Region.

$\epsilon_{Nd}(T)$ and $^{87}Sr/^{86}Sr$ values of small shelly fossils from maidiping section are -6.5 to -7.1 and 0.709624 to 0.709812, respectively. $\epsilon_{Nd}(T)$ and $^{87}Sr/^{86}Sr$ values of small shelly fossils from Meishucun section are -6.1 to -7.1 and 0.709310 to 0.709700, respectively. $\epsilon_{Nd}(T)$ and $^{87}Sr/^{86}Sr$ values of small shelly fossils from Kalpin section are -6.1 to -6.5 and 0.709436 to 0.709576, respectively. $\epsilon_{Nd}(T)$ and $^{87}Sr/^{86}Sr$ values of small shelly fossils from three section are very similar.

The palaeoseawater in the three areas of China was co-oceanic during the Precambrian-Cambrian transitional period, with an average $\epsilon_{Nd}(T)$ value of -6.6 ± 0.5 . The Nd model age of the tested samples is about 1.8Ga, which represents the mean age of the continental source sres surrounding China's seawater.

This work is granted by the National Natural Science Foundation of China (No. 40872028) and by the Analysis Testing Foundation of Nanjing University

[1] Yang Jiedong *et al.* (1989). *Chinese Science Bulletin*, Vol. 34, 63

Surfacial geochemical features of elements in Qinghai-Tibet Plateau

WANG YONGHUA¹ AND WANG MINGQI²

¹Chengdu center, China Geological Survey, Sichuan, China 610082

²China University of Geosciences, Beijing, China

Qinghai-Tibet Plateau in China covers the area about 2,400,000km². Different landscapes including high-cold mountain, high-cold lake and swamp plateau, desert, deep valley are developed in the area. National geochemical mapping results show that there are typical distribution patterns of elements in different terrains.

High-cold mountain landscape, which is about 900,000km², over 4,000m high and less than 0°C annual temperature, is situated in the heart of the plateau. Most elements including Ag, Au, Ba, Be, Bi, Cd, Co, Cr, Cu, F, Hg, La, Li, Mn, Mo, Nb, Ni, P, Pb, Sn, Sr, Th, U, V, Y, Zn, Zr, SiO₂, Al₂O₃, TFe₂O₃, MgO and Na₂O in the stream sediments are quite close to the average value of the whole area and only As, B, Sb, W and K₂O are slightly enriched.

High-cold lake terrain is over 800,000km², 4500m high, 100-400mm rainfall and 0°C-4°C annual temperature. Most elements including Cr, La, Li, Nb, P, Sn, Sr, V, Zr, Al₂O₃, TFe₂O₃, Ag, B, Ba, Be, Bi, Cd, Co, F, Hg, Li, Mn, Mo, Ni, Pb, Th, U, W, Y, Zn, K₂O, MgO, Na₂O in the terrain are decreased and only CaO is strongly enriched and As, Sb, Sr are slightly increased.

Desert is widespread in west part of China and over 800,000km² in the plateau, in which annual rainfall is less than 400mm and the annual temperature is about 0 °C. The many elements like As, B, Cd, Hg, Li, Ni, Sb, Ti, U, V, W, Zn, Ag, Be, Bi, Co, Cr, Cu, F, La, Mn, Mo, Nb, P, Pb, Sn, Th, Y, Zr, TFe₂O₃ in the terrain are low than the average value of whole plateau; but Ba, Sr, CaO, MgO, Na₂O and K₂O are increased.

Deep valley landscape, which is 640,000 km² and over 1500m relief, is distributed around the plateau. The average contents of most elements including Ag, Au, Be, Cd, Co, Cr, Cu, F, Hg, Mn, Mo, La, Li, Mn, Mo, Nb, Ni, P, Pb, Sn, Th, Ti, U, V, W, Y, Zn, Zr, Al₂O₃, TFe₂O₃ and K₂O in the terrain are much higher than that in whole plateau.

n-Alkan-2-ones of lacustrine sediments and its climate significance in Linxia Basin, NE Tibetan Plateau, NW China

YONGLI WANG^{1,2}, XIAOMING FANG², YUANMAO LI¹, DAXIANG HE¹, YINGQIN WU¹, HUI YANG¹ AND YOUXIAO WANG¹

¹Key Laboratory of Petroleum Resources Research, Institute of Geology and Geophysics, Chinese Academy of Sciences, Lanzhou 730000, China

²Center of Basin-Mountain System and Environment, Institute of Tibetan Plateau Research, Chinese Academy of Sciences, Beijing 100085, China
(correspondence:Fangxm@itpcas.ac.cn)

Abundant n-alkan-2-ones were detected in all samples and the distribution ranging was from C17 to C31 in the lacustrine sediments of Maogou section in the Linxia Basin, NE Tibetan Plateau, NW China. The maxima peaks of C27, C29 and C31 were especially obvious and the odd carbon number predominance was remarkable from C25 to C31. The different maxima peaks of n-alkan-2-one from relative higher to lower carbon-numbered compounds were changed obviously and six climate stages could be identified in entire depositional section. Abundant isoprene-ketones (i.e., isomeric C18 ketones, iKC18) were detected in all samples. The relative abundance of isoprene-ketones for MG5 and MG8 to MG11 were higher, while that for MG1 to MG4 and MG6 to MG7 were lower. The isoprene-ketone can be regarded as recorder of temperature changes of the sedimentary environment. The higher abundance of isoprene-ketones indicates the low temperature of the sedimentary environment. The greatest change showed for MG7 to MG8 when the relative abundance of isoprene-ketones increased sharply, indicating the climate turned to cold condition at ~8Ma suddenly. Another obvious change in the relative abundance of isoprene-ketones was higher in MG5 indicating a cold condition at ~13Ma.

Based on the distribution characteristics of these biomarkers, we suggest that they record information related to climate change.

Supported by grants No. KZCX2-YW-Q05-05, XDA05120204, KZCX2-EW -104(2), NSFC No.40672123 and 2005CB422001.

Water hydrogen and oxygen isotope composition characterization in the tea ditch of Anxian, China

WANG YONGLI, NI SHIJUN AND ZHANG CHENGJIANG

¹Department of Geochemistry, Chengdu University of Technology, Sichuan Province, (wangyl@cdut.edu.cn, nsjl@cdut.edu.cn, zcj@cdut.edu.cn)

This paper studies isotopic composition in the Chayuan Gou of Anxian area. The results showed that the water body δD is between -68‰ ~ -54‰ , $\delta^{18}O$ in between -11‰ ~ -8‰ ; Sample put above global rainfall line and distribute in two different area (ChuBa Gou water area, Chayuan Gou water area). these show the groundwater and surface water originated in the meteoric waters of supply; according to $\delta^{18}O$ isotopic composition water Supplies elevation are about 1400 ~ 1500m.

ChuBa Gou water system and Chayuan Gou water system has different hydrogen and oxygen isotopic composition, the front is enrich lighter isotopes and the later is enrich heavy isotopes. S15 isotopic composition of spring water showed that the groundwater come from different two type groundwater mixing, the mixing ratio of 3:2.

Mechanism of uranium accumulation in a mining-impacted acidic peatbog

Y. WANG^{1*}, M. FRUTSCHI¹, V. PHROMMAVANH²,
M. DESCOSTES² AND R. BERNIER-LATMANI¹

¹Ecole Polytechnique Fédérale de Lausanne (EPFL),
Environmental Microbiology Laboratory (EML), Station
6, CH-1015 Lausanne, Switzerland
(*correspondence: yuheng.wang@epfl.ch)

²AREVA NC - Business Group Mines, Direction R&D, BAL
3720C, Tour AREVA, 1, place Jean Millier, 92084 Paris
La Défense Cedex, France

Uranium can accumulate in peatbogs from both natural and anthropogenic sources [1, 2]. An acidic peatbog located in central France was affected by historical uranium mining activities as well as by continued uranium leaching from granite rocks. As a result, this site displays areas, referred to as hotspots, in which uranium concentration can reach up to 4,000 mg/kg [3]. The first-order question for this site is the mechanism leading to this remarkable accumulation. Microbially-driven reductive immobilization is a possible route but so is the complexation of U(VI) by solid phase organic matter that is abundant in the peat soil.

In order to unravel this mechanism and to evaluate the impact of proposed remediation strategies, extensive depth-resolved sampling of soil and porewater have been carried out at hotspots as well as at U-free background areas. Core samples were analyzed for chemical composition, mineralogy and uranium speciation using a combination of x-ray diffraction, gamma spectrometry, sequential chemical extractions, electron microscopy of petrographic sections, cryo electron microscopy of plunge-frozen samples and bulk and micro-scale X-ray absorption spectroscopy. Moreover, the microbial community present in the soil was characterized phylogenetically and probed for its metabolic potential for U(VI) reduction. Additionally, porewater physico-chemical parameters (e.g., pH, Eh, DO, Fe(II), SO_4^{2-} , sulfide, U, Mn(II), major inorganic cations and anions, TOC, TIC) were obtained from the same spots to allow correlation of the water and soil characteristics as a function of depth. This approach is the basis for a delineation of the redox transition from oxic to anoxic and the corresponding microbial activity in each redox zone and provides the information needed to understand the mechanism of accumulation of U in this site.

[1] Krachler and Shotyk (2004). *J Environ Monit* **6**, 418-426.
[2] Regenspurg *et al.* (2010). *Geochim Cosmochim Acta* **74**, 2082-2098. [3] Moulin (2008). PhD, Ecole Centrale de Paris.

Modeling hydrogen and carbon isotopes of thermogenic gases from different kerogens in closed system

YUNPENG WANG¹, CHANGYI ZHAO², HONGJUN WANG²
AND JINZHONG LIU¹

¹SKLOG, Guangzhou Institute of Geochemistry, Chinese
Academy of Sciences, Guangzhou 510640, China

²RIPED of PetroChina, Beijing 100083, China

For better characterizing the hydrogen and carbon isotopes of thermogenic gases, we studied three selected lacustrine, marine and terrigenous kerogen (coal) samples using gold-tube closed system. We found the obvious fractionation mutation of hydrogen isotope at higher conversion rate for lacustrine and marine kerogen. How to model the isotopic variation is a key issue. Here, we take Rayleigh's method proposed by Rooney (1995) [1], and the isotopic variation was modeled by using two Rayleigh's functions and the results are showing in Fig. 1. In Rayleigh's function, we fitted the experimental results through adjusting the initial isotope compositions of the gas precursors (δ_0) and fractionation factors ($\epsilon=1000(\alpha-1)$, α is the ratio of reaction rates of isotopes). It is clear that there exist variations for evolution trend of lacustrine and marine kerogen while conversion rate (F) reaches around 0.6, but the variation is not obvious for coal in comparison. Figure 1 suggests that the initial isotope and fractionation factor changed for type I/II kerogen. Inspecting the generation and cracking record, we found these variations are corresponding to the onset temperature of massive secondary cracking of heavy hydrocarbons to methane. This study implies that the secondary cracking of oil in closed system will change the hydrogen and carbon isotopes of thermogenic gases.

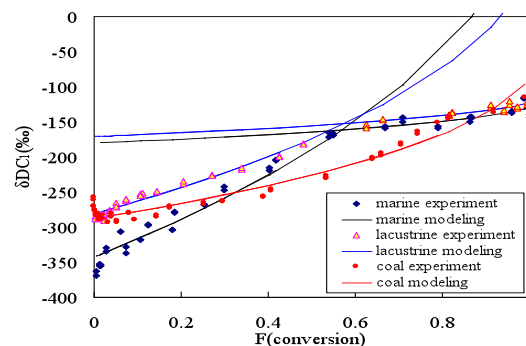


Figure 1: The experimental and modeling results

[1] Rooney *et al.* (1995) *Chem. Geology*. **126**, 219-232.

Fractionation of highly siderophile elements, selenium and tellurium in peridotites from the Baldissero and Balmuccia peridotite massifs, Ivrea Zone (Northern Italy)

Z. WANG*, H. BECKER AND T. GAWRONSKI

Freie Universität Berlin, Institut für Geologische Wissenschaften, Malteserstrasse 74-100, D-12249 Berlin, Germany (*correspondence: zaicongwang@gmail.com)

Peridotites from the Ivrea Zone (Northern Italy) are known for their excellent preservation and absence of low temperature alteration features. We have determined abundances of highly siderophile elements (HSE), Se and Te, and $^{187}\text{Os}/^{188}\text{Os}$ in depleted and fertile spinel lherzolites and a harzburgite (loss on ignition <1 %) from the Balmuccia and Baldissero massifs in order to study the behaviour of elements such as Au, Re, Se and Te that are otherwise easily affected by alteration processes. The lherzolites ($\text{Al}_2\text{O}_3=2.0\text{-}3.1\%$) have absolute and relative abundances of Os, Ir and Ru ($\text{Os}/\text{Ir}=1.13\pm 0.04$, $\text{Ru}/\text{Ir} = 2.02\pm 0.08$, $n=10$), consistent with typical mantle lherzolites. Incompatible HSE are relatively depleted (e.g., $\text{Re}/\text{Ir} = 0.04\pm 0.02$, $\text{Au}/\text{Ir}= 0.30\pm 0.10$, $\text{Pd}/\text{Ir}=1.90\pm 0.40$). Balmuccia peridotites show limited variation and Baldissero peridotites larger scatter, with a harzburgite showing the lowest abundances of incompatible HSE and chalcophiles. All samples show a systematic depletion pattern in CI chondrite normalized diagrams with $\text{Pd} > \text{Au} > \text{Re}$, but no systematic variation with lithophile tracers exist. Se concentrations of lherzolites range between 54 and 89 ng/g and Te contents from 12 to 18 ng/g, resulting in Se/Te (4.2-7.3) below CI chondrite values. Initial $\gamma_{\text{Os}}(300\text{Ma})$ (-2.3 to +2.0) are consistent with the notion that the last partial melting event occurred during the Phanerozoic. The data on lherzolites can be explained by moderate degrees of partial melting and control of partitioning by sulphide-silicate equilibrium with $D_{\text{Re}} < D_{\text{Au}} < D_{\text{Pd}}$ and $D_{\text{Se}} < D_{\text{Te}}$.

In situ stable isotopic detection of anaerobic oxidation of methane in Monterey Bay cold seeps via integrated cavity output spectroscopy

SCOTT D. WANKEL^{1*}, MANISH GUPTA², J. BRIAN LEEN², ROBERT PROVENCAL², VIMAL PARSOTAM² AND PETER R. GIRGUIS³

¹Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138

(*correspondence: sdwankel@fas.harvard.edu)

²Los Gatos Research, Inc., Mountain View, CA 94041

³Department of Organismic and Evolutionary Biology, Harvard University, Cambridge, MA 02138

Anaerobic methane oxidation (AOM) plays an important role in the global methane cycle by governing the release of CH_4 from anoxic sediments into the global ocean and ultimately the atmosphere. Thus, gaining an accurate understanding of both the distribution of CH_4 sources and the occurrence of AOM as well as the spatial and temporal variability of cycling pathways is critical. Environmental analyses of methane stable isotopic composition ($\delta^{13}\text{C}_{\text{CH}_4}$) provide just such an indicator of CH_4 source, whether biogenic or thermogenic, as well as a spatial and temporal integrator of microbial cycling pathways, such as AOM. Here we present results from several deployments of a newly developed *in situ* methane stable isotope analyzer (Off-Axis ICOS) capable of measuring $\delta^{13}\text{C}_{\text{CH}_4}$ to full ocean depths. Deployments to cold seep environments (960m) in Monterey Canyon (California) revealed a distinct separation between $\delta^{13}\text{C}_{\text{CH}_4}$ in advecting fluids relative to sediment pore fluids. Multiple visits to two sites revealed $\delta^{13}\text{C}_{\text{CH}_4}$ in advecting fluids ranging from -70.2 to -63.8‰, while fluids sampled from adjacent pushcore holes exhibited higher $\delta^{13}\text{C}_{\text{CH}_4}$ (-64.2 to -50.2‰). While advective flux of CH_4 from the central seep orifice is substantial, these data implicate the importance of AOM in consuming a minimum of 57 to 70% of the diffusive flux of CH_4 in the surrounding sediments.

Crustal accretion on mid-ocean ridges revealed through volatile concentrations in olivine-hosted melt inclusions

V.D. WANLESS*, A. SHAW AND M. BEHN

Department of Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA
(*correspondence: dwanless@whoi.edu)

We present volatile (H₂O, CO₂, Cl, S, and F) and major element data from melt inclusions in olivines found in crustal xenoliths and crystal clots from the fast-spreading East Pacific Rise to determine the depths of crystallization on mid-ocean ridges (MOR). The melt inclusions are generally, more primitive compared to the host glasses, with MgO concentrations ranging from 7.5 to 11.5 wt% and 6.6 to 8.4 wt%, respectively. Vapor saturation pressures calculated from equilibrium CO₂-H₂O concentrations suggest crystallization depths ranging from the crust-mantle transition (~6 km bsf) to above the seismically imaged, shallow melt lens (~600 m bsf). Minimum pressures estimates indicate that most of the melt inclusions (~70%) cluster between 1 and 2.5 km, consistent with crystallization in the shallow melt lens. However, the remaining melt inclusions show minimum equilibration pressures deeper than 2.5 km, implying that olivine crystallization beneath fast-spreading centers is not limited to the shallow melt lens.

Vapor-saturation pressures are also used to determine how volatile and major element concentrations vary with depth in the ocean crust. In general, volatile concentrations are much more variable in the upper 4 km of crust compared to the lower crust. For instance, Cl concentrations in melt inclusions formed in the upper crust range from 10 to 66 ppm, compared to only 42 to 51 ppm in melt inclusions formed deeper in the crust. This may result from higher degrees of fractional crystallization and/or increased fluid-rock interaction in the shallow crust. Major elements show no systematic variations with depth; however, more evolved olivines (Fo <86) are restricted to pressures within the shallow crust.

Several models have been proposed for crustal accretion beneath MORs (e.g., gabbro glacier or stacked sills), however there is no consensus on how the lower crust is formed at MORs or the depths over which crystallization occurs. Our volatile data imply that crystallization on fast-spreading ridges occurs throughout the crust, favoring models of in-situ crystallization or stacked sills and is inconsistent with a purely top-down, gabbro glacier model for lower crustal accretion on fast-spreading MORs.

A role of plant biomass-derived black carbon in electron transfer processes?

T. WANZEK¹, M. KEILUWEIT^{1,2}, D. PIERSON,¹
J. BAHAM¹ AND M. KLEBER^{1*}

¹Oregon State University, Department of Crop and Soil Science, Corvallis, OR 97331

(*correspondence: Markus.Kleber@oregonstate.edu)

²Lawrence Livermore National Laboratory, Physical and Life Sciences Directorate, Livermore, CA 94550

Recent work by Roden *et al.* [1] has provided strong evidence for a role of aromatic compounds in providing solid-state electron shuttles for electron transfer between bacteria and metal oxide surfaces. Historically, such materials are considered to be part of operationally defined "humic" substances [2] and are thought to result from "humification", i.e., from processes of secondary synthesis in the course of organic matter decomposition. However, there is increasing evidence that soils and sediments are subject to large imports of aromatic carbon on a global scale [3,4] through vegetation fires and additions of industrial black carbon. Future additions of aromatic carbon to soils are expected to rise in the wake of the evolving "Biochar" movement [5].

Up to one fifth of oxygen-containing functional groups on industrial black carbon can have quinonic functionality [6], and a number of studies suggest that quinone functionalities within natural organic matter can be a suitable electron transfer mediator for iron bioreduction and contaminant degradation [7]. It has been determined that the efficiency of quinone redox mediators is controlled by their reduction potential, stability towards side reactions and kinetic reactivity in electron transfer reactions [7].

Here we take a first step towards identifying a potential role of plant biomass-derived black carbon in generating aromatic compounds with the ability to serve as electron transfer media. Titrations and spectroscopic information were used to test the hypothesis that redox potentials of chars vary as a function of quinone group abundance. Grass and wood chars generated across a range of heat treatment temperatures [8] allowed us to represent the varying amounts of oxygenated surface groups known to occur in natural chars.

- [1] Roden *et al.* (2010). *Nature Geoscience* **3**:417-421. [2] Lovley *et al.* (1996). *Nature* **382**:445-448. [3] Schmidt & Noack. (2000). *Global Biogeochem. Cycles* **14**:777-793. [4] Rodionov *et al.* (2010). *Global Biogeochem. Cycles* **24**:Gb3013. [5] Lehmann J. (2007). *Nature* **447**:143-144. [6] Studebaker *et al.* (1956). *Ind. & Eng. Chemistry* **48**:162-166. [7] Uchimiya & Stone. (2009). *Chemosphere* **77**:451-458. [8] Keiluweit *et al.* (2010). *ES&T* **44**:1247-1253.

Modelling phase behaviour in the geological storage of carbon dioxide

O. WARR^{1*}, C.J. BALLENTINE¹ AND A. MASTERS²

¹SEAES, University of Manchester, M13 9PL, UK

(*correspondence:

oliver.warr@postgrad.manchester.ac.uk)

²CEAS, University of Manchester, M13 9PL, UK

Global warming is currently accepted as a key issue facing man. One potentially viable solution is carbon dioxide sequestration in shallow aquifers [1] where carbon dioxide is expected to exist as a supercritical phase above an underlying water phase [2]. It is essential therefore that this binary phase system is fully understood. One technique is to use trace inert proxies (i.e. noble gases) which can coexist as solute particles within both phases, the partitioning of which is affected by the extent of phase interactions (groundwater contact) and the magnitude/rate of carbon dioxide dissolution. These proxies can therefore be used to yield essential information on these processes [3].

It is however imperative that noble gas partitioning between the two phases is well constrained. We are constructing a Gibbs-Ensemble Monte Carlo simulation to model this binary phase system which will include noble gas tracers to generate the partitioning coefficients for all noble gases for the wide range of conditions expected in storage sites. This simulation simultaneously samples the molecular configurations in both water-rich and carbon dioxide-rich phases. Particles are exchanged between the two systems. At steady state the two phases are at thermodynamic equilibrium and the corresponding compositions and overall densities can be calculated. Models selected for water [4] and carbon dioxide [5] have already been extensively tested across the temperatures and pressure ranges of interest (40-150 Bar, 320-360 K) with average simulated densities being within 1.1% and 5% respectively of experimental values and thus are considered sufficiently accurate thermodynamically for incorporation into the model. Further ground-truthing for the model is being provided by lab experiments under simulated shallow aquifer conditions. We present the current progress in creating this model and discussion of the challenges which have arisen as a result of modelling such a complex system.

[1] IPCC (2005) [2] Holloway & Savage (1993) *Energy Convers. Mgmt* **34**, 925-932. [3] Ballentine & Burnard (2002) *RiMG* **47** 481-538. [4] Berendsen *et al.* (1987) *J. Phys. Chem* **91**, 6269-6271. [5] Zhu *et al.* (2009) *Chin. J. Chem. Eng.* **17**, 268-272.

Mantle heterogeneity constraints from abyssal peridotite sulfide Pb and Os isotopic compositions

JESSICA M. WARREN^{1*} AND STEVEN B. SHIREY²

¹Geological and Environmental Sciences, Stanford University

(*correspondence: warrenj@stanford.edu)

²Department of Terrestrial Magnetism, Carnegie Institution of Washington

Convection over the history of the Earth has led to multiple cycles of mantle depletion and enrichment, which are preserved as ancient chemical compositional anomalies in the oceanic mantle. Studies of long-lived radiogenic isotopes in basalts, such as Pb, have indicated significant mantle heterogeneity in both the depleted upper mantle and the mantle source of ocean island basalts. The basalt data array defines a ~2 Ga age that has been interpreted as recording mixing of ancient subducted slabs with depleted mantle.

In contrast to basalts, abyssal peridotites from oceanic ridges have the potential to constrain the sub-kilometer lengthscale of mantle variability. Analysis of Pb isotopes in peridotites has been limited by the very low concentration of Pb in these residues of mantle melting. We have employed a technique for the determination of Pb and Re-Os isotopes and concentrations in peridotite sulfides using a modified version of the Re-Os technique for sulfide inclusions in diamonds.

The Pb and Re-Os isotopic composition of 21 sulfide grains were determined for abyssal peridotites from the Gakkel and Southwest Indian Ridges. Concentrations of Pb and Os in sulfides are correlated, with a correlation coefficient of ~0.8. The relatively lower mantle normalized concentrations of Pb (27, for an average of 4 ppm) with respect to Os (470, for an average of 1.6 ppm) indicates that Pb is much less compatible in sulfide during mantle melting than previously thought. Sulfide Pb concentrations are so low that sulfides cannot be the main reservoir of mantle Pb, storing only ~2%, with the remainder hosted in silicates.

Sulfide Pb isotopic compositions extend to unradiogenic values that plot to the left of the geochron and cover a wider range than associated basalts. Pb and Os isotopic compositions are correlated, also with a coefficient of ~0.8. The Re-Os data in sulfides fall along a 2 Ga model age, similar to the age given by the Pb-Pb system for the same sulfides. Multiple grains from the same peridotite have different isotopic compositions and elemental concentrations. Taken together, these results indicate that the mantle is heterogeneous down to the sub-sample lengthscale, with the Pb-Os correlation requiring that these heterogeneities were created by prior ridge melting events at ~2 Ga.

Suspended floc: Links between microbial ecology, FeOOH and trace element dynamics

L.A. WARREN*, A.V.C. ELLIOTT AND J.M. PLACH

SGES, McMaster University, 1280 Main St West, Hamilton ON L8S4K1 Canada

(*correspondence: warrenl@mcmaster.ca)

The linkages between microorganisms and geochemical processes in environmental systems hinge on ecological relationships associated with the microbial consortia involved. These ecological relationships are often highly cooperative and macroscopically structured to enable microscale redox cycling not favourable under bulk system conditions. Suspended floc, highly microbially active, trace element (TE) rich and interactive with bulk aqueous solution, are poorly studied with respect to microbial-mineral-TE biogeochemistry. Characterization of suspended floc TE abundance and partitioning for Ag, As, Cu, Ni and Co across six variably impacted aquatic ecosystems identify floc to be a key TE sequestration sedimentary compartment, concentrating TE ~55x above that of surficial bed sediments. Further, floc TE-geochemical partitioning patterns were conserved across systems, with amorphous Fe oxyhydroxides (FeOOH) consistently as the most important sorbent phase for TE retention, irrespective of physico-chemical conditions or TE involved. Results indicate that floc TE uptake is biologically linked to floc microbial components. Floc organic concentration directly predicts floc FeOOH concentration while imaging analysis shows bacterial exopolymeric substances (EPS) fibrils, a major floc constituent, to be heavily mineralized. Thus while floc FeOOH are the dominant floc TE sequestration phase, EPS and microbial constituents are the critical foundation underpinning floc TE behaviour through their structural role in floc FeOOH occurrence, ultimately creating a distinctly different solid than bed sediments with differing controls on TE uptake. Further, the enrichment of both iron reducing and iron oxidizing microorganisms from all flocs collected across a spectrum of systems widely variant in [O₂] and pH indicate previously unconstrained Fe cycling occurs at the floc scale that is controlled by floc ecology, not by system geochemistry. These results add to the growing evidence that ecological partnership enables consortial microbes to “sidestep” geochemical constraints predicted to occur at the bulk scale.

Carbonation of artificial silicate minerals: Passive removal of atmospheric CO₂

C-L. WASHBOURNE¹*, P. RENFORTH² AND D.A.C. MANNING¹

¹School of Civil Engineering and Geosciences, Newcastle University, NE1 7RU, United Kingdom

(*correspondence: carla-leanne.washbourne@ncl.ac.uk)

²Department of Earth Sciences, University of Oxford, Oxford, OX1 3AN, United Kingdom

Artificial silicate minerals present an accessible source of material for enhanced weathering. Silicate ‘wastes’ may perform carbon sequestration through *in situ* carbonation of calcium (Ca) and magnesium (Mg) phases. Maximum carbon (C) capture potential using artificial silicates is 190-332Mt C a⁻¹ [1]. Soil engineering, promoting CO₂ sequestration by inclusion of these reactive mineral substrates, has the potential to capture a portion of the C turnover of the global pedologic system; 75 Gt C a⁻¹ [2][3][4].

Stable isotope data (δ¹³C, δ¹⁸O) confirm that >50-90% of C in pedogenic carbonates, formed on artificial silicates, is atmospherically derived. Field observations and laboratory data demonstrate that anthropogenic soils accumulate 20-30 kg C m² as carbonates (≥organic carbon content in natural soils). Flow-through experiments (25°C, 1 atm.) using fresh basic steel slag show pH buffered at ~11.6 as Ca leaches at a rate of log₁₀-8.9 – log₁₀-9.3 mol⁻¹sec⁻¹cm⁻², several orders of magnitude faster than ‘natural’ silicates. Once portlandite (Ca(OH)₂) has been consumed pH is reduced to ~9.1 and calcium carbonate precipitation continues.

Effective, low-energy field-scale implementation of mineral carbonation through soil engineering could assuage current constraints on economic performance [5][6][7]. Proof of principle for carbonation of artificial silicates in engineered soils has been demonstrated [4]; proof of field scale feasibility will be demonstrated through continued empirical and experimental observation including extensive analysis of carbon in urban soils at the Science Central development site, Newcastle upon Tyne, UK.

[1] Renforth *et al.* (2011), *Environ Sci Technol* **45** (6) 2035-41
 [2] Schlesinger *et al.* (2000), *Biogeochem*, **48**; 7-20 [3] Manning (2008), *Min Mag*, **72**; 639-649 [4] Renforth *et al.* (2009), *Applied Geochem*, **24** (9) 1757-1764 [5] Butt *et al.* (1997), *Global Warming International Conference*, Columbia NY. [6] Huijgen *et al.* (2005), *Environ Sci and Technol* **39**: 9676-9682 [7] Lackner *et al.* (1997), *Energy Conversion and Management* **38**: S259-S264

Pathways of dissolved organic matter in the subterranean estuary: Evaluation of organic geochemical tracers

HANNELORE WASKA^{1*}, MICHAEL SEIDEL¹,
THORSTEN DITTMAR¹ AND GUEBUEM KIM²

¹Max Planck Research Group for Marine Geochemistry,
ICBM, University of Oldenburg, Germany
(*correspondence: hwaska@mpi-bremen.de,
mseidel@mpi-bremen.de, tdittmar@mpi-bremen.de)

²Environmental and Marine Biogeochemistry Laboratory,
School of Earth and Environmental Sciences, Seoul
National University, South Korea (gkim@snu.ac.kr)

The mixing zone of fresh terrestrial groundwater and recirculating seawater in a coastal permeable aquifer, the so-called “subterranean estuary”, is a powerful bioreactor which determines the fate of dissolved compounds as they are transported into the ocean via submarine groundwater discharge (SGD). Dissolved organic matter (DOM) plays a crucial role in driving microbial remineralization processes, and through its breakdown contributes to the groundwater nutrient pool. Until recently, DOM in the subterranean estuary was mostly determined as bulk dissolved organic carbon, providing limited information on sources and degradation states. Studies of chromophoric DOM (CDOM) and biomarkers such as lignin provide information on DOM origin. Other traditional parameters, such as amino acid D/L ratios and degradation indices, and stable isotopic composition (e.g. $\delta^{13}\text{C}$), can be used to track the processing of DOM. Emerging analytical techniques, e.g. ultra-high resolution Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), improve our understanding of the chemical composition of DOM by providing molecular fingerprints. We investigated two intertidal subterranean estuaries, in Hampyeong Bay along the Yellow Sea coast of South Korea and on Spiekeroog Island, a barrier island in the German Wadden Sea. The major objective was to characterize pathways of DOM as it travels through the aquifer. In Hampyeong Bay, amino acid and CDOM data pointed to a mostly marine DOM source, whereas on Spiekeroog, $\delta^{13}\text{C}$ values indicated both a marine and a terrestrial DOM source. Molecular fingerprinting showed that a large amount of DOM was processed in the aquifer of Spiekeroog Island, whereas several components were passing the subterranean estuary unaltered, possibly forming a source of refractory DOM.

Is your clean lab full of zinc?

L.E. WASYLENKA^{1*}, E.B. WILKES² AND A.D. ANBAR³

¹Dept. of Geological Sciences, Indiana University, 1001 East
Tenth Street, Bloomington, IN 47405-1405 USA

(*correspondence: lauraw@indiana.edu)

²Dartmouth College, Hanover, NH 03755 USA

³School of Earth and Space Exploration and Dept. of
Chemistry and Biochemistry, Arizona State University,
Tempe, AZ 85287 USA

Contamination of samples with extraneous zinc is likely much more common and severe than many metal isotope geochemists expect. Bottles, tubes, pipette tips, and especially disposable gloves are often produced with Zn stearate as the mold release agent. By far the largest amount of zinc is introduced by gloves. Dilute HCl will effectively rid other items of Zn, but gloves cannot be cleaned easily, and their use can lead to surface contamination throughout the lab.

We recently conducted experiments in which dissolved Zn was partly adsorbed onto Mn-oxide particles. The dissolved and adsorbed pools were separated by filtration, and isotope ratios were analyzed by MC-ICP-MS. A commercial ICP solution was both our standard ($\delta^{66/64}\text{Zn} = 0$) and the source of Zn in the experiments. When gloves were worn for sample handling, blanks contained as much as 150 ng Zn, and both the dissolved and adsorbed pools came out enriched in heavy isotopes relative to the starting pool, in apparent violation of mass balance. Without gloves, blanks were lower, but still variable, and mass balance was more closely satisfied. Zinc leached from two brands of allegedly low-zinc vinyl gloves was +10‰ relative to our standard ($\delta^{66/64}\text{Zn}$). We conclude that glove Zn in our lab contaminated our samples, even when gloves were not worn for sample processing.

We were only able to see clear evidence of contamination because (1) we had an expectation of mass balance, and (2) we happened to use a standard strongly enriched in light isotopes relative to our gloves. We caution others who measure unknown, natural samples that most natural samples are similar in isotopic composition to the gloves we measured and to JMC-Lyon Zn, which is becoming an accepted Zn isotope standard. Knowing whether variable amounts of glove zinc are contaminating samples is therefore a challenge. We recommend very careful monitoring of blanks and column chemistry yields, and we plan to designate and clean a glove-free workspace within the clean lab for further zinc isotope work.

Raman spectroscopic insight into structural changes in berlinite with high pressure and temperature

ANKE WATENPHUL^{1*} AND CHRISTIAN SCHMIDT²

¹Deutsches Elektronen-Synchrotron DESY, Notkestr. 86, 22603 Hamburg, Germany (anke.watenphul@desy.de)

(* correspondence: anke.watenphul@desy.de)

²Deutsches GeoForschungsZentrum (GFZ), Telegrafenberg, 14473 Potsdam, Germany (hokie@gfz-potsdam.de)

Berlinite (AlPO₄) and α -quartz are structural isotypes, which are related to each other by the coupled substitution 2 Si = Al + P. The SiO₄ tetrahedra along the *c*-axis in α -quartz are replaced in berlinite by alternating AlO₄ and PO₄ tetrahedra. This preferred ordering results in a doubled *c* unit-cell parameter. The frequencies of Raman modes of berlinite and α -quartz are very similar because the atomic masses of Al + P are almost the same as that of two Si atoms [1]. However, detailed inspection reveals a greater complexity in the Raman spectrum of berlinite [2]. To obtain more information on the relationships to the berlinite structure, we studied the strong A₁-Raman lines at 462 and the 1111 cm⁻¹ at temperatures up to 800 °C and pressures up to 10 GPa.

The positions of both bands shift in the opposite direction with pressure (*P*) and, likewise, with temperature (*T*). The 1111 cm⁻¹ Raman line is accompanied by a less intense band at 1104 cm⁻¹. With increasing *P*, the 1111 cm⁻¹ band shifts towards lower wavenumbers and that at 1104 cm⁻¹ to higher wavenumbers. Both lines thus display the same frequency at about 1.4 GPa at 23 °C. With further increase in *P*, they become fully separated above 5 GPa. Both Raman lines originate from stretching vibrations of the PO₄ tetrahedra. The opposed behavior with pressure is tentatively interpreted as being caused by the alternate succession of the AlO₄ and PO₄ tetrahedra along the *c*-axis, which permits a different compression/extension of the P-O1 and P-O2 distances.

The results also indicate the great potential of berlinite as a pressure sensor for diamond-anvil cell experiments, including studies at elevated *T*. A relative shift, defined by the difference of the shifts in the wavenumber between the 462 and the 1111 cm⁻¹ lines with *P* and *T*, can be used as pressure gauge. Moreover, this sensor may be applicable at higher pressures than α -quartz [3] because no high-pressure polymorph isomorphic to coesite or stishovite is known.

[1] Scott (1971), *Phys. Rev. B* **4**, 1360-1366. [2] Gregora *et al.* (2003) *J. Phys.: Condens. Matter* **15**, 4487–4501. [3] Schmidt & Ziemann (2000), *Am. Mineral.* **85**, 1725-1734.

Effect of ionic strength on Ca isotope and Sr incorporation into calcite

J. WATKINS^{1*}, D.J. DEPAOLO^{1,2}, F.J. RYERSON³ AND M. GONZALES⁴

¹Univ. of California-Berkeley, Berkeley, CA 94720, USA (*correspondence: jwatkins@berkeley.edu)

²Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

³Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

⁴The Pennsylvania State, University Park, PA 16802, USA

Chemical reactions in nature lead to stable isotope variations in part because diffusivities and reaction rates are mass-dependent. For crystals grown from aqueous solution, there is no general theory that relates reaction rate to mass, but the contribution of isotope-specific reaction rates to the net isotope composition of a mineral must be related to processes occurring at the mineral-fluid interface.

Laboratory experiments have shown that the Ca isotope composition ($\delta^{44}\text{Ca}$) of calcite precipitated from aqueous solution varies considerably (up to 1.5‰) and correlates with the crystal growth rate (*R*). Generally, inorganic calcite precipitation experiments yield calcite crystals that are enriched in the light isotope of Ca relative to the parent solution. The degree of light isotope enrichment correlates with Sr/Ca in calcite. These observations indicate that variations in $\delta^{44}\text{Ca}$ in calcite reflect a mass dependence on reaction rate coefficients (*k*) and that the physical process responsible for mass discrimination is also responsible for trace element discrimination. We postulate that dehydration/rehydration kinetics of Ca²⁺ and Sr²⁺ and/or the presence of impurities on the mineral surface are controlling the kinetic isotope and trace element effects. If true, the presence of other ions (e.g. NH₄⁺) in solution should perturb the stability of the hydration shell of Ca²⁺ and Sr²⁺ and also interfere with their incorporation into the mineral lattice.

We present results from inorganic calcite precipitation experiments using two solutions that differ in ionic strength (*I*=0.095 vs. *I*=0.485 mol/l). In low ionic strength experiments, we observe correlations between $\delta^{44}\text{Ca}$, Sr/Ca and *R* that are in excellent agreement with results from a previous study that used a similar parent solution composition (Tang *et al.*, *GCA*, 2008). In our initial experiments at high ionic strength, values of $\delta^{44}\text{Ca}$ vs. *R* and Sr/Ca vs. *R* lie off the previous trends, but $\delta^{44}\text{Ca}$ and Sr/Ca co-vary such that $\delta^{44}\text{Ca}$ vs. Sr/Ca is relatively independent of solution composition. Additional experiments are underway and results will be discussed in the context of molecular-scale processes - and their liquid composition-dependence - controlling isotopic and trace element incorporation into minerals.

Sum Frequency Vibrational Spectroscopy (SFVS) of water and hydroxyls on the corundum (1 $\bar{1}$ 02) surface: Acid-base properties from direct observation of protonation states

G. A. WAYCHUNAS^{1*}, J. SUNG² AND Y. R. SHEN²

¹Earth Sciences Division, LBNL, Berkeley, CA 94720, USA

(*correspondence: gawaychunas@lbl.gov)

²Physics Department, UC Berkeley, Berkeley, CA 94720 USA

SFVS is a powerful tool for quantitative measurement of protonated functional groups on mineral surfaces, especially when used in a phase-sensitive mode [1]. This is demonstrated for the corundum (1 $\bar{1}$ 02) interface where the orientation and nature of surface hydroxyls on the dry protonated surface can be obtained and compared with models for the surface termination derived from crystal truncation rod (CTR), X-ray reflectivity (XRR) measurements, and with the most likely functional group assignments [2]. Hydroxyl orientations are determined from pole-figure type measurements of the magnitude of the non-linear optical susceptibility for each band, and the polar orientation (up-down with respect to the z-direction) is determined from measurements of the imaginary part of the susceptibility. A scheme for describing the hydrogen bonding among these protonated groups is found to be consistent with surface symmetry and the particular vibrational frequencies observed. The addition of water to the interface alters the hydrogen bonding of the hydroxyls and introduces water-functional group hydrogen bonding [3]. Direct measurement of the SFVS hydroxyl and water band amplitudes as a function of pH can be used to test the expected pKa values for the functional groups, and hence link interfacial acid-base properties to precise molecular surface entities and their protonation states.

This research has been in part supported by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy.

[1] Shen & Ostroverkhov (2006) *Chem. Rev.* **106**, 1140-1154.

[2] Sung *et al.* (2011) *J. Amer. Chem. Soc.* **133**, 3846-3853.

[3] Sung *et al.* (in review, *J. Amer. Chem. Soc.*)

Evolution of the lower crust from S. Mexico: Constraints from Lu-Hf isotopes and U-Pb ages in zircon

B. WEBER^{1*}, E. SCHERER², K. MEZGER³ AND J. RUIZ⁴

¹CICESE, 22860 Ensenada B.C., México

(*correspondence: bweber@cicese.mx)

²Mineralogie, WWU, D-48149 Münster, Germany

³Geologie, Uni Bern, CH-3012 Bern, Switzerland

⁴Geosciences, Univ. Arizona, Tucson AZ, 85721 USA

Unraveling the origin and tectonic evolution of lower continental crust is often complicated by granulite facies metamorphism that obscures petrogenetic features and resets isotopic systems. In order to reconstruct the assemblage of ancient supercontinents (like Rodinia), it is crucial to understand the evolution of individual crustal blocks, its relations, and its position with respect to the cratons. Four isolated lower crustal complexes of mid-Proterozoic (Grenville) age also referred to as "Oaxaquia" [1] are exposed in E and SE Mexico. Oaxaquia was interpreted in terms of arc magmatism, followed by backarc rifting, and migmatization, predating AMCG (anorthosite-mangerite-charnockite-granite) intrusions and granulite facies metamorphism [2].

U-Pb zircon dating by laser ablation MC-ICPMS and single-grain Lu-Hf analysis by solution MC-ICPMS was applied to elucidate crustal growth and igneous history of Oaxaquia. Typical Oaxaquia rocks include AMCG suite rocks as well as arc-type migmatites and orthogneisses, all of which having zircon cores at ~1.2 Ga, additional igneous growth zones migmatite zircons, and granulite facies rims at ~1.0 Ga. Hafnium isotopes of typical Oaxaquia rocks display little variations yielding $T_{DM(Hf)}$ model ages from 1.50 to 1.65 Ga [3]. Significant differences could be observed in zircons from E Mexico orthogneiss (Huiznopala) with $T_{DM(Hf)}$ at ~1.8 Ga [3]. New detailed laser dating of such zircons revealed mostly ~1.4 Ga and older zircon cores, surrounded by ~1.2 Ga igneous zones, indicating melting of crustal precursors different from typical Oaxaquia.

The results lead to a new model in which typical Oaxaquia evolved as juvenile arc in the early mid-Proterozoic. Continental crustal slices, probably from the continental arc of Amazonia, were thrust over or attached to the Oaxaquia oceanic arc, which was then buried and partially melted to produce AMCG rocks prior to the collision with Baltica during the final stage of Rodinia assemblage.

[1] Ortega-Gutiérrez *et al.* (1995) *Geology* **23**, 1127-1130. [2]

Keppie *et al.* (2003) *Precambrian Res* **120**, 365-389. [3]

Weber *et al.* (2010) *Precambrian Res* **182**, 149-162.

Airborne measurements of volcanic particles and gases with small aircrafts — Examples of measurements in the Eyjafjallajökull ash plume over Germany and Iceland

K. WEBER^{1*}, J. ELIASSON², A. VOGEL¹, C. FISCHER¹, M.F. MEIER³, B. GROBÉTY³ AND D. DAHMANN⁴

¹University of Applied Science, 40474 Düsseldorf, Germany
(*correspondence: konradin.weber@fh-duesseldorf.de)

²University of Iceland, 107 Reykjavik, Iceland

³University of Fribourg, 1700 Fribourg, Switzerland,

⁴IGF, 44789 Bochum, Germany

During the 2010 eruption period of the Eyjafjallajökull the University of Applied Sciences of Duesseldorf and the University of Reykjavik performed several measurement flights with small aircraft in the volcanic plume. Whereas the University of Applied Sciences mapped the distal plume over Germany, the University of Iceland explored the airspace over western Iceland and near the Eyjafjallajökull, partly entering the volcanic plume boundary directly.

The use of the small piston-motor driven research aircraft in the special situation of volcanic plumes has several advantages over jet engine driven research aircrafts:

The piston-motor driven aircraft are robust enough to operate even at elevated ash concentration levels.

The small aircrafts allow a low cruising speed during the measurements and have thus the advantage of delivering results with a high spatial resolution.

The low possible aircraft cruising speed during the measurements simplifies the intake of even bigger ash particles into the measurement systems.

Small aircraft allow a very cost effective operation.

The aircraft were equipped with optical particle counters (OPCs) for on-line in-situ results. Moreover, the German aircraft was equipped with a DOAS system for SO₂ and a NDIR analyzer for CO₂ measurements.

The measurement flights revealed that the ash plume over Germany had a very inhomogeneous structure. Sub-plumes and different vertical plume layers could be identified. Regional elevated SO₂ concentrations could be detected. Peak ash particle concentrations of more than 330 µg/m³ could be found during the measurement flights over northern Germany, whereas the flights over Iceland showed low concentrations outside the plume, but values of about 2000 µg/m³ within the boundary of the plume.

A “cradle to grave” analysis of geothermal arsenic in a lowland river system

J.G. WEBSTER-BROWN^{1*}, N.J. WILSON², A.F. HEGAN³, H.K. CHRISTENSON¹ AND P.J. SWEDLUND⁴

¹Waterways Centre for Freshwater Management, University of Canterbury, Christchurch, New Zealand
(*jenny.webster-brown@canterbury.ac.nz, hannah.christenson@pg.canterbury.ac.nz)

²University of Bayreuth, Bayreuth, Germany
(nathaniel.wilson@uni-bayreuth.de)

³SEAES, University of Manchester, United Kingdom.
(aimee.hegan@manchester.ac.uk)

⁴Department of Chemistry, University of Auckland, New Zealand (p.swedlund@auckland.ac.nz)

In the central North Island of New Zealand, arsenic is released from geothermal hot springs into the large lowland Waikato River, and thereafter into the Tasman Sea. Aspects of arsenic geochemistry in the geothermal fluids, and in the river and its lake waters, have been previously studied but a catchment-scale analysis of factors affecting geothermal arsenic on its journey to the sea has highlighted the importance of biological as well as geochemical processes.

Evidence for biological interactions with arsenic occurs on a different timescale to that typically used to identify geochemical interactions. For example, when arsenic is released into the surface environment via the Champagne Pool hot spring at Waiotapu, it occurs predominantly as arsenite ion. In the outflow arsenic is immediately exposed to a regime of decreasing temperature, attended by increasing oxygen and periodic influxes of H₂S from small fumeroles, favouring oxidation to arsenate ion or removal as orpiment (As₂S₃) respectively. However, diurnal variations in arsenic concentrations in the outflow confirm the influence of photosensitive microorganisms, evidently through their intervention in dissolved sulphide-sulphate equilibria. Similarly, after discharging into the Waikato River, geothermal arsenic appears to be most immediately controlled by adsorption to the iron oxide component of SPM. However, long term adsorption experiments under light/dark conditions, and a more detailed assessment of the competitive adsorption of important diatom nutrients; silica and phosphate, indicate that arsenic concentration is not regulated simply by the availability of iron oxide adsorption sites. In a river such as the Waikato, enriched in both geothermal silica and agricultural phosphate, diatom growth and decay also influences arsenic speciation and mobility.

Thermophilic anaerobic oxidation of methane performed by novel microbial consortia

G. WEGENER^{1,2}, K. KNITTEL¹, T. HOLLER¹,
V. KRUKENBERG¹, F. WIDDEL¹ AND A. BOETIUS^{1,2,3}

¹Max Planck Institute for Marine Microbiology, Bremen, Germany

²MARUM, Center for Marine Environmental Sciences, Bremen, Germany

³Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany

The anaerobic oxidation of methane with sulfate (AOM) controls the emission of the greenhouse gas methane from the ocean floor and is performed by microbial consortia of archaea (ANME) associated with bacterial partners [1]. So far, *in vitro* propagation of AOM was documented for temperatures up to approx. 25°C, but the presence of molecular ANME markers in hydrothermal sediments suggests higher temperature ranges for this process [2, 3]. In natural enrichments from Guaymas Basin hydrothermal sediments we show *in vitro* propagation of AOM up to 70°C with a growth optimum of 50°C and doubling times of around 60 days. We performed microbiological experiments and genetic, microscopic and mass spectrometric analyses to characterize the key agents in thermophilic AOM. The hot Guaymas enrichments are dominated by filamentous ANME-1 archaeal cells, which form individual sheaths around their bacterial partners. These belong to the deep-branching HotSeep-1 cluster which closest relatives are thermophilic sulfur reducers, e.g. *Desulfurella*. So far the interaction between these novel ANME-1 types and their bacterial partners is not resolved, but the highly structured consortia support previous hypotheses of an obligate syntrophic partnership. Furthermore, our results indicate that AOM might be more widespread than previously assumed including hot subsurface sediments and gas reservoirs [4,5].

[1] Knittel & Boetius (2009) *Annu Rev Microbiol* [2] Teske *et al* (2002) *AEM* [3] Schouten *et al* (2003) *AEM* [4] Speed & Clayton (1975) *Geology* [5] Werner *et al* (1988) *Chem Geol*

Spinels under elevated pressures and temperatures – A synchrotron study

M. WEHBER^{1*}, C. LATHE² AND F. SCHILLING³

¹DESY/HASYLAB, Notkestrasse 85, 22607 Hamburg, Germany (*correspondence: michael.wehber@desy.de)

²Helmholtz-Centre Potsdam, GFZ German Research Centre for Geosciences, Telegrafenberg, 14473 Potsdam, Germany (christian.lathe@desy.de)

³KIT Karlsruhe Institute for Technology, Institute for Applied Geosciences, Kaiserstrasse 12, 76131 Karlsruhe, Germany (frank.schilling@kit.edu)

Spinels have the general formula AB_2O_4 and crystallize in the cubic spacegroup Fd-3m. They play important roles in geosciences and technical applications. The aim of this study was to make simultaneous high-pressure/high-temperature (HP/HT) measurements to find out how the thermal expansion behave under high pressure.

In this study, the three different spinels magnetite ($FeFe_2O_4$), franklinite ($ZnFe_2O_4$) and gahnite ($ZnAl_2O_4$) were investigated with energy-dispersive powder XRD using two different multi-anvil-presses at HASYLAB. Isothermal experiments were performed up to 15 GPa using MAX200x, thermal experiments up to 5 GPa and 1100 K using MAX80. Diffraction data were evaluated with the Rietveld-method to obtain the cell parameter of the sample and the pressure medium. Pressure-volume-data were fitted to second and third order Birch-Murnaghan equation of state to obtain the bulk moduli of each sample. In addition, the thermal expansion coefficient were calculated at different pressures.

Evaluation of the HP measurements yielded the following bulk moduli. For magnetite: $K_{T2nd} = 187(6)$ GPa, $K_{T3rd} = 184(7)$ GPa with $K' = 4.5(2)$, for franklinite $K_{T2nd} = 180(5)$ GPa, $K_{T3rd} = 178(6)$ GPa with $K' = 4.6$ and for gahnite $K_{T2nd} = 207(7)$ GPa, $K_{T3rd} = 204(9)$ GPa with $K' = 4.9$. HP/HT experiments showed a linear pressure dependence of the thermal expansion at least up to 5 GPa ($-1.3 \cdot 10^{-6}$ (K/GPa)⁻¹ for magnetite, $-1.7 \cdot 10^{-6}$ (K/GPa)⁻¹ for franklinite and $-3.0 \cdot 10^{-6}$ (K/GPa)⁻⁶ for gahnite). There seems to be an additional connection to the iron content of the spinels whereat the increase of the iron content decreases the slope of the pressure dependence.

On the fluid-mobility of molybdenum, tungsten, and antimony in subduction systems

H. WEHRMANN^{*1}, R. HALAMA²,
D. GARBE-SCHÖNBERG², K. HOERNLE^{1,3}, G. JACQUES¹,
K. HEYDOLPH^{1,3}, J. MAHLKE^{1,3} AND K. SCHUMANN^{1,3}

¹Sonderforschungsbereich 574, IFM-GEOMAR, Kiel,
Germany (*hwehrmann@ifm-geomar.de)

²Sonderforschungsbereich 574, Institute of Geosciences of the
University of Kiel, Germany

³IFM-GEOMAR, Kiel, Germany

Molybdenum (Mo) and tungsten (W) have long been regarded as being more or less immobile during slab fluid-induced arc magma generation. Here we characterize about 180 samples of young, predominantly mafic to intermediate tephros and lavas for their Mo, W, and antimony (Sb) concentrations, to examine the fluid-mobility of these elements in subduction systems. Samples were taken along the active arcs of the Chilean Southern Volcanic Zone (SVZ) and the Central American Volcanic Arc (CAVA). When relating Mo, W, and Sb to trace element ratios typically used to constrain the involvement of subduction fluids in magma formation, such as Ba/La or U/Th, Mo, W, and Sb are enriched in the most fluid-influenced, highest-degree melts. W/Mo ratios correlate positively with Pb/Ce, which is established to reflect a recent subduction signal or assimilation of crustal material with an ancient subduction signature, suggesting that subduction processes promote enrichment of W over Mo. This is well expressed at the SVZ and most of the CAVA; while few OIB-type rocks from Central Costa Rica form an opposite trend. Moreover, Mo/W ratios co-vary with Cl contents derived from melt inclusions, indicating that the relative degree of mobilization responds to the composition of the subduction fluid. To evaluate the mobility of Mo, W, and Sb during metamorphism in the slab, eclogites with no or minor metasomatic overprint and a fluid-induced overprint in an eclogite-blueschist sequence were investigated. None of the three elements shows a systematic variability related to metasomatism and the minor variations are interpreted to reflect protolith heterogeneity. This suggests that Mo, W and Sb remain relatively immobile up to depths of 70 km in the subduction zone.

Long-term development of diagenetic signals of past sulfate-methane transition zones in subseafloor sediments

L. M. WEHRMANN^{1*}, C. MÄRZ², P. MEISTER¹,
C. OCKERT³, B. BRUNNER¹, N. GUSSONE³,
B.M.A. TEICHERT³ AND T.G. FERDELMAN¹

¹Max Planck Institute for Marine Microbiology, Bremen,
Germany (*correspondence: lwehrman@mpi-bremen.de,
pmeister@mpi-bremen.de, bbrunner@mpi-bremen.de,
tferdelman@mpi-bremen.de)

²Newcastle University, UK (christian.maerz@newcastle.ac.uk)

³University Münster, Germany
(charlotte.ockert@uni-muenster.de,
Nikolaus.Gussone@uni-muenster.de,
barbara.teichert@uni-muenster.de)

Anaerobic oxidation of methane (AOM) coupled to sulfate reduction in the sulfate-methane transition zone (SMTZ) leaves prominent diagenetic carbon and sulfur signatures in pore-water and solid-phase chemistry that are preserved over geological time scales. We report on the evolution of these signals in the sediments of Site U1341 drilled during Integrated Ocean Drilling Program (IODP) to the Bering Sea to a depth of 600 meters below seafloor (mbsf). At this site, present-day microbial activity associated with organic carbon mineralization is comparably low as evidenced in low dissolved inorganic carbon (DIC) concentrations, and a minor decrease in sulfate concentrations in the top 50 mbsf. Strong decrease of sulfate concentrations below 140 mbsf mirrored by pronounced ³⁴S-sulfate enrichment at the depth of minimum sulfate concentrations suggest that the extent of microbial sulfate reduction was high in this sediment interval during a period of elevated primary productivity in the water column between 2.48 and 2.56 Ma. Elevated sulfate reduction rates drove sulfate to depletion and facilitated the onset of methanogenesis, AOM and the installation of a SMTZ. Rates of these processes apparently declined as a consequence of decreased availability of organic carbon during later time periods. This interpretation is consistent with ³⁴S-enriched pyrite, ¹³C-depleted dolomite phases and barium depletion to detrital background in distinct sediment intervals. Close examination of the diagenetic pore-water and solid-phase signals, however, revealed that their relative positions in the sedimentary sequence considerably diverge. Also, pore-water DIC, sulfate, Ca and Mg concentrations and isotope profiles do not covary systematically. Our results suggest variable responses of diagenetic signals produced by past SMTZs in the pore-water and sediment over prolonged time scales.

Seawater pH records from a fringe coral reef in southern Hainan Island, the Northern South China Sea: Implications for ocean acidification

GANGJIAN WEI¹, LUHUA XIE¹, WEIZHONG WU¹, WENFENG DENG¹ AND MALCOLM T. MCCULLOCH²

¹State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

²School of Earth Environment, The University of the Western Australia, WA 6009, Perth, Australia

The observations for seawater pH time-series have been conducted since 2008 in Luhuitou coral reef, fringed to Sanya in the southern Hainan Island, the northern South China Sea (SCS). Diurnally cycles are the most significant variations for seawater pH on coral reef, with amplitudes up to 0.3~0.6 in general. High pH generally occur at noon (12 am ~ 2 pm), while low pH generally occur at mid-night (0 am ~ 2 am). The pH variations are highly correlated to those of dissolved inorganic carbon (DIC) and dissolved oxygen (DO) concentrations in seawater, as well as $\delta^{13}\text{C}$ of DIC and sea surface temperature (SST). This suggests that such seawater pH changes are mainly controlled by photosynthesis and respirations of the bio-mass on coral reef. Seasonal seawater pH variations on this coral reef are of ~0.3, and an ~0.1 pH decrease trend from 2008 to 2010 can be figured out. Such variation patterns apparently correlate to changes in atmospheric CO_2 concentration, but the variation amplitudes are significantly larger than that contributed from the increasing $p\text{CO}_2$. Ecosystem decline on this coral reef possibly resulted from rapid urbanization in this region may account such seawater pH decrease.

A seasonal-resolution seawater pH record from 1980 to 1996 has also been reconstructed by the $\delta^{11}\text{B}$ of a *Porites* coral from this reef. No decline trend of seawater pH has been observed during this period. Periodical variation with an apparent 10-yr period is clearly presented in this record, which is similar to that from the Great Barrier Reefs of Australia [2]. This indicates that natural variations for seawater pH with large annual amplitude (0.1~0.3) are generally observed on coral reefs in the west Pacific. Such variations are comparable to the predicted ocean acidification trend in the following century (0.3~0.4 for global ocean: [1]).

[1] Caldeira and Wickett, 2003 *Nature*, , **425**:365. [2] Wei *et al.*, 2009 *Geochim. Cosmochim. Acta*, , **73**:2332–2346

Deltaic landforms and stratigraphic controls on groundwater arsenic

B. WEINMAN^{1*}, S.L. GOODBRED², A. VAN GEEN³ AND A.K. SINGHVI⁴

¹Univ of Minnesota, St. Paul, MN 55108, USA
(*correspondence: bweinman@umn.edu)

²Vanderbilt Univ., Nashville, TN 37235, USA

³Lamont Doherty Earth Observatory, Palisades, NY 10964, USA

⁴Physical Research Laboratory, Ahmedabad 380-009, India

Sediment deposits can have physical (hydraulic conductivity and anisotropy) and chemical (diagenetic) effects on biogeochemical cyclings. In Asian deltas, our sedimentological work shows that groundwater arsenic heterogeneity can be explained by an aquifer's depositional history. In Bangladesh, variable thicknesses of the floodplain's mud-capping (0-13m) allows for differential flushing in the shallow aquifer [1]. In turn, this allows for differential groundwater arsenic concentrations over 10's of meter distances, supporting more of a physical (flushing) control on arsenic by the sediments. In Vietnam, there is a more "chemical" type of sedimentary control, with higher groundwater arsenic sourced in Holocene sands, while lower arsenic is seen in water from Pleistocene units. This is different than the more "physical" sedimentary control observed in Bangladesh, indicating more of a reactive-transport or chemical (weathering) control by the sediments [2, 3].

Despite these differing chemical and physical effects on groundwater arsenic by their host sediments, one commonality between these and other arsenic-prone regions is that abandoned-channel facies consistently serve as local depocenters for muds and/or Holocene sand units, which both correlate to higher groundwater arsenic. This raises an ancillary concern about hydroelectric and other river-diverting projects, which can leave downstream areas starved for both sediments and water [4,5]. In the case of groundwater arsenic, we see these types of diversions as potentially mimicking the natural waning associated with the abandonment by a river, leaving a potential for new landforming events favoring higher arsenic concentrations in the groundwater.

[1] Weinman *et al.* (2008) *GSA Bulletin* **120**,1567-1580. [2] White & Brantley (2003) *Chemical Geology* **202**, 479-506. [3] Davis *et al.* (2004) *Eos* **85**(44), 449,455. [4] Vorösmarty *et al.* (2009) *Bull. Atomic Sci* **65**(2), 31-34. [5] Khalequzzaman (1994) *Nat Hazards* **9**, 65-80.

Isotopic fractionation of Cu in plants

CHARLOTTE WEINSTEIN*¹, FREDERIC MOYNIER¹,
KUN WANG¹, RANDAL PANNELLO¹, JULIEN FORIEL¹ AND
SYLVAIN PICHAT²

¹Department of Earth and Planetary Sciences, Washington University in St. Louis, 1 Brookings Dr., St. Louis, MO 63130, USA (*correspondence: cbweinstein@wustl.edu)
²Laboratoire de Sciences de la Terre, Ecole normale supérieure de Lyon, 46 allée d'Italie, 69007 Lyon, France

Knowledge of the copper cycle in the plant-soil-water system is needed in order to better constrain proper plant micronutrient nutrition, control pollution, and determine sustainable soil management practices. Here, we will report the Cu isotopic compositions of different components (seeds, germinated seeds, leaves, and stems) of the dicot, lentil (*Lens culinaris*), and of two monocots, Virginia wild rye (*Elymus virginicus*) and hairy-leaved sedge (*Carex hirsutella*). The isotopic measurements were done by multi-collection inductively coupled plasma-mass spectrometry at Washington University following the procedure described in [1,2,3]. Our data are reported in permil deviation ($\delta^{65}\text{Cu}$) from the standard, NIST 976. The isotopic compositions of these plants ($\delta^{65}\text{Cu} \approx -0.43, -0.41$) are systematically enriched in the lighter isotope of Cu (^{63}Cu) in comparison to the soil in which they grow ($\delta^{65}\text{Cu} \approx +0.19$), suggesting a preferential uptake of ^{63}Cu into the plant. Furthermore, different components within the plants themselves are isotopically fractionated. The shoots (stems, leaves and seeds) are systematically lighter than the underground parts of the plants and the Cu isotopic compositions of individual leaves become lighter in correlation with their heights on the plant. These results are similar to what has been observed for Zn isotopes, which are assumed to be transported through plants by means of diffusion and kinetic fractionation across cell membranes [4]. Because of this similarity, we suggest that the same transport mechanisms (diffusion and transport through cell membranes) are also responsible for the observed isotopic fractionation of Cu. Furthermore, the Cu isotopic variations measured in plants are similar in magnitude to the differences previously measured in various soils, and therefore should be taken into account in order to accurately interpret the isotopic compositions of Cu in soils.

[1] Marechal *et al.* (1999) *Chem Geol.* **156**, 251-273. [2] Moynier *et al.* (2006) *Geoch. Cosmo. Acta*, **70**, 6103-6117. [3] Moynier *et al.* (2010) *Geoch. Cosmo. Acta* **74**, 799-807. [4] Moynier, F. *et al.* (2009) *Chem. Geol.*, **267**, 125-130.

ULVZ as repository for the enriched component in the Hawaiian source

D. WEIS¹, M.O. GARCIA², J.M. RHODES³, M. JELLINEK¹
AND J.S. SCOATES¹

¹PCIGR, EOS, University of British Columbia, Vancouver BC, V6T1Z4, Canada (dweis@eos.ubc.ca)
²Geology & Geophysics, Univ. Hawai'i, Honolulu, HI 96822
³Geology & Geography, Univ. Massachusetts, Amherst, MA 01003, USA

The origin, scale and location of mantle heterogeneities have been debated for over 50 years. Improved analytical precision for radiogenic isotopes, combined with statistical data analysis, allow for more detailed investigations into the geochemical variations of basalts related to mantle plumes and for modeling of the shallow and deep plume conduit and structure. Identification of two clear geochemical trends (Loa and Kea) among Hawaiian volcanoes [1, 2] in all radiogenic isotope systems [3], together with the recurrence of similar isotopic signatures at >350 kyr intervals, has implications for the dynamics and internal structure of the Hawaiian mantle plume [4] and for the scale of heterogeneities in the deep mantle. Recent isotopic data for over 850 samples from the shield, post-shield and rejuvenated stages on Hawaiian volcanoes indicate source differences between the Loa- and Kea-trend volcanoes that are maintained throughout the ~1 Myr activity of each volcano and that extend back in time on all the Hawaiian Islands (to ~5 Ma). Hawaiian post-shield and rejuvenated lavas have more Kea-like geochemical characteristics than the underlying shield lavas with only two exceptions. Loa-trend volcanoes have more heterogeneous compositions than Kea-trend volcanoes in all isotopic systems by a factor of ~1.5 and present an EM-component (most expressed in Ko'olau) as well as different geochemical trends with time (increase of Pb isotopic ratios in Loa). The Loa-Kea distinction reflects differences in the plume source, at the core-mantle boundary, where the Mauna Loa side of the Hawaiian plume samples a more heterogeneous source that may correspond to the northeast end of the Pacific ultra-low velocity zone (ULVZ). Kerguelen, an EM-I oceanic island, is located on the eastern end of the ULVZ African anomaly. We infer that these deep velocity anomalies at the CMB are the repositories for EM components brought to the surface by strong mantle plumes.

[1] Tatsumoto (1978) *Earth Planet. Sci. Lett.* **38**, 63-87. [2] Abouchami *et al.* (2005) *Nature* **434**, 3401-06. [3] Weis (2010) Abs V41F-01 Fall AGU Meeting. [4] Farnetani & Hofmann (2009, 2010) *Earth Planet. Sci. Lett.* **282**, 314-322; **295**, 231-240.

Bacterial physico-chemical controls on As-Pb iron hydroxy sulfates in reduced environments

C.G. WEISENER^{1*}, C.M. SMEATON¹, G.E. WALSH¹,
A.M.L. SMITH^{2,3,4}, E.C. FRU¹ AND B.J. FRYER¹

¹Great Lakes Institute for Environmental Research, University of Windsor, ON, Canada (*weisener@uwindsor.ca)

²Dept. of Mineralogy, The Natural History Museum, Cromwell Road, London, SW7 5BD, UK

³Davy Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London, UK

⁴Dept. of Earth and Planetary Sciences, Birkbeck, University of London, Malet Street, London, WC1E 7HX, UK

We recently demonstrated the intracellular precipitation of Pb by *Shewanella putrefaciens* CN32 during the reductive dissolution of Pb-jarosite [1]. In the present study, we build upon earlier research which focused on the abiotic dissolution of Pb-As-jarosite [2]. In this study we examine the reductive dissolution of Pb-As-jarosite ($\text{PbFe}_3(\text{AsO}_4)(\text{SO}_4)(\text{OH})_6$) by bacteria under anaerobic circumneutral conditions. Microbial biomass, SEM, ATP, [Pb] and solution chemistry including As and Fe speciation were monitored over time to assess the influence of *S. putrefaciens* on As-Pb jarosite. The work will discuss the rates of Fe reduction versus As reduction and the fate of Pb providing new insight into Pb, Fe and As biogeochemical cycling in reduced environments.

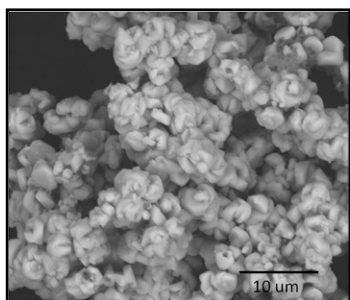


Figure 1: a) SEM image and b) EDS spectra of Pb-As-jarosite

[1] C.M. Smeaton *et al.*, (2009) *Env. Sci. Tech.* **43**, 8091-8096. *Journal*, **25**, 415- 421. [2] A.M.L. Smith *et al.*, (2006) *Chemical Geology*, **229**, 344-61.

High-Mg carbonatitic HDFs, kimberlites and the SCLM

Y. WEISS^{1*}, W.L. GRIFFIN², D.R. BELL³ AND O. NAVON¹

¹The Institute of Earth Sciences, the Hebrew University of Jerusalem, Israel (*yakov.weiss@mail.huji.ac.il)

²GEMOC, Macquarie University, NSW, Australia

³School of Earth and Space Exploration, Arizona State University, AZ, USA

Trace-element patterns of high-Mg carbonatitic high-density fluids (HDFs) trapped in Siberian fibrous diamonds are similar to those of Group I kimberlites, but are slightly more fractionated. The patterns of both are comparable in shape to the average pattern of peridotite xenoliths from the sub-continental lithospheric mantle (SCLM) [1].

Possible scenarios for explaining these similarities include mixing, fractionation and melting:

- 1) Adding 2.5% of kimberlitic magma or 0.7% of the Siberian high-Mg HDFs to a highly depleted peridotite closely reproduces the SCLM pattern.
- 2) The formation of the high-Mg HDFs through fractionation of kimberlitic magma calls for 70% crystallization of olivine, pyroxene garnet and carbonate. However, the alkalis and Ba of the calculated fluid are too low and the middle to heavy REE, Zr, Hf, Ti and Y are too high compared to the Siberian high-Mg HDFs.
- 3) Simple batch melting of 0.5% of a source with average SCLM modal abundance and trace-element composition closely reproduces the trace-element pattern of the Siberian high-Mg HDFs. Higher degrees of melting (~2%) of the same source yield patterns similar to those of Group I kimberlite.

High-Mg HDFs in diamonds from Kankan, Guinea have major-element compositions comparable to that of the Siberian high-Mg carbonatitic HDFs. However, they are depleted in K, Rb, Cs, Nb and Ta and enriched in Ba, Th, U and LREE relative to the Siberian ones. These differences closely correspond to those between the patterns of Group II and Group I kimberlites, respectively. Extending the melting scenario to the Kankan HDFs and Group II kimberlites, the two can be produced by 0.2 and 1% melting of SCLM that carries phlogopite (0.3% and 0.1%, respectively) and a trace of rutile.

Whether it is mixing, melting or combination of both, the new constraints indicate a very close genetic relation between high-Mg carbonatitic HDFs, kimberlites and the average SCLM.

[1] McDonough (1990) *EPSL* **101**, 1-18.

Photolysis of iron(III) carboxylate complexes — Quantum yield determination and reactivity simulation in clouds and atmospheric particles

C. WELLER, A. TILGNER AND H. HERRMANN

Leibniz-Institut für Troposphärenforschung, 04318, Leipzig, Germany (weller@tropos.de)

Iron is always present in the atmosphere in concentrations from $\sim 10^{-9}$ M (clouds, rain) up to $\sim 10^{-3}$ M (fog, particles). Sources are mainly mineral dust emissions. Iron complexes are very good absorbers in the UV-Vis actinic region and therefore photo-chemically reactive. Iron complex photolysis can be an important degradation pathway for organic compounds with the ability to bind iron.

Absorption spectra and Fe^{2+} quantum yields of iron(III) coordination compounds with oxalate, malonate, succinate, glutarate, tartronate, tartrate, glyoxalate and pyruvate were experimentally determined. Complex solutions were irradiated in a 1 cm quartz cell by excimer laser flash photolysis at wavelengths of 308 and 351 nm or by Hg(Xe) lamp photolysis at 436 nm (for Fe(III) oxalate system). Photochemically produced Fe^{2+} was spectroscopically detected at 510 nm as $[\text{Fe}(\text{phenanthroline})_3]^{2+}$.

Measured quantum yields of malonate and glutarate complexes are in the range of $0.02 < \Phi < 0.05$, while succinate, tartrate, pyruvate, glyoxylate and tartronate complexes show values between $0.12 < \Phi < 1.21$. The measured overall quantum yields include contributions from secondary thermal reactions. Furthermore, in some systems a dependence of the measured quantum yield on the amount of the incident photons was determined. In the case of oxalate, a dependence of the quantum yield on the initial concentration of iron(III) oxalate complexes was observed. A kinetic simulation of the reaction system after the photolysis was performed for oxalate, succinate, glyoxalate and tartrate complexes to characterize the influence of secondary thermal reactions on the quantum yield.

A tropospheric chemistry simulation with the multi-phase chemistry mechanism CAPRAM (Chemical Aqueous Phase Radical Mechanism) involving the photolysis of the studied complexes and subsequent reactions of the resulting fragments showed that Fe(III) complex photolysis represents a major sink for the ligands oxalate, tartronate, tartrate and pyruvate in addition to the oxidation via free radicals.

Technical and policy challenges in deep vadose zone remediation of metals and radionuclides

DAWN M. WELLMAN AND MICHAEL J. TRUOX

Pacific Northwest National Laboratory, Richland, Washington 99354; (dawn.wellman@pnl.gov, mj.truex@pnl.gov)

Deep vadose zone contamination is a significant issue in many regions of the world, although much of the focus has been on arid and semiarid regions where that zone is thickest. Contamination in deep vadose zone environments is isolated from exposure such that direct contact is not a factor in its risk to human health and the environment; rather, movement of contamination from the deep vadose zone to the groundwater creates the potential for exposure and risk to receptors. Therefore, while the deep vadose zone is not necessarily considered a resource requiring restoration, limiting flux from contaminated vadose zone is key for protection of groundwater resources and down-gradient receptors. However, technical challenges complicate the decision process for deep vadose zone remedial actions.

Remediation of metal and radionuclide contamination in the deep vadose zone is complicated by heterogeneous contaminant distribution and the preferential saturation-dependent flow in heterogeneous sediments. Thus, efforts to remove contaminants have generally been unsuccessful; and as a result, the magnitude of contaminant discharge (mass per time) from the vadose zone to the groundwater must be maintained low enough by natural attenuation (e.g., adsorption processes or radioactive decay) or through remedial actions (e.g., contaminant mass or mobility reduction) to meet the groundwater concentration goals.

Contaminant transport mechanisms through the vadose zone can attenuate the overall contaminant flux to the groundwater, and vadose zone contamination may not necessarily require remediation if the natural flux results in sufficiently low contaminant concentrations in the groundwater. In some cases, remediation to control transport, enhance attenuation mechanisms, or remove contaminants may be needed to limit flux so groundwater or surface water protection standards are maintained. This presentation reviews major processes viable for deep vadose zone metal and radionuclide remediation that form the practical constraints on remedial actions.

Lithium self-diffusion in $\text{LiAlSi}_2\text{O}_6$ glass and single crystals

A.-M. WELSCH¹* H. BEHRENS¹, I. HORN¹, S. ROSS¹,
P.J. VULIĆ², D. MURAWSKI¹ AND A. KREMENOVIC²

¹Institut für Mineralogie, Leibniz Universität Hannover,
Callinstr. 3, 30167 Hanover, Germany, (*correspondence:
a.m.welsch@mineralogie.uni-hannover.de)

²Department of Crystallography, University of Belgrade,
Dušina 7, 11000 Belgrade, Serbia

Understanding the mechanisms of lithium diffusion is of great interest for geo- and material sciences. Optimizing the performance of Li-bearing solid media has a significant impact in developing new technologies. Knowledge of kinetic Li-isotopic fractionation leads to better understanding of geological processes in which lithium geochemistry plays a major role.

Our ongoing research is aimed to investigate Li diffusion in aluminosilicate media. In the scope of this study, spodumene ($\text{LiAlSi}_2\text{O}_6$) like materials were selected as representative model system since lithium, as the only mobile species, migrates through a static aluminosilicate network. Crystalline and glassy materials are compared in order to determine the effect of structural order on Li-diffusion. Glasses were produced by melting of oxide and carbonate mixtures as well as by melting natural spodumene. Natural crystals are from different pegmatites worldwide. Synthetic single crystals were obtained in a slow crystallization process using a flux method. The samples were tested by impedance spectroscopy for ionic conductivity in the range between 1 Hz to 10 MHz at temperatures up to 940 K. Additionally, lithium self-diffusion coefficients were determined by diffusion couple experiments using two halves with same base composition but different Li isotopic abundancies. Li isotope profiles were measured using UV fs laser ablation coupled with ICP-MS. Raman spectroscopy aided in better understanding the local structural features which coordinate lithium migration.

Ionic conductivity was found to be 6 - 7 orders of magnitude slower in natural spodumene crystals than in the glasses while the activation energy for Li conduction is about the same for both materials (0.66 kJ/mol for the glass, 0.76. kJ/mol for the crystal). This implies that the barrier for Li-migration is not sensitive to structural order in aluminosilicate materials. Comparison of Li isotope diffusion data and dc ionic conductivity yields a correlation factor of 0.5 for Li-diffusion in $\text{LiAlSi}_2\text{O}_6$ -glasses.

Basin evolution, lithofacies palaeogeography and manganese mineralization in Heqing basin, Yunnan province, Southwest of China

XING-PING WEN¹, RUN-SHENG HAN^{1,2} AND
XIAO-FENG YANG³

¹Faculty of Land Resource Engineering, Kunming University of Science and Technology, Kunming, 650093, P. R. China (wfxyp2008@gmail.com)

²Southwest Institute of Geological Survey, Geological Survey Center for Non-ferrous Mineral Resources, Kunming, 650093, P. R. China

³Research Center for Analysis and Measurement, Kunming University of Science and Technology, Kunming, 650093, P. R. China

Heqing basin is located in the northwest of Yungui plateau, southwest of China, a geological conjunction zone of three tectonic units separated by Jinshajiang, Honghe and Xiaojinhe-Lijiang fault belts. Heqing manganese deposit is situated in southwestern margin of Heqing basin. The Songgui formation of the Late Triassic series is the principal ore-host strata, composed mainly of mudstone, limestone and siltstone [1].

Heqing sedimentary manganese deposit formation is associated with Heqing basin evolution. The lithofacies paleogeography of Heqing basin is reconstructed. Sedimentary facies and palaeogeography of the Late Permian Changxingian ages reveal littoral deposits in Heqing manganese deposit. Then the sea level is continuously elevated in the Middle Triassic Ladinian age. Sedimentary facies and palaeogeography of the Late Triassic Carnian age expose shallow sea platform marginal bank facies in Heqing manganese deposit, which is beneficial to accumulation of ore-forming minerals under more stable geological and physicochemical conditions. In the Late triassic Norian age, the region marine regression lead to littoral deposits facies in Heqing manganese deposit, which terminates mineralization.

This study was jointly supported by the crisis of resource exploration mining project, China (20089943) and the innovation team of ore-forming dynamics and prediction of concealed deposits, KMUST, Kunming, China (2008).

[1] Fan, Delian and Yang, Peiji. (1999), *Ore Geology Reviews* **15**, 1-13.

Biogeochemical patterns and processes in buoyant, deep-sea hydrothermal plumes

KATHLEEN WENDT¹, KARTHIK ANANTHARAMAN²,
JOHN A. BREIER³, GREGORY J. DICK²,
KATRINA J. EDWARDS⁴, PETER R. GIRGUIS⁵,
JEFFRY V. SORENSEN¹, JASON SYLVAN⁴ AND
BRANDY M. TONER^{1,*}

¹University of Minnesota, St. Paul, MN, USA,
(*corresponding: toner@umn.edu)

²University of Michigan, Ann Arbor, MI, USA

³Woods Hole Oceanographic Institution, Woods Hole, MA,
USA

⁴University of Southern California, Los Angeles, CA, USA

⁵Harvard University, Cambridge, MA, USA

Along the global mid-ocean ridge, sub-seafloor hydrothermal circulation results in the exchange of heat and chemical species between seawater and the ocean crust. The resulting thermally and geochemically altered fluids are vented at the seafloor. The mixing of cold, oxic deep-ocean waters with hydrothermal fluids creates plumes with physically and chemically dynamic features. Hydrothermal plumes represent a globally distributed interface where marine hydrothermal circulation exerts its biogeochemical influence on elemental budgets of ocean basins.

The goal of the present study is to describe the microbiological niches created by physical and geochemical gradients in plumes. One of our central hypotheses is that microorganisms respond to and alter the geochemistry of hydrothermal plumes. To achieve this goal and test our hypothesis, a field study was undertaken at the Eastern Lau Spreading Center (ELSC). While multiple vent sites along the ELSC are included in the larger study, here we report on an integrated, biogeochemical investigation of a single buoyant plume within ABE vent field.

A series of replicate sample sets were collected by *in situ* filtration at 0.5m, 40m, 200m within a buoyant plume using the ROV JASON. Above plume background and near bottom background sample sets were also collected. Hydrothermal plume particles in sample replicates or splits have been queried for bulk geochemistry, particle-by-particle mineralogy, and microbial community composition. These three data streams are being evaluated individually to characterize the geochemical and microbiological changes throughout the plume with respect to above and below plume backgrounds. In addition, an iterative and integrated analysis is being used to compare: (1) calculated mineralogy to direct measurements; and (2) predicted energy yields from chemoautotrophy to observed microbial composition.

Biogeochemical cycling of iron, sulfur and carbon in the nutrient-rich meromictic acid pit lake Cueva de la Mora (Spain)

K. WENDT-POTTHOFF^{1,*}, M. KOSCHORRECK¹,
M. DIEZ ERCILLA² AND J. SÁNCHEZ ESPAÑA²

¹UFZ – Helmholtz Centre for Environmental Research,
Department Lake Research, D-39114 Magdeburg,
Germany

(*correspondence: katrin.wendt-potthoff@ufz.de)

²Instituto Geológico y Minero de España (IGME), 28003
Madrid, Spain

Cueva de la Mora is a meromictic, nutrient-rich acid pit lake with pronounced vertical gradients of physicochemical parameters in the chemocline and monimolimnion [1]. We studied microbial activity, abundance and biomass, and biogeochemical cycling of iron, sulfur and carbon to find out if (1) the high nutrient content influenced alkalinity-producing microbial processes compared to other acid pit lakes, and (2) if sediments in the shallow, mixed and the deep, stagnant parts of the lake exhibited biogeochemical differences related to meromixis. We hypothesized that redox cycling was more intense in the mixed part and higher amounts of reduced components would accumulate in the stagnant part.

Several biogeochemical reaction rates were higher than in typical acid pit lakes and fell rather within the range of neutral or weakly acidic lakes, probably a consequence of nutrient levels. Anaerobic processes occurred mainly in the sediments, and methanogenesis was negligible for the carbon budget of the lake. Sediments from the mixed and stagnant parts of the lake differed markedly. Mixolimnetic sediments showed high iron and sulfate reduction rates, and they appeared to undergo substantial recycling, as supported by reactive Fe(II) and Fe(III) profiles, relation between sulphate reduction and accumulation of reduced sulphur, and viable counts of iron and sulphur reducing and oxidising bacteria. Monimolimnetic sediments exhibited lower anaerobic microbial activities, and surprisingly accumulated more Fe(II) than mixolimnetic sediments, but less carbon and reduced sulfur. This might be explained by a strong separation of the monimolimnetic water body, resulting in comparably less input of energy (light) and allochthonous matter. The effect of alkalinity-generating microbial processes is not sufficient to neutralize the lake within a few decades.

[1] Sánchez España J, López Pamo E, Diez M, Santofimia E (2009), *Mine Water Environ* **28**:15-29

Tracing N₂O transformation pathways in a lake ecosystem by N₂O isotopomer analysis

C.B. WENK^{1*}, H.J.R. BLEES¹, K. Koba²,
K.L. CASCIOTTI³, C.J. SCHUBERT⁴, M. VERONESI⁵,
C.V. FREYMOND¹, H. NIEMANN¹, J. ZOPFI⁶ AND
M.F. LEHMANN¹

¹Institute of Environmental Geosciences, University of Basel, Switzerland (*correspondence: christine.wenk@unibas.ch)

²Faculty of Agriculture, Tokyo University of Agriculture and Technology, Japan

³Department of Environmental Earth System Science, Stanford University, USA

⁴Swiss Federal Institute of Aquatic Science and Technology (Eawag), Switzerland

⁵Institute of Earth Sciences, University of Applied Sciences of Southern Switzerland, Switzerland

⁶Laboratory of Microbiology, University of Neuchâtel, Switzerland

In terrestrial and aquatic ecosystems, N₂O can be produced through two pathways: nitrification and incomplete denitrification. The measurement of the stable isotopic and isotopomeric composition of N₂O can help determine the relative importance of these processes in net N₂O production. To date, relatively little is known about the role of lakes as N₂O source to the atmosphere, and N₂O isotopomer dynamics in lakes have barely been studied.

Lake Lugano (South Basin) is a monomictic, eutrophic lake, where high bottom water N₂O concentrations are observed (900nM; 100x equilibrium saturation). Sediment core incubations with ¹⁵N-labeled substrates suggest that sedimentary denitrification is the main N₂O source. These incubation data, however, appear to conflict with water column observations. A N₂O concentration maximum at the aerobic/anaerobic interface, together with the intramolecular distribution of ¹⁵N (SP of ~33‰) in N₂O suggests that N₂O in the water column is mainly produced by nitrification. The investigated redox-transition zone is a net sink for NO_x, and N₂O gradients suggest N₂O reduction just below this zone. Yet, isotopomeric signatures that were previously assumed to be characteristic for N₂O production by denitrifying organisms were not observed. Our results raise doubts about the general validity of previously reported N₂O isotopomer effects from laboratory experiments for lake ecosystems.

Spins deep in the Earth

RE NATA WENTZCOVITCH

Department of Chemical Engineering and Materials Science,
Minnesota Supercomputing Institute, University of
Minnesota, MN, USA, 55403

There has been much interest in spin crossovers found in 2003 and 2004 in the most abundant minerals of Earth's lower mantle ((MgFe)O and (MgFe)(Si,Fe)O₃-perovskite) under pressure. Spin crossovers depend on thermodynamic conditions and a full understanding of this problem requires its investigation as function of pressure and temperature. There are several controversies, especially in the perovskite systems, and surprises are revealed by electronic structure calculations. The geophysical consequences of these crossovers are yet to be fully understood. I will review recent progress in the study of spin crossovers and give an overview of this phenomenon and its potential implications for the Earth.

Research carried out in collaboration with H. Hsu, K. Umemoto, P. Blaha. Research supported by the MRSEC Program of NSF under Award Number DMR-0212302 and DMR-0819885, and by NSF/ATM-0428774, EAR-0810212, and EAR-1047629.

The Santa Quitéria Batholith, NE Brazil: A mantle–crust interaction

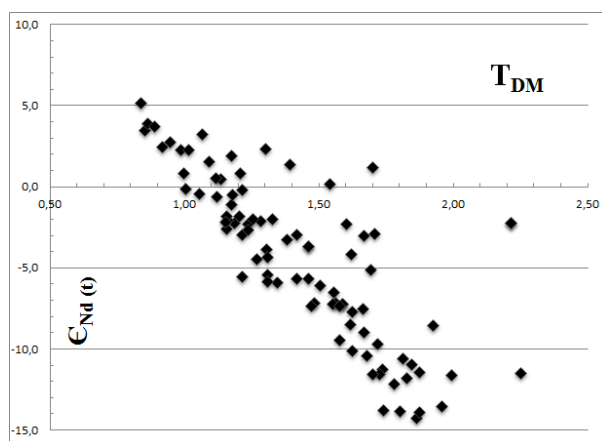
E. WERNICK^{1*}, S.A. ZINCONE² AND T.J.S. SANTOS²

¹Instituto de Geociências, UNESP, Rio Claro, SP, Brazil

(*correspondence: wernick@uol.com.br)

²Instituto de Geociências, UNICAMP, Campinas, SP, Brazil

Granitoid magmatism is an important tool for the characterization of mantle–crust interaction, a process which extremes are represented by M- type (mantelic) and S- type (crustal) granites. The huge (~15.000km²) Brasiliano Santa Quitéria batholith (SQB) from the Borborema Province, state of Ceará, NE Brazil, comprises mainly high-K/shoshonitic megaporphyritic/evengrained monzodiorites, monzogranites and granites. Its long lasting (650–470 Ma.) magmatic evolution reflects part of the closure of the Pharusian Ocean and the collision between the Amazonas, São Luiz, São Francisco and West Congo cratons. 90 Sm–Nd data for SQB rocks [1–4] show that their parent magma represents an isotopic mixture of a juvenile mantelic component with older, mainly Paleoproterozoic, crustal rocks. The geological, petrographic and geochemical evidences for the mixture change from the syncolliisional, via the syntranscurrent, to the late magmatic stage of the batholith, the last one related to the regional relaxing and collapsing of the orogen.



[1] Fetter (1999) Ph.D. thesis, Kansas University, USA, 164p.

[2] Castro (2004) Ph.D. thesis. USP, Brazil, 221 p.

[3] Teixeira (2005) Master Dissertation, UNB, Brazil, 128p.

[4] Santos *et al.* unpublished.

Probing the silicon isotope signature of supply limited chemical weathering in the Cordillera Central of Costa Rica

A. JOSHUA WEST^{1,2}, SOPHIE OPFERGELT¹,
RACHAEL JAMES³, PHILIP POGGE VON STRANDMAN⁴ AND
KEVIN BURTON¹

¹University of Oxford, Department of Earth Sciences, South Parks Road, Oxford OX1 3AN, UK

²University of Southern California, Department of Earth Sciences, Los Angeles, CA, 90089, USA;
(correspondence: joshwest@usc.edu)

³National Oceanography Centre Southampton, European Way, Southampton, SO14 3ZH, UK

⁴University of Bristol, Department of Earth Sciences, Queen's Road, Bristol, BS8 1RJ, UK

The fractionation of silicon isotopes during tropical, supply-limited weathering remains incompletely understood, a key missing link in being able to use the Si isotope system to infer the rates and character either of primary mineral weathering, or of biogeochemical cycling of Si. Samples of rock, soil, vegetation, and water from La Selva Biological Preserve, on the flanks of Volcan Barva in the Cordillera Central of Costa Rica, provide the opportunity to (i) better constrain the isotopic signature of dissolved Si associated with supply-limited weathering, and (ii) understand the mechanisms generating the observed isotopic characteristics in these settings. We collected samples from La Selva and analysed these samples for $\delta^{30}\text{Si}$ by MC-ICP-MS. Si-isotope analyses of samples from La Selva confirm that weathering in tropical, supply-limited environments generates the isotopically lightest dissolved Si that has been observed in stream and river waters measured globally. Streams with significant groundwater contribution, with flowpaths through less altered volcanic bedrock, have significantly higher isotopic compositions, reflecting primary mineral weathering. Analysis of bedrock and soils, including clay separates from soils, indicates that this light isotopic composition of dissolved Si is a consequence of the dissolution of clay minerals formed during previous weathering cycles. Contemporary weathering processes in the soil at La Selva are associated with precipitation of even lighter neo-formed clays, driving the bulk soil to increasingly light Si isotope ratios. Weathering of secondary minerals in such locations, as confirmed in this study, may complicate interpretation of the variability in dissolved riverine Si isotopes over large spatial scales and long temporal scales.

Mo isotope signature of OAE 1a: New insights from the Western Tethys

S. WESTERMANN^{1*}, D. VANCE¹, C. ARCHER¹
AND S. ROBINSON

¹Bristol Isotope Group, School of Earth Sciences, University
of Bristol, Wills Memorial Building, BS8 1RJ, UK
(*correspondence: stephane.westermann@bristol.ac.uk)

²University College London, Gower Street, London, WC1E
6BT (stuart.robinson@ucl.ac.uk)

Oceanic anoxic events (OAEs) record profound and rapid changes in the chemistry of the world ocean. Quantifying the oxygenation state of the oceans through OAEs is of fundamental importance to understanding the global perturbation of the carbon cycle observed during these events. The aim here is to trace global redox change in the world ocean through the early Aptian anoxic event (OAE 1a, Selli event), one of the most significant and widespread black shale events of the Cretaceous.

We selected the Gorgo a Cerbara section (Italy), where evidence of euxinic conditions has recently been provided by biomarkers [1-2], and investigated the redox-sensitive trace element (RSTE) distribution and the molybdenum (Mo) isotopes variations through the section.

All RSTE measured present similar behaviour, with a low background level contrasted by maxima in concentrations within the Selli level. A relatively good correlation is observed between total organic carbon (TOC) values and RSTE accumulation, suggesting well-developed anoxia. However, Mo isotopes show surprisingly negative values through the section. An increasing trend in $\delta^{98/95}\text{Mo}$ is observed before the Selli interval, with values ranging from -0.89 up to 0.06 ‰. Then, $\delta^{98/95}\text{Mo}$ values remain more or less constant fluctuating around -0.23 ‰, but with a shift towards more negative values within the Selli level. This trend is interrupted by a positive peak to 0.13 ‰, corresponding to samples with the highest Mo content (up to 94 ppm).

The RSTE behaviour indicates variations in the oxygenation state of the western Tethys, reaching anoxic/euxinic conditions during OAE 1a. However, the light $\delta^{98/95}\text{Mo}$ values suggest that the redox conditions may not have been fully euxinic. Iron speciation measurements will be performed to further investigate the redox conditions during the deposition of the Selli interval, and its relationship to sedimentary Mo isotope evolution.

[1] Pancost, R. *et al.* (2004). *Journal of the Geological Society* 161, 353–364. [2] van Breutel *et al.* (2007). *Paleoceanography* 22, PA1210.

Melting and melt/rock reaction of sulphides in Middle Atlas spinel peridotite xenoliths

K.J. WESTNER^{*1}, N. WITTIG^{1,2}, R. KLEMD¹, H. BRÄTZ¹
AND I. OSBAHR¹

¹GeoZentrum Nordbayern, Mineralogie & Endogene
Geodynamik, Universität Erlangen, Schlossgarten 5(a),
91052 Erlangen (*correspondence:
katrin.westner@geo.stud.uni-erlangen.de)

²National High Magnetic Field Laboratory & Department of
Earth, Ocean, and Atmospheric Science, FSU, 1800 E.
Paul Dirac Drive, Tallahassee, FL 32310, USA

The major and siderophile and chalcophile trace element composition (n=25) in sulphides (58 analyses) and Fe-hydroxides (7 analyses) of seven spinel-facies peridotite xenoliths from the Moroccan Middle Atlas was determined at the University of Erlangen by electron microprobe and in-situ LA-ICP-MS. The sulphide assemblage comprises monosulphide solid solution, pentlandite and minor isocubanite. Sulphides occur as: (i) inclusions (eu- to subhedral) in primary silicates, usually associated with sulphide melt trails; (ii) anhedral grains on silicate grain boundaries, and (iii) within silicate glass in discrete melt pockets formed during the ascent of the xenoliths. Variably pervasive alteration of sulphides to hydroxides is generally associated with cracks in the peridotite matrix. Three PGE patterns were identified – often within the same sample and irrespective of the petrographic occurrence: [a] IPGE > PPGE; [b] no PGE fractionation and [c] PPGE > IPGE. Hydroxides show nearly identical PGE patterns with similar PGE abundances to their host sulphides. Relatively incompatible chalcophile elements correlate with the degree of PGE fractionation. The presence of such PGE fractionation ([a] & [c]) on thin-section scale is consistent with mantle melting experiments [1], which predict residual IPGE-rich sulphides and (trapped) PPGE-rich melt blebs. The close proximity of interstitial and enclosed grains with these patterns suggests contemporaneous sulphide-silicate crystallisation due to melt-rock reaction of olivine and pyroxene, hence trapping sulphide melt as inclusions and leaving potentially earlier residual IPGE-rich sulphides intact. Whole rock major and siderophile trace elements and Os isotopes are also in accordance with coupled sulphide-silicate introduction [2]. Our results allow deciphering the mobility and transport of upper mantle sulphide melts, which is a crucial prerequisite for understanding the generation of crustal noble metal deposits.

[1] Bockrath *et al.* (2004) *Science* **305**, 1951-1953. [2] Wittig *et al.* (2010) *Lithos* **115**, 15-26.

Noble gases and halogens in Icelandic basalts

B. WESTON*, R. BURGESS AND C.J. BALLENTINE

SEAES, The University of Manchester, Manchester, U. K.
(*bridget.weston@postgrad.manchester.ac.uk)

We present noble gas and halogen data from a suite of samples taken from across Iceland. Iceland combines hotspot volcanism, a spreading ridge and abundant sub-glacially erupted basaltic samples. This combination allows for samples which erupted under high enough pressures to retain a measurable noble gas content, and also display signatures representing interaction between ocean island and mid-ocean ridge basalt mantle sources. In terms of the isotopic composition of the light noble gases, this interaction has been the subject of a number of studies. However, the elemental heavy noble gas composition of Icelandic basalts has been less well investigated. Studies are hampered by the large, isotopically atmospheric component typically found in Icelandic sub-glacial samples; this late-stage contamination can swamp other signatures. In addition, the degassing process results in both elemental fractionation and loss of the noble gases. Taking full account of both these processes is crucial to resolving the elemental noble gas composition of Iceland's source mantle: Evidence for volatile recycling, volatile sources during the Earth's history and the nature of different mantle source zones are just a few topics that require elemental data as well as isotopic.

Isotopic neon and argon ratios show mixing between air and mantle components, allowing corrected abundances of krypton and xenon to be calculated: Although isotopically indistinguishable from air, these are elementally non-atmospheric, allowing the fit of the data to degassing models to be assessed. We use a variation on the model of Gonnermann and Mukhopadhyay to define possible degassing trends for these samples [1]. Known mantle production ratios for $^4\text{He}/^{40}\text{Ar}$ and $^4\text{He}/^{21}\text{Ne}$ then allow limits to be placed on elemental ratios from Iceland's source mantle.

In contrast to the noble gas analyses, elemental fractionation is not apparent in the halogen data; for example, I/Cl ratios are consistently close to the bulk earth value of 72×10^{-6} across a broad range of samples [2]. However, halogen concentrations vary widely, with the highest values found towards central Iceland. Combined with the noble gas results, this data can provide an insight into the halogen composition of the different mantle sources interacting at Iceland.

[1] Gonnermann and Mukhopadhyay (2007) *Nature* **449**, 1037-1040. [2] Burgess *et al.* (2002) *EPSL* **197**, 193-203.

C-solubility in magmas at low $f\text{O}_2$

D.T. WETZEL^{1*}, M.J. RUTHERFORD¹, S.D. JACOBSEN²,
E.H. HAURI³ AND A.E. SAAL¹

¹Dept. of Geological Sciences, Brown University, Providence RI 02912 (*correspondence: Diane_Wetzel@brown.edu)

²Dept. of Earth and Planetary Sciences, Northwestern University, Evanston, IL 60208
(steven@earth.northwestern.edu)

³DTM Carnegie Institute of Washington, DC 20015
(hauri@DTM.ciw.edu)

Available evidence suggests that in the absence of water, carbon is the element responsible for generating the gas phase that drives fire-fountain eruptions in low oxidation-state magmas [1, 2]. For example, recent experiments show that C forms a CO-rich gas phase in ascending lunar picritic magmas at 40 MPa [3]. Indigenous H (H_2O), discovered in a range of lunar picritic glasses [4], affects this conclusion. Our study was designed to determine the solubility and speciation of C in H-bearing graphite-saturated picritic magmas and the effect of H on the initial gas phase generated.

Experimental A15 green glass samples were pre-set at IW, enclosed in graphite, and run in an IHPV. C and H contents determined by SIMS show 3-150 ppm C and 6-140 ppm H at lower pressures and up to 1400 ppm C and 1250 ppm H at 1 GPa. Carbon in the green glass has a strong positive correlation with pressure. Analyses also show a positive correlation between dissolved C and H in the experimental glasses. Raman spectroscopy indicates CH_4 present in the melt, which confirms the observed trend between C and H in the glasses. These results are consistent with experiments on Na-silicate [5] and haplobasaltic [6] melts. Magmatic C contents greater than ~20 ppm will cause the first gas phase to form from C-H (CH_4) species saturation assuming H contents were in the range 200-1000 ppm. Thermodynamic models [7] predict a CH_4 - and H_2 -rich gas phase in equilibrium with a reduced melt at $P > 40$ MPa and CO-rich gas at lower pressures.

[1] Sato M. (1976) *PLSC 7th*, p.1323-25. [2] Fogel R.F. and Rutherford M.J. (1995) *GCA*, **59**, 201-15. [3] Nicholis M.G. and Rutherford M.J. (2009) *GCA*, **73**, 5905-17. [4] Saal A.E. *et al.* (2008) *Nature*, **454**, p.192-95. [5] Mysen *et al.* (2009) *GCA*, **73**, 1696-1710. [6] Ardia P. *et al.* (2011) *LPSC XLII*, Abst. #1659. [7] Zhang C. and Duan Z. (2009) *GCA*, **73**, 2089-2102.

Diatom Si isotope variations from the Atlantic Sector of the Southern Ocean (ODP Site 1093) record environmental changes of the last 170 ka

F. WETZEL^{1*}, A. SHEMESH², B.C. REYNOLDS¹

¹Institute of Geochemistry and Petrology, Department of Earth Sciences, ETH Zurich, Switzerland (*correspondence: wetzel@erdw.ethz.ch)

²Department of Environmental Sciences & Energy Research, The Weizmann Institute of Science, Rehovot, Israel

A number of recent studies utilized silicon isotopes to trace changes in the biogeochemical cycling of silicon in the paleocean [1, 2]. The main controlling process on this cycle is the uptake of silicon by opal-precipitating phytoplankton. Accounting for about 60% of the oceanic primary production, diatoms link the dissolved silicon (nutrient) pool and oceanic CO₂ uptake from the atmosphere. Since the Southern Ocean plays a key role in ocean circulation and deep-sea ventilation, its underlying opal-rich sediments are particularly suitable for studying the link between atmospheric CO₂ variations and phytoplankton nutrient utilization. The degree of surface silicon utilization is to a first order a function of nutrient supply from below and should be reflected in the diatom silicon isotope composition. In combination with carbon isotope ($\delta^{13}\text{C}$), nitrogen isotope ($\delta^{15}\text{N}$) and micronutrient (esp. Fe) information it is possible to reconstruct the efficiency of the biological pump that determines whether the surface ocean acts as a net source or sink for atmospheric CO₂.

Here, we present down-core (0-170 ka) silicon isotope variations of diatoms from the Atlantic Sector of the Southern Ocean (ODP Site 1093) and examine the impact of glacial-interglacial climate change on the degree of silicon isotope utilization. The results show that the degree of silicon isotope utilization during interglacial periods is different from that of peak glacial periods. During peak glacial periods, silicon utilization is inefficient at a time where an efficient biological pump is assumed to draw down additional atmospheric CO₂, implying a more complex relationship between silicon in frustules and nutrients contributing to organic tissues. In addition, ambiguity exists as to whether the increased efficiency in the biological pump during glacials was, as commonly believed, a contributor to the low atmospheric CO₂ concentrations or a consequence and therefore 'only' a positive feedback.

[1] Ellwood *et al.* (2010) *Science* **330**:1088-1091; [2] Hendry *et al.* (2010) *EPSL* **292**:290-300;

The extent of oceanic anoxic events revealed by correlated Mo- and U isotope records

S. WEYER^{1*}, C. MONTOYA-PINO², G.W. GORDON³,
B. VAN DE SCHOOTBRUGGE², W. OSCHMANN², J. PROSS²
AND A.D. ANBAR³

¹Institut für Mineralogie, Leibniz Universität Hannover, 30167 Hannover, Germany

(*correspondence: s.weyer@mineralogie.uni-hannover.de)

²Institut für Geowissenschaften, Universität Frankfurt, 60431 Frankfurt a. M., Germany

³School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287, USA

Isotopic signatures of redox-sensitive trace metals in black shales (e.g. Mo and U) have become a frequently used tool to estimate the extent of anoxic or euxinic conditions in ancient oceans [1-5]. A disadvantage of these tools is that they are sensitive to local redox conditions or other effects [4-6]. Here we show that combining Mo- and U isotopes provide a much more robust approach.

We studied black shales from and around both the Cretaceous OAE2 (Demerara Rise, Central Atlantic ocean) and the early Jurassic T-OAE (Dotternhausen, Germany, and Truc de Balduc, France) and compared our results with those from "recent" sapropels of the Black Sea (unit I and unit II). Samples from all investigated units display a distinct negative correlation of Mo- and U isotope records. This coupling of Mo- and U isotopes is likely generated during black shale formation under variable (redox) conditions.

Samples from the OAE2 and those from below- and above OAE2 together define a single trend of Mo- versus U isotopes. Individual trends are defined by sample suites from different subzones of the lower Toarcian (during- and slightly after the T-OAE). All these trends are significantly shifted towards lighter isotope compositions compared to the trend defined by Black Sea samples, except samples from the *bifrons* zone (the youngest lower Toarcian) which display almost modern Mo- and U isotope records. Our findings indicate significant enhancement of seafloor anoxia (5-10-fold compared to present) during both OAE2 and T-OAE. For both periods, enhancement of seafloor anoxia exceeded the duration of the OAEs, as defined by their $\delta^{13}\text{C}_{\text{org}}$ excursions.

[1] Arnold *et al.* (2004), *Science* **304**, 87-90; [2] Pearce *et al.* (2008), *Geology* **36**, 231-234; [3] Kendall *et al.* (2009), *GCA* **73**, 2534-2558; [4] Gordon *et al.* (2009), *Geology* **37**, 535-538; [5] Montoya Pino *et al.* (2010); *Geology* **38**, 315-318; [6] Poulson *et al.* (2006) *Geology* **34**, 617-620.

Occurrence of reduction induced sulfide saturation in oxidised arc magmas

TARUN H.E. WHAN*, JOHN A. MAVROGENES AND RICHARD J. ARCULUS

Research School of Earth Sciences, Australian National University, ACT Australia 0200
(*correspondence: tarun.whan@anu.edu.au)

It has been previously well documented that solubility of sulfur in silicate melts increases by order of magnitude as the sulfate (SO₄)₂ compared to the sulfide (S₂) species [1]. Also established is magnetite saturation, the first phase to appear on the liquid line of descent during fractional crystallisation that subtracts significant amounts of total Fe and also lowers the Fe₃₊/Fe₂₊ of the residual magma, may trigger reduction in the evolving silicate melt [2]. This process of reduction induced sulfide saturation (RISS) can lead to a melt attaining sulfide saturation in a closed system, without the need of any external input i.e., crustal assimilation of sulfur or an enriched slab component.

We have explored the details of the processes subsequent to magnetite saturation in arc magmas. For example, preliminary analysis of melt inclusions contained within titanomagnetite separated from a suite of subaqueous quenched volcanic glasses from the Pual Ridge recovered during Marine National Facility Voyage (FR08-1991), while confirming predicted Cu and S abundances at peak enrichment of these elements, require some finite amount of magnetite fractionation before sulfide saturation is achieved.

Relatively oxidised sulfate-saturated, representative basaltic andesite compositions doped with a suite of chalcophile trace elements, have been experimentally equilibrated under reducing conditions to simulate RISS. The experiments yield Cu-Ag-Au rich sulfides, experimentally validating for the first time the plausibility of this process in evolving arc magmas.

[1] Jugo, P. J., R. W. Luth & J. P. Richards (2005a). *Journal of Petrology* **46**(4): 783-798. [2] Jenner, F. E., O'Neill, H. ST. C., Arculus, R. J., Mavrogenes, J. A. (2010) *Journal of Petrology* **51**(12): 2445- 2464.

Fluid pressure versus rock pressure: Their influence on metamorphic reactions

JOHN WHEELER¹, SERGIO LLANA-FUNEZ² AND DAN FAULKNER¹

¹School of Environmental Sciences, University of Liverpool, Liverpool, L69 3GP, UK
(*correspondence: johnwh@liv.ac.uk)

²Departamento de Geología, Universidad de Oviedo, calle Arias de Velasco s/n, 33005 Oviedo, Spain

In the upper part of the Earth aqueous and other fluids interact physically and chemically with their surroundings, naturally or during fluid disposal and extraction. Differences between rock and fluid pressure are common in the upper few km of the crust. Pressure affects chemical equilibrium: so how do these two different pressures affect chemical processes? Despite the fundamental nature of this question, there are no agreed answers and systematic tests are lacking. Here we discuss results from a set of experiments on gypsum dehydration, where confining and fluid pressure are independently varied.

Because they involve significant volume change, dehydration reactions are sensitive to pressure. Most dehydration reactions involve a net volume increase; hence in confined conditions overpressure develops unless the fluid can drain away. Thus, porosity and permeability development are key processes in nature and experiment. In addition, when confining pressure is greater than fluid pressure, the solids may compact. Reaction, fluid flow and compaction will all influence the evolving fluid pressure field and feedbacks are inevitable. Despite this we show how we can distinguish the effects of reaction rate from those of other processes.

We have run an extensive set of experiments on gypsum dehydration (to bassanite) and, in parallel, have developed a numerical model for dehydration. We show two results.

1. Experiments show that the rate of gypsum dehydration is strongly influenced by pore fluid pressure and not by confining pressure. This means that, even as the bassanite becomes the dominant load supporting phase, the confining pressure it supports is not influencing the thermodynamics of the reaction.

2. Experiments and the numerical model both show that under some conditions a reaction *front* develops, separating unaltered gypsum from substantially reacted regions. Such fronts, if they develop, exert a strong influence on behaviour in experiments and will equally influence natural systems.

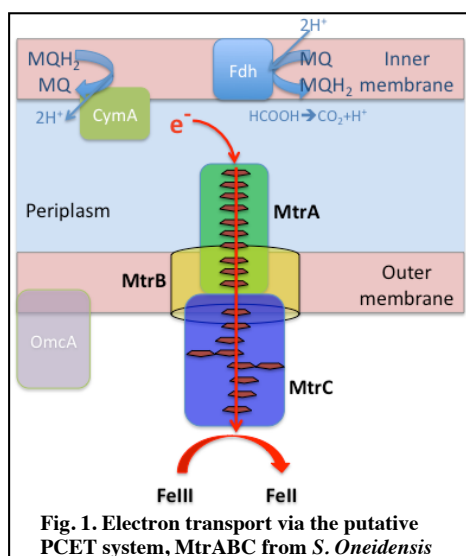
Liposome study of MtrABC: A Porin cytochrome electron transport system from *Shewanella oneidensis*

G.F. WHITE*, M.J. EDWARDS, N.A. BAIDEN, A. HALL, J.N. BUTT, D.J. RICHARDSON AND T.A. CLARKE

University of East Anglia, Norwich NR4 7TJ, UK

(*correspondence: gaye.white@uea.ac.uk)

S. Oneidensis are able to respire in the absence of oxygen because they can use oxidised metals, external to the cell, as terminal electron acceptors. This involves electron transfer across the bacterial cell envelope to the surface of minerals such as Fe(III) and Mn(IV) oxides. Genetic knockout studies have identified a suite of proteins associated with electron transport through the outer membrane [1]. This includes the MtrABC complex. Studies of these proteins led to the putative model for Porin-Cytochrome Electron Transport (PCET) shown in Fig. 1 below [2, 3].



In this model the decaheme cytochromes MtrA and MtrC meet inside the transmembrane sheath, MtrB. The 20 hemes are closely aligned allowing electrons to flow through the MtrAC “wire”. To test this model, we have inserted MtrABC into liposomes containing a hydrophilic electron source, reduced methyl viologen, that also acts as a redox indicator. We describe the development of this technique and present our investigations into PCET via MtrABC across a lipid bilayer to a range of soluble and insoluble minerals.

[1] Myers *et al.* (2002) *App. Env. Microbiol.* **68**, 2781-2793.

[2] Ross *et al.* (2007) *App. Env. Microbiol.* **73**, 5797-5808. [3]

Hartshorne *et al.* (2009) *PNAS.* **106**, 22169-22174.

Correlated uranium concentration, radiation damage, and increased SHRIMP U/Pb ages of zircon

LLOYD T. WHITE* AND TREVOR R. IRELAND

Research School of Earth Sciences, The Australian National University (*correspondence: lloyd.white@anu.edu.au)

SHRIMP U-Pb age calibrations require an accurate calibration of the observed ion ratios. Previous work has shown that there is a correlation between highly elevated uranium concentrations (>3000 ppm) and an increase in apparent age [1]. This “high uranium effect” has been attributed to U, Pb gain or loss, matrix-dependent sputtering, and changes in secondary ionisation efficiency of different species. If this process is systematic, then it may be possible to obtain a calibration that will allow correction of high U spots and allow comparison with more normal zircon.

We report results from SHRIMP I, II and RG analyses of several samples of varying uranium concentration and age (~20 Ma, ~50 Ma, ~100 Ma and ~180 Ma). Our results suggest that the “high uranium effect” can vary between different geometries of SHRIMP (i.e. I, II and RG) and may (at least in part) relate to how the machine is calibrated. It also appears that the “high-uranium effect” is more pronounced in the older zircons.

Raman spectroscopy was used to analyse some of the zircons that had been analysed previously with SHRIMP. This was done so that the uranium concentration and U/Pb age was known for each Raman analysis. The Raman results suggest that the correlation between uranium concentration and age is complex, but implies that the older apparent ages obtained from SHRIMP are related to zircons that have lost some, or all of their crystalline structure. Thus, the “high-uranium effect” is more problematic in older zircons because of accumulated radiation damage, which will also promote Pb redistribution.

[1] Williams & Hergt (2000), *Beyond 2000: New Frontiers in Isotope Geoscience*, Woodhead, Hergt, & Noble (eds), Lorne, Abstract Proceedings, p. 185-188.

Implications of a non-chondritic Earth for terrestrial heat production and geodynamics

WILLIAM M. WHITE AND JASON PHIPPS MORGAN

Dept. of Earth & Atmospheric Sciences, Cornell University,
Ithaca, NY 14853 USA (wmw4@cornell.edu,
jp369@cornell.edu)

Previous geochemical estimates of terrestrial radiogenic heat production were based on the assumption that refractory lithophile elements, such as the REE, U, and Th are present in the Earth in chondritic relative proportions (the “modified chondritic Earth’ model). However, $^{142}\text{Nd}/^{144}\text{Nd}$ ratios in modern terrestrial materials imply that the Sm/Nd ratio in the Earth, or at least the observable part of it, that is about 6% higher than chondritic, and hence the Earth is non-chondritic, even for ratios of refractory lithophile elements. The most likely explanation is that a low Sm/Nd igneous protocrust that formed as the Earth accreted was lost through collisional erosion. A protocrust 6% enriched in Nd relative to Sm would have been more strongly enriched in the more highly incompatible elements K, U, and Th. Calculations based on a model of protocrust formation and collisional erosion that satisfy both Sm-Nd and Lu-Hf isotopic constraints imply U and Th concentrations in the bulk silicate Earth (BSE) about 40% lower than in the ‘modified chondritic Earth’ model. Assuming a $K/U = 13800$ for the BSE, the K concentration is 30% lower than previously believed. This corresponds to a terrestrial heat production of 11.9 TW, compared to estimates ranging from 16 to 20 TW based on ‘modified chondritic Earth’ model. Of this, some 5 to 10 TW of heat production is in the continental crust, leaving <6 TW of heat production in the mantle. For comparison, recent estimates of U, Th, and K in the depleted mantle imply heat production in the range of 0.6–1.0 $\mu\text{W}/\text{kg}$; if the depleted mantle occupies the entire mantle, this translates into mantle heat production of 3–4 TW. Mantle heat losses are roughly 33 TW, hence the mantle Urey ratio (ratio of heat production to heat loss) is in the range of 0.09 to 0.19. At present, heat generated by viscous dissipation of the gravitational energy released by sinking slabs is 12 to 15 TW, and <5 TW is released by the cooling core. Of this energy, only a fraction, 3.8 to 4.8 TW can produce new gravitational power to drive convection and plate tectonics. Thus gravitational energy is being consumed at a much higher rate than it is being regenerated. This is a clear indication that the present rate of slab subduction is not sustainable and that the mantle is in a phase of faster than normal slab subduction and plate spreading.

Hygroscopic and CCN properties of marine aerosol

J.D. WHITEHEAD^{1*}, J.D. ALLAN¹, N. GOOD² AND G. McFIGGANS¹

¹Centre for Atmospheric Science, SEAES, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK
(*correspondence: James.Whitehead@manchester.ac.uk).

²Centre for Atmospheric and Instrumentation Research, University of Hertfordshire College Lane, Hatfield, AL10 9AB, UK

The impact of marine aerosols on cloud properties is the subject of active research due to the high level of uncertainty associated with their effect on the climate. In order to quantify these effects more accurately, it is important to measure and understand aerosol water uptake, which can vary greatly with particle size and composition. The tools available for this task include the Hygroscopicity Tandem Differential Mobility Analyser (HTDMA) and the Cloud Condensation Nuclei counter (CCNc), however consistency between the aerosol water uptake derived with these instruments can be affected by the composition in particular due to the presence of organic components [1].

Both instruments were operated at Mace Head, during winter 2010 and summer 2011. The site’s location on the west coast of Ireland makes it ideal for sampling air masses from over the North Atlantic without significant local anthropogenic influence. During the winter, the aerosol particles in the clean marine air at this location consist largely of inorganic components, so it is expected that reconciliation between the hygroscopic and CCN properties of the aerosols will be straightforward. Owing to hotly-debated impacts of the contribution of organic aerosol components to droplet activation and to the expected higher summertime contribution to primary marine particulate of biogenically derived organic matter [2], reconciliation of aerosol water uptake derived with each instrument presents additional challenges. This can be examined with reference to aerosol composition data from an Aerosol Mass Spectrometer (AMS) simultaneously operating at the same location.

Recent progress with the analysis and comparison of the winter and summertime data will be presented and discussed in the context of previous marine experiments.

[1] Good *et al.* (2010) *Atmos. Chem. Phys.* **10**, 3189–3203. [2] Yoon *et al.* (2007) *J. Geophys. Res.* **112**, doi:10.1029/2005JD007044.

Quadruple sulfur isotope determination by SIMS: Limitations, progress and prospects

M.J. WHITEHOUSE

Swedish Museum of Natural History, Stockholm, Sweden
(martin.whitehouse@nrm.se)

The discovery of mass independent fractionation effects in sulfur isotopes leading to what is commonly referred to as “anomalous” or “MIF” sulfur has revolutionised our understanding of the evolution and interaction of sulfur reservoirs. Of the four naturally occurring sulfur isotopes, variations in the abundance of ^{33}S and ^{36}S may be produced by upper atmosphere photo-catalysed reactions acting on SO_2 . The distinctive and irreversible signatures preserved in sulfides or sulfates in the geological record are key to understanding the evolution of Earth’s atmosphere [1], and provide important tracers in geobiological [2] and ore-forming processes [3]. Recent studies have also investigated ^{36}S abundance as a potential tracer of the MIF process [4].

Among the various methods available to measure sulfur isotopes, secondary ion mass spectrometry (SIMS) combines high-spatial and -volume resolution with a precision adequate for many studies, as well as the ability to efficiently analyse a large number of *in situ* targets. To date, SIMS studies have been limited to the three most abundant isotopes, ^{32}S , ^{33}S and ^{34}S , all of which may be measured simultaneously using Faraday cups (FC’s) with typical precision on $\delta^{33}\text{S}$ (and $\Delta^{33}\text{S}$) and $\delta^{34}\text{S}$ of $<0.2\text{‰}$ (1σ). The low abundance of ^{36}S (ca. 0.02%) however presents a significant analytical challenge to SIMS. Under typical analytical conditions used for triple-sulfur isotope analysis, a ca. 10^9 cps ^{32}S will be accompanied by only 2×10^5 cps ^{36}S which is too low to yield acceptable precision using FC’s. Furthermore, the ~ 5 - 10 -fold signal increase needed to reach such precision can only be achieved with a considerable loss of spatial resolution. An alternative approach is to measure ^{36}S in a pulse-counting electron multiplier (EM) but the small Hamamatsu EM’s on the IMS1270/80 experience significant gain drift at high count rates. Nonetheless, with appropriate within and between run drift correction, usable internal precision on $\Delta^{36}\text{S}$ of $\sim 0.5\text{‰}$ (1σ) can be achieved with spatial resolution $<10 \mu\text{m}$, as will be demonstrated with case studies from both early- and late-Archean sulfides. Lower noise FC amplifiers or substitution of a more robust EM can eventually improve precision.

[1] Farquhar & Wing (2003) *EPSL* **213**, 1-13. [2] Kamber & Whitehouse (2007) *Geobiology* **5**, 5-17. [3] Bekker *et al* (2009) *Science* **326**, 1086-1089. [4] Shen *et al.* (2009) *EPSL* **279**, 383-391

Geomicrobiology of hyperalkaline Cr(VI) contaminated land

ROBERT A. WHITTLESTON¹, IAN T. BURKE¹,
DOUGLAS I. STEWART² AND R.J.G. MORTIMER¹

¹School of Earth and Environment, University of Leeds,
Leeds, LS2 9JT, UK

²School of Civil Engineering, University of Leeds, Leeds, LS2
9JT, UK

Chromium in the form of its carcinogenic anion, chromate, has been entering the soils beneath a chromite ore processing residue (COPR) disposal site in the north of England for over 100 years, as a hyper alkaline (pH 13.5) liquor. This study reports the findings of a multi-disciplinary investigation into the biogeochemical processes occurring within the subsurface that influence contaminant fate.

The soil immediately beneath the waste was found to have a pH of 11→12.5, and contain 0.3→0.5% w/w chromium, and 45→75% of the microbially available iron is Fe(II). The soil pH and Cr concentrations were found to decrease with distance from the waste. XAS and (S)TEM analysis indicated that Cr is present throughout the soils as a mixed Cr(III)-Fe(III) oxy-hydroxide phase, resistant to air oxidation. This suggests that the elevated soil Cr content is due to reductive precipitation of Cr(VI) by Fe(II), producing a stable long term host for Cr(III). 16s rRNA community analysis of the soil immediately beneath the waste found a microbial population dominated by *Proteobacteria*, *Firmicutes* and *Bacteroidetes* species. Addition of this soil to alkaline Fe(III) containing growth media (pH=9.2) produced a consortium of iron reducing microorganisms dominated by the *Firmicutes* species, particularly *Anaerobranca*, *Anaerovirgula* and *Tissierella*.

Microcosm experiments demonstrated the capacity of COPR affected soil to abiotically remove all Cr(VI) from COPR leachate within 40 days. Amendment of the pH (\sim pH 9) resulted in the development of a cascade of microbially mediated terminal electron accepting processes, reaching Fe(III) reduction after complete Cr(VI) removal. A *Firmicutes* dominated population (73%) was identified in the pH amended microcosm systems during Fe(III) reduction, with *Dethiobacter sp* dominant, but *Anaerobranca sp* also present.

This work suggests that abiotic reductive precipitation of Cr(VI) by microbially produced Fe(II) can be effective at preventing the spread of chromium from COPR waste sites.

Lithium and its isotopes in Central European Rivers

U. WIECHERT^{1*}, C.V. ULLMANN^{1,2}, D. UHLIG¹,
T. PFAHL¹, M. RICKING¹ AND H. BECKER¹

¹Freie Universität Berlin, Germany

(*correspondence: wiechert@zedat.fu-berlin.de)

²University of Copenhagen, Denmark

Lithium isotopes are a promising new means to study silicate weathering. To date most lithium isotope work on river systems has been done on ocean islands [1] or remote regions of, for example, the Himalayas [2] where human influence on rivers is minor. In this study we present lithium abundances and isotopic ratios for the central European rivers Danube, Elbe, and Rhine. The catchments of these rivers are highly populated, densely industrialised, and affected by a highly developed farming industry. The goal of this ongoing project is to identify major processes and anthropogenic sources which control lithium and its isotopes in central European rivers. The investigated waters show lithium concentrations (dissolved load) between ~2 and 22 µg/l and $\delta^7\text{Li}$ from +4 to +22 ‰ relative to L-SVEC. Some Danubian and upper Rhine waters have lithium abundances close to 2 µg/l and high $\delta^7\text{Li}$ up to +22 ‰. Similar concentrations (0.2-4.0 µg/l) and $\delta^7\text{Li}$ ~+23 ‰ are reported for more pristine river systems worldwide [3] indicating that lithium in the upper Danube and upper Rhine is largely controlled by silicate weathering. The catchments of the lower Elbe, in particular waters of the river Saale, are characterized by high lithium concentrations and $^7\text{Li}/^6\text{Li}$. These waters have also high sulfate concentrations and $\delta^{34}\text{S}$ up to +8.5 ‰ CDT indicating a contribution from Permian evaporites. This is reasonable because evaporites have been mined in the region for more than a century. Samples from the river Elbe near Dresden, all Rhine and Danube samples show a good correlation between lithium isotope ratios and silicon fraction in the dissolved load ($r^2 = 0.7$). The highest molar fractions of silicon are connected to low $\delta^7\text{Li}$ ~5 ‰ and $\delta^{34}\text{S}$ ~3.4 ‰ in catchments of the river Elbe near Dresden. This is consistent with very intense weathering or a distinct style of weathering probably related to oxidation of sulfides and formation of highly acidic waters in old mining districts of the Erzgebirge.

[1] Pogge von Strandmann *et al.* (2008) *EPSL* **274**, 462-471;
[2] Kisakurek *et al.* (2005) *EPSL* **237**, 384-401. [3] Huh *et al.* (1998) *GCA* **62**, 2039-2051.

Shale gas potential of the Upper Jurassic strata in the central part of the Polish Lowlands

D. WIĘCŁAW* AND P. KOSAKOWSKI

AGH University of Science and Technology, Al. Mickiewicza
30, 30-059 Krakow, Poland

(*correspondence: wieclaw@agh.edu.pl)

The Upper Jurassic strata, rich in organic matter, are regarded as the main source rock of the large hydrocarbon accumulations in the Nowegian sector of the North Sea [1]. Also in Poland the Kimmeridge and Tithonian strata were subject of a large-scale exploration. In numerous wells only oil and gas shows were recorded. [2]. Our present study shows a new point of view on the possibility of shale gas accumulation in these strata. The investigations were conducted in the central part of the Polish Lowlands where the analysed strata are covered by thick Cretaceous deposits.

In total, 126 samples (66 from the Kimmeridgian and 60 from the Tithonian strata, respectively) were collected. Rock-Eval pyrolysis indicates a large diversity in the total organic carbon (TOC) content, from 0.14 to 6.6 wt% (median 1.1 wt%) and from 0.19 to 10.2 wt% (median 1.6 wt%) in the Kimmeridgian and Tithonian strata, respectively. The total hydrocarbon content in the analysed rocks is not high and medians equal 1.32 and 4.2 mg HC/g rock, respectively. Hydrocarbon potential of the Kimmeridgian strata is usually low with the median value of 121 mg HC/g TOC indicating the presence of gas-prone kerogen, whereas for the Tithonian strata, the median of this index equals 272 mg HC/g TOC (mixed gas- and oil-prone kerogen). Maturity of organic matter corresponds with the initial phase of "oil window". The BasinMod® 1-D modelling revealed that the generation of hydrocarbons from the Upper Jurassic source rocks occurred in the Late Cretaceous time. This process was interrupted by inversion on the Polish Lowlands.

In the selected areas of the Polish Lowlands the Kimmeridgian and Tithonian strata have generated sufficient amount of hydrocarbons to saturate rock and can be considered as a potential shale gas source.

The investigations were financed by the Ministry of Science and Higher Education (Project No. N307 3141 39).

[1] Justwan & Dahl (2005) *Proc. 6th Petrol. Geol. Conf.*, 1317-1329. [2] Karnkowski (1999) *Oil and gas deposits in Poland*, 380pp.

Primary shape and nanomechanical properties of natural Fe-colloids studied by AFM and SEM

A.K. WIECZOREK*, A. FRITZSCHE AND K.U. TOTSCHKE

Institut für Geowissenschaften, Hydrogeologie, Friedrich-Schiller-Universität Jena, Burgweg 11, D-07749 Jena, (*correspondence: arkadiusz-krzysztof.wieczorek@uni-jena.de)

Natural colloids and nanoparticles are involved in a multitude of biogeochemical and physicochemical processes and act as mobile reactive carriers [1]. Interactions with each other and with the immobile phase not only affect hydraulic properties, but may change geometric, mechanic and physicochemical properties of the pore network and its interfaces. Of particular importance are the nanoparticulate mineral-organic mixed phases, formed either by the way of heterogeneous nucleation, sorption or co-precipitation [2][3]. We studied natural colloids sampled from soils subjected to redoximorphosis combining Scanning Electron Microscopy, Energy-Dispersive X-ray Spectroscopy and Atomic Force Microscopy. We identified three types of material, i.e. bulky Fe-aggregates, linear-aligned Fe-aggregates and flat, circular, soft and adhesive patches, presumably pure organic in nature. The majority belongs to the bulky-type with mean sizes around 50nm. Yet they are formed of much smaller subunits. The linear-aligned aggregates, presumably representing the subunits of the bulky aggregates, have mean diameters around 20 nm with large variety of lengths. They seem to be "chained" along linear structures, which we hypothesize to be of biotic origin. Thus, biotic material may be important in the geometric structuring of the aggregation process of natural colloids.

[1] Totsche & Kögel-Knabner (2004) *Vadose Zone Journal* **3(2)**, 352-367. [2] Eusterhues *et al.* (2008) *Environ. Sci. Technol.* **42**, 7891-7897. [3] Eusterhues *et al.* (2011) *Environ. Sci. Technol.* **45**, 527-533.

Sequential extractions as a tool to investigate stable metal isotope fractionation between soil pools

JAN G. WIEDERHOLD^{1,2*}, BERNARD BOURDON^{2,3} AND RUBEN KRETZSCHMAR¹

¹Institute of Biogeochemistry and Pollutant Dynamics, ETH Zurich, Switzerland (*correspondence: wiederhold@env.ethz.ch)

²Isotope Geochemistry, Institute of Geochemistry and Petrology, ETH Zurich, Switzerland

³ENS Lyon and CNRS, France

Stable isotope ratios contain information about sources and transformations in the biogeochemical cycle of metals in the environment. The recent development of high-precision methods to resolve metal isotope fractionation (e.g., Fe, Hg) now allows to apply these new isotope tracers to a variety of natural systems and sample matrices including soils. Biogeochemical metal cycling in soils plays an important role in chemical weathering processes, nutrient dynamics, and the fate of pollutants in terrestrial ecosystems.

The stable isotope signature of bulk soil samples can be assessed relatively easily by analysing total digest solutions. However, metals in soil samples are often present in various "pools" which can have very different histories and chemical properties. Thus, valuable information on isotopic differences between soil pools and fractionation between them is lost by analyzing only the isotope signature of bulk samples. Sequential chemical extractions are an established tool to separate metal pools from natural samples. However, the application of sequential extractions in stable isotope studies bears the risk of introducing fractionation artifacts during the extraction procedure. Thus, a careful method development is required to assess the suitability of specific extraction steps.

Here, we present iron isotope ($\delta^{56}\text{Fe}$) and mass-dependent (MDF) and mass-independent (MIF) mercury isotope ($\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$) data from sequential extractions of different environmental samples measured by MC-ICP-MS. Newly-developed extraction methods were able to trace the evolution of secondary iron phases in young initial soils from a granitic glacier forefield, revealing that the imprint of a kinetic isotope effect during silicate weathering is preserved in pedogenic minerals. Mercury isotope ratios of sequential extracts from contaminated mine samples demonstrated that isotopically-distinct Hg pools exist within different tailing materials, exhibiting strong positive MDF and small negative MIF signatures in the more soluble extraction steps relative to the bulk isotopic composition. Future applications as well as potential limitations and pitfalls of sequential extraction methods in metal isotope studies will be discussed.

Life at the dry limit: Microbial colonization of evaporites in the Atacama Desert

J. WIERZCHOS^{1*}, A. DE LOS RÍOS¹, A.F. DÁVILA², S. VALEA¹, B. CÁMARA¹, O. ARTIEDA³ AND C. ASCASO¹

¹MNCN-CSIC, 28006 Madrid, Spain

(*correspondence: j.wierzchos@mncn.csic.es)

²SETI Institute, Mountain View, CA 94043-2172, USA

(adavila@seti.org)

³Universidad de Extremadura, 10600 Plasencia, Spain

(oartieda@unex.es)

The hyper-arid core of the Atacama Desert is considered the driest region on Earth, one of the most challenging environments for life, and a Mars analog, due mainly to water scarcity. While Atacama soils are essentially lifeless, we have shown that hygroscopic halite crusts are colonized by endolithic communities composed of cyanobacteria, heterotrophic bacteria and archaea [1, 2]. The interior of the crusts provides shelter against extreme temperatures and UV radiation, and facilitates cell hydration through mineral deliquescence [3]. We also found that microporous and translucent gypsum crusts represent another evaporitic habitat for life in Atacama. This substrate is colonized by endolithic and hypoeolithic free living algae, fungi, cyanobacteria and heterotrophic bacteria, as well as by epilithic lichens [4]. The colonization of gypsum crusts appears to be controlled by atmospheric water potential. Based on our work in Atacama, we propose that putative Martian microorganisms withdrew to similar evaporitic micro environments as the planet dried out [5]. As such, evaporitic deposits would be primer targets for the search for life.

[1] Wierzchos *et al.* (2006) *Astrobiol.* **6**, 415-422. [2] De los Ríos *et al.* (2010) *Int. Microb.* **13**, 79-89. [3] Dávila *et al.* (2008) *J. Geophys. Res.* **113**, G01028. [4] Wierzchos *et al.* (2011) *Geobiol.* **9**, 44-60. [5]. Dávila *et al.* (2010) *Astrobiol.* **10**, 617-628.

Trace element mobilisation in a natural analogue CO₂ storage site

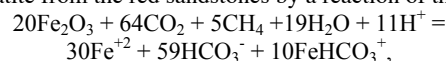
MAX WIGLEY*, MIKE BICKLE, NIKO KAMPMAN, BENOIT DUBACQ AND HAZEL CHAPMAN

Dept. Earth Sciences, Downing Street, Cambridge CB2 3EQ, UK (*correspondence: mmw36@cam.ac.uk)

Natural analogues present a unique opportunity to study fluid-mineral interactions and transport processes that may occur in geological CO₂ storage systems [1,2]. Near Green River, Utah, USA, regionally extensive portions of the red-bed Entrada sandstone have been locally bleached white/yellow by low temperature diagenetic fluids [3]. Fluid inclusion studies [3], field relationships and modelling suggest that the fluid responsible for the bleaching is a low Eh-pH, CO₂-rich brine, containing variable amounts of methane.

Analyses reveal systematic patterns of trace element mobilisation and transport resulting from CO₂-promoted oxide dissolution (Fig. 1). Trace metals and REE concentrations are enriched at the transition from bleached to red facies. Element distribution is controlled by partitioning between the fluid and secondary minerals (carbonate, oxide, and clay phases), that precipitate as geochemical fronts propagate through the host rock. These fronts separate reduced, acidic fluid from oxidized groundwater.

Modelling suggests that bleaching results from dissolution of hematite from the red sandstones by a reaction of the form:



in which CO₂ and a small fraction of methane complex the iron in solution. This reaction combined with Eh-pH diagrams suggest the precipitation of an iron-bearing carbonate and/or iron oxide phase, consistent with petrological observations.

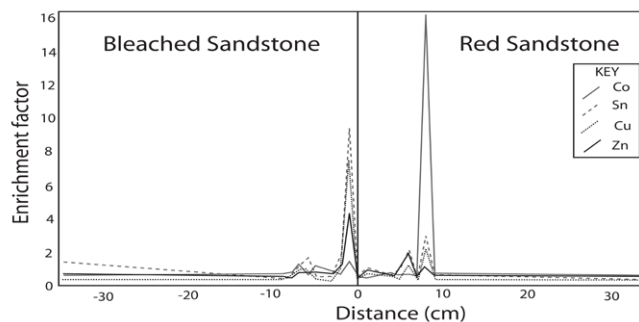


Figure 1. Plot of enrichment factor of metals relative to unaltered Entrada sandstone, versus distance from the bleached-unbleached contact.

[1] Moore *et al* (2005), *Chem. Geol.* **217**, 365-385. [2] Kampman *et al* (2009), *Earth Planet. Sci. Lett.* **284**, 473-488. [3] Kampman (2010), PhD thesis.

Chemical composition of biomass used in co-combustion with coal in Polish power-plants

W. WILCZYŃSKA-MICHALIK^{1*}, R. GASEK¹ AND M. MICHALIK²

¹Institute of Geography, Pedagogical University, ul. Podchorążych 2, 30-085 Kraków, Poland
(*correspondence: wmichali@up.krakow.pl; rgasek@ap.krakow.pl)

²Institute of Geological Sciences, Jagiellonian University, ul. Oleandry 2a, 30-063 Kraków, Poland; (marek.michalik@uj.edu.pl)

Biomass is considered as important non-fossil renewable energy source. Potential biomass resources in Poland are estimated to be around 30 millions Mg per year and the share of biomass in electricity production and other applications is increasing systematically. Lack of complex life cycle assessment studies is the reason that real environmental value of biomass usage as fuel is not fully understood.

Concentration of major and trace elements in biomass is very important in prediction of technological problems during combustion and usage of combustion co-products as well as their environmental impact. Composition of biomass is related to many factors, e.g.: type of biomass, age of plant, growth process, fertilizers and pesticides used, soils composition and contamination, atmospheric pollution of plantation area, harvesting, transportation and storage.

The study is based mineralogical (optical and electron microscopy, XRD) and chemical analyses of samples of biomass used in power-plants in southern Poland.

The content of mineral component is low. Mineral particles can be considered as detrital (i.e. introduced by water or wind during plant growth) and anthropogenic (introduced during harvesting, transportation, storage and processing).

Chemical variation of studied samples of biomass is significant (e.g. Ca from 0.1 to 1.1wt%; P from 0.2 to 0.89wt%; Al from <0.01 to 0.09wt%; Na from <0.001 to 0.106wt%; K from 0.05 to 2.4wt%; S from <0.01 to 0.22wt% and for selected trace elements: Mn from 7 to 333 ppm; Pb from 2.9 to 25.6 ppm; Zn from 8.3 to 79.4 ppm; Cu from 2.2 to 25.2 ppm; Mo from 0.03 to 0.72 ppm; Hg from <1 to 21 ppb). The content of several trace elements is within the range comparable with Polish coals (e.g. Mn, Cr, Cu, Ni, Pb, Zn).

Significant differences in chemical composition of various types of biomass suggest that it is possible to expect different behaviour during combustion and different environmental impact. It also suggests that careful blending of biomass may be important.

Hydrothermal alteration and Ni sulphide formation in the Bon Accord Ni-oxide body, Barberton, South Africa

ANTJE WILDAU^{1*}, A.E. WILLIAMS-JONES² AND MARIAN TREDoux¹

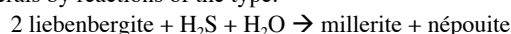
¹Department of Geology, University of the Free State, Bloemfontein, 9300, South Africa
(*correspondence: antje@geologie-leipzig.de)

²Department of Earth and Planetary Sciences, McGill University, Montreal, QC, H3A 2A7, Canada

The Bon Accord deposit is a 3.5Ga Ni-oxide body in the Barberton Greenstone Belt, South Africa. This small, lens-shaped orebody (6 x 3 x 0.35 m) was discovered in 1920, and mined out in the 1960s. The Ni concentration ranged from 35wt.% NiO in the center to 10wt.% NiO at the rim. The deposit has attracted considerable attention because of its very unusual mineralogy (e.g., bonaccordite, cochromite, nimite, liebenbergite, willemseite, trevorite). The orebody is hosted by a talc-carbonate-serpentinite and is located in the contact metamorphic aureole of a younger granite. The genesis of the deposit is unknown and the two main hypotheses that have been advanced for its formation are controversial. One of these is that the deposit is the product of a meteorite impact and the other is that it is an oxidized body of nickel-iron from the Earth's core.

Petrographic and geochemical studies of the Bon Accord deposit show the influence of hydrothermal fluids. In the centre of the deposit, there are relicts of primary liebenbergite (Ni₂SiO₄), which was serpentinized and later altered to willemseite ((Ni,Mg)₃Si₄O₁₀(OH)₂). The rest of the orebody is completely devoid of liebenbergite (Ni₂SiO₄) but much richer in népouite (Ni₃Si₂O₅(OH)₄) and willemseite ((Ni,Mg)₃Si₄O₁₀(OH)₂). The outer parts contain abundant millerite (NiS) and heazlewoodite (Ni₃S₂), plus a number of Ni-arsenide and Cu-sulphide minerals (10 vol.%), whereas the centre is almost devoid of Ni-sulphide minerals (<1vol.%). These minerals occupy cracks in the ferroan trevorite (NiFe₂O₄) and nickeloan magnetite ((Ni,Fe)₃O₄). In some places, the secondary minerals replace these oxides.

The mineralogical and textural relationships described above are consistent with alteration of the primary silicate minerals by reactions of the type:



These observations suggest that the Bon Accord deposit formed from Ni-rich komatiite that was altered by circulating hydrothermal fluids, forming secondary sulphide minerals.

A comparison of mm scale resolution techniques for sediment core analysis

D. WILHELMS-DICK^{1*}, T. HANEBUTH¹, U. RÖHL²,
T. WESTERHOLD², M. KRIEWS³, H. RÖMMERMANN³ AND
S. KASTEN¹

¹Bremen University, Postfach 330 440, 28334 Bremen,
Germany (*correspondence: wilhelms@uni-bremen.de)

²Marum, Postfach 330 440, 28334 Bremen, Germany

³Alfred Wegener Institute for Polar and Marine Research,
Postfach 120161, 27515 Bremerhaven, Germany

To study high-frequency variability in the Arabian Monsoon intensity, laminated sediments from the oxygen minimum zone (200–1200m) of the Arabian Sea offer a high-resolution climate archive [1]. The chemical signature which is used to reconstruct past climate can be obtained using several different analysing techniques. In the presented study a 5.3 m long sediment core from the northern Arabian Sea (GeoB12309-5: 24:52.3°N; 62:59.9°E, 960 m water depth), covers the past 4,900 cal yrs BP. The XRF core scanner data show highly varying signals in the upper 1.6 m core depth. Based on these results and radiograph images, samples were taken for LA-ICP-MS and ICP-MS/OES analysis.

The big advantages of analysing a sediment core via XRF core scanning are non-destruction and speed, but only relative variations for chemical elements are obtained and not element concentrations. The LA-ICP-MS methods is quasi non-destructive, you obtain element concentrations but is more time consuming. The most precise, but also most time consuming methods for main and trace element analysis are the ICP-MS/OES techniques after full acid digestion.

Results from all 3 methods show similar chemical patterns at distinct sediment structures (e.g. turbidites) for Ca, Rb and Sr. However, the comparability between the 3 methods is worse for Al, K, Ti, Fe and Zr. The particle size, water content of the sediment and surface roughness highly influences the XRF method, to some extent also the LA-ICP-MS technique. These results suggest that the soft sediment cores including its overall quality and surface conditions limit the ability of the sub-mm scale XRF scanning method to receive reliable data for Ca, Rb and Sr. However, the LA-ICP-MS technique as it was used here shows problems with long term drift, hence making it very difficult to accurately compare the 3 high resolution methods. Due to the relatively large amount of sediment digested, the ICP-MS/OES method delivers the most accurate results which are assumed to best serve as input data for frequency analysis.

[1] Von Rad *et al.* (1999) *Quat. Res.* **51**, 39-53.

Zircon solubility in Na-Si-Al-O-H fluids by *in situ* SR-XRF analysis

M. WILKE¹, C. SCHMIDT¹, J. DUBRAIL¹,
K. APPEL² AND M. BORCHERT²

¹Deutsches GeoForschungsZentrum GFZ, Potsdam, Germany
(max@gfz-potsdam.de)

²Deutsches Elektronen-Synchrotron, Hamburg, Germany

The geochemical budget of high-field-strength elements (HFSE, i.e., Ti, Zr, Hf, Nb and Ta) in rocks is largely controlled by accessory phases such as zircon or rutile. Thus, the mobility of HFSE during processes in the Earth's crust and mantle is closely linked to solubility and stability of these phases. Fluid composition appears to be the most important parameter because it may drastically affect the complexation of HFSE. Earlier studies ([1],[2]) on rutile report enhanced solubility for aqueous fluids with Na₂Si₃O₇ (NS3) or NaAlSi₃O₈. Complexing of Ti with alkalis and silica (siloxan groups) dissolved in the fluid has been suggested as an important mechanism to explain these high solubilities. A similar mechanism for enhanced solubility can be expected for the zircon-hafnon series.

Synthetic zircon was equilibrated with fluids containing Na₂Si₃O₇, Na₂Si₃O₇ + 5 wt% Al₂O₃, or NaAlSi₃O₈ at *T* up to 750 °C and *P* up to 1.5 GPa using hydrothermal diamond-anvil cells. The Zr content of the fluids was determined *in situ* at *P* and *T* by confocal synchrotron radiation μ XRF analysis at beamline L, HASYLAB. At *P* of 450–950 MPa and *T* of 500–750°C, Zr concentrations range from 20 to 90 ppm in H₂O + 10 wt% NS3 fluids. In H₂O + 18 wt% NS3 solutions, they increase to 200 to 500 ppm and drop to 100–150 ppm upon addition of Al. The highest concentrations of up to 1000 ppm were measured in fluids containing 30 wt% NS3. At constant NS3 content, the Zr concentration generally decreases with *P* and increases with *T*. One experiment with zircon *and* hafnon was done to measure Zr-Hf fractionation. At a NS3 content of 27 wt%, a molar Hf/Zr ratio of 2.7 was determined, which indicates significant Hf-Zr fractionation in these fluids. For a fluid with 6 wt% NaAlSi₃O₈ at ~1.45 GPa and 600°C, the XRF signal was at the detection limit, i.e. ~1 ppm Zr or below. These solubility data are qualitatively consistent with those on rutile ([1],[2]) and indicate strong differences in Zr speciation with *P*, *T*, and fluid composition. They represent another example for which efficient complexation of HFSE by siloxan-like units in the fluid is indicated (see also ref. [3]).

[1] Manning *et al.* (2008) *Earth Planet. Sci. Lett.* **272**, 730-737. [2] Antignano & Manning (2008) *Chem. Geol.* **255**, 283-293. [3] Dubrail *et al.* (2011) *MinMag*, this volume.

Compound-specific isotopic evidence of paleoenvironmental change Lake El'gygytgyn, NE Russia

K. WILKIE*, S.T. PETSCH, S. BURNS AND J. BRIGHAM-GRETTE

Dept. of Geosciences, University of Massachusetts, Amherst, MA, USA (*correspondence: kwilkie@geo.umass.edu)

Recent successful drilling operations at Lake El'gygytgyn, NE Russia have recovered sediment cores back to 3.6Ma, representing the longest time-continuous sediment record of past climate change in the terrestrial Arctic. Compound-specific isotopic analysis of sedimentary lipids from this remote basin spanning the last 120ka allows reconstruction of past hydrological conditions, thereby providing a powerful tool for reconstructing past Arctic climate changes.

The hydrogen isotopic composition of lipid biomarkers was determined from previously obtained Lake El'gygytgyn sediment cores and compared with other multi-proxy evidence of past climate change within the lake basin. Here we present δD measurements of individual sedimentary fatty acids representing aquatic and terrestrial sources (e.g. aquatic, δD_{AQ} : nC_{20} , nC_{22} ; terrestrial, δD_{TER} : nC_{30}) over the past 120 ka. The δD_{AQ} record shows little variation on glacial-interglacial cycles, possibly due to perennial ice cover during full glacial conditions and/or changes in aquatic community structure and aquatic organic matter sources. The data from terrestrial components show significant variation (up to 70‰) between glacial-interglacial intervals as well as variation on millennial timescales (~200 yr resolution). The most negative δD_{TER} values occur during glacial conditions (i.e. the Last Glacial Maximum and MIS 4) while enriched values are observed during interglacial intervals (i.e. most notably during the Holocene and MIS 5e). Preliminary reconstruction of the isotopic composition of precipitation from these results allows for comparison with the δD ice core records from both Greenland and Antarctic to assess high latitude environmental change and global teleconnections. Initial comparison of these records shows high fidelity with speleothem records from Hulu and Dongge caves [1] as well as with δD_{GRIP} [2] and δD_{VOSTOK} [3] records.

[1] Wang *et al.* (2005), *Science* **308**, 854-857. [2] Masson-Delmotte *et al.* (2005), *Science* **309**, 118-121. [3] Petit *et al.* (1999), *Nature* **399**, 429-436.

The W isotopic composition of the Hadean mantle – Evidence for the late heavy bombardment

M. WILLBOLD¹, T. ELLIOTT¹ AND S. MOORBATH²

¹University of Bristol, School of Earth Sciences, Wills Memorial Building, Queens Road, Bristol, BS8 1RJ, United Kingdom

²University of Oxford, Department of Earth Sciences, South Parks Road, Oxford, OX1 3AN, United Kingdom

The contrasting behaviour of its daughter and short-lived ($t_{1/2}$ ~9Ma) parent has made the ^{182}Hf - ^{182}W system invaluable in determining the timescales of planetary core formation. However, Hf is also considerably less incompatible than W in many melting and crystallisation scenarios in purely silicate systems. Thus the ^{182}Hf - ^{182}W pair has also been used with success in examining the evolution of the silicate portion of planetesimals. Recent $\epsilon^{142}\text{Nd}$ data demonstrate that Hadean mantle fractionation events are recorded in the isotopic signatures of samples from Isua, Greenland. Notably one interpretation of terrestrial ^{142}Nd - ^{143}Nd systematics invokes the formation of an enriched, deep reservoir within the first 30Ma of Earth History. It has further been suggested that the contrast between $\epsilon^{142}\text{Nd}$ in the most ancient Greenland samples and present day mantle (~20ppm) is a result of partial remixing between this hidden reservoir and convecting mantle after ~3.5Ga. If so, the Greenland samples derived from mantle that pre-dates this event would be expected to show a difference in $\epsilon^{182}\text{W}$ relative to modern mantle.

We have made high-precision (<5ppm; 2σ) $\epsilon^{182}\text{W}$ measurements on some Isua samples. These document significant differences between these samples and modern mantle values (~13ppm). In contrast to previous studies [1,2] our analyses are considerably more precise and we are the first to document significant differences. However, the magnitude of the difference in our $\epsilon^{182}\text{W}$ is smaller than predicted for a remixing scenario of early enriched reservoir with the convecting mantle that can account for the difference in $\epsilon^{142}\text{Nd}$ between Isua and present mantle. We thus re-emphasise the conclusions of [1], that this change in $\epsilon^{142}\text{Nd}$ with time does not provide good evidence for the existence of an early enriched reservoir. We further note that the addition of ~0.5% of primitive chondritic material after core formation, as suggested by the late veneer model, is sufficient to account for the lowering of $\epsilon^{182}\text{W}$ from values we report in the Isua samples to present-day.

[1] Iizuka, T. *et al.* (2010) *Earth and Planetary Science Letters* **291**, 189-200. [2] Moynier, F. *et al.* *Proceedings of the National Academy of Sciences* (2010) **107**, 10810-10814.

From thermochronometric ages to exhumation rates

S.D. WILLET¹, M.T. BRANDON², M. FOX¹ AND F. HERMAN¹

¹Geological Institute, ETH, 8092 Zurich, Switzerland
²Yale University, New Haven, CT, USA

To render a thermochronometric age into a more useful exhumation rate, it is necessary to process that age through a thermal model. We present a set of analytical and numerical thermal modelling methods of increasing complexity; which we feel are as simple as possible, while still retaining the essential physics of the thermal processes. We consider first the simple case of converting a single age into an exhumation rate. We include the dependence of the closure temperature on cooling rate (Dodson, 1973) and the upward advection of heat and derive some simple, analytical expressions relating exhumation rate to age through the kinetic parameters of the thermochronometric system, first, by assuming the geothermal gradient has been constant in time, and, second, using the transient analytical solution for an advecting halfspace. The second problem we consider is the effects of topographic relief on the closure isotherm. We calculate the mean depth to a closure isotherm using the solution described above, and then use spectral methods to calculate topography on this isotherm in response to topography of the surface. Finally, we consider the problem of spatially-varying exhumation rate. For this problem we combine the approaches given above, calculating perturbations to isotherms using spectral methods, combined with 1-D models of heat advection and diffusion. The 1-D models are linked by imposing a spatial correlation structure on the exhumation rate, which is otherwise free to vary in space and time. This approach provides an efficient method to “invert” a large number of thermochronometric ages, distributed in space and elevation, providing maps of time-varying exhumation rate. We illustrate each of these methods with data from the European Alps.

Novel approaches to organic aerosol chemical characterization

B.J. WILLIAMS^{1*}, Y. ZHANG¹, R. MARTINEZ¹, K.S. DOCHERTY^{2,3}, I.M. ULBRICH², J.L. JIMENEZ², S.V. HERING⁴, N.M. KREISBERG⁴, A.H. GOLDSTEIN⁵, AND D.R. WORSNOP⁶

¹Washington University, St. Louis, MO 63130, USA
(*correspondence: brentw@seas.wustl.edu)

²University of Colorado and CIRES, Boulder, CO 89309, USA

³Alion Science and Technology, Research Triangle Park, NC 27709, USA

⁴Aerosol Dynamics Inc., Berkeley, CA 94710, USA

⁵University of California, Berkeley, CA 94720, USA

⁶Aerodyne Research Inc., Billerica, MA 01821

In recent years several new approaches have been introduced to improve the chemical characterization of atmospheric organic aerosol (OA). Here, we highlight two techniques, the thermal desorption aerosol gas chromatograph (TAG) for automated in-situ molecular level OA speciation [1], and the high resolution time-of-flight aerosol mass spectrometer (AMS), which in addition to inorganic speciation, measures total fine OA mass concentrations and determines O/C, H/C, and N/C elemental ratios [2]. While each technique has its strengths, the TAG system is not capable of complete OA analysis without prior chemical derivatization, and the AMS is not capable of separating individual compounds. Here, we will describe recent efforts to create a combined TAG-AMS system to provide measurements of total OA, elemental ratios, and individual compounds. Finally, we discuss our efforts to develop novel data analysis approaches. Positive matrix factorization (PMF) has been used to deconvolve timeseries of AMS mass spectra [3] and timeseries of TAG source-marking compounds [4] into major components contributing to atmospheric OA concentrations. The desire to have combined TAG-AMS input parameters for a single PMF analysis have inspired novel measurement ideas that will be introduced here.

- [1] Williams *et al.* (2006) *Aerosol Sci Technol* **40**, 627-638.
[2] DeCarlo *et al.* (2006) *Anal Chem* **78**, 8281-8289. [3] Ulbrich *et al.* (2009) *Atmos Chem Phys* **9**, 2891-2981. [4] Williams *et al.* (2010) *Atmos Chem Phys* **10**, 11577-11603.

Isotopic evidence for internal oxidation of the Earth's mantle during accretion

HELEN M. WILLIAMS^{1,2*}, BERNARD J. WOOD¹,
JON WADE¹, DANIEL J. FROST² AND JAMES TUFF¹

¹Department of Earth Sciences, The University of Oxford,
South Parks Road, Oxford OX1 3AN, UK

²Department of Earth Sciences, Durham University, Science
Labs, Durham DH1 3LE, UK (*correspondence:
h.m.williams2@durham.ac.uk)

³Bayerrisches Geoinstitut, Universität Bayreuth, D-95440
Bayreuth, Germany

The Earth's mantle is currently oxidised and out of chemical equilibrium with the core. Why this should be the case, and why the Earth's mantle should be oxidised relative to other terrestrial planets is poorly understood. It has been proposed that the oxidised nature and high ferric iron (Fe³⁺) content of Earth's mantle was produced internally by disproportionation of ferrous iron (Fe²⁺) into Fe³⁺ and metallic iron by perovskite crystallisation during accretion [1]. Here we show that there is a substantial Fe isotope fractionation between experimentally equilibrated metal and perovskite, which can account for the heavy Fe isotope compositions of terrestrial basalts relative to equivalent samples derived from Mars and Vesta [2,3] as the latter are too small to stabilise perovskite. Mass balance calculations indicate that all of the mantle's Fe³⁺ could have been generated from a single disproportionation event, which is consistent with complete dissolution of perovskite in the lower mantle during the Moon-forming giant impact. The similar Fe isotope compositions of terrestrial and lunar basalts [2,3] is consistent with equilibration between the mantles of the Earth and Moon in the aftermath of the giant impact [4] and suggests that the heavy Fe isotope composition of the Earth's mantle was established prior to, or during the giant impact. The oxidation state and ferric iron content of the Earth's mantle was therefore plausibly set by the end of accretion, and is decoupled from later volatile additions [5], tectonic plate recycling and the rise of oxygen in the Earth's atmosphere at 2.45 Ga [6].

[1] Frost, D. J. *et al.*, (2004). *Nature* **428** (6981), 409 [2] Poitrasson, F. *et al.*, (2004). *EPSL*. **223** (3-4), 253 [3] Weyer, S. *et al.*, (2005). *EPSL* 240 (2), **251** [4] Pahlevan, K. and Stevenson, D. J., (2007) *EPSL*. **262** (3-4), 438. [5] Schonbachler *et al.*, (2010) *Science* **328** (5980), 884. [6] Kump, L. R., (2008) *Nature* **451** (7176), 277.

Characterization of elemental sulfur reducing bacteria using transmission electron microscopy and their impact on sulfur isotope fractionation

KENNETH H. WILLIAMS^{1*}, MICHAEL J. WILKINS^{2*},
ALICE C. DOHNALKOVA², JENNIFER L. DRUHAN¹,
AND MARK E. CONRAD¹

¹Lawrence Berkeley National Laboratory, Berkeley, CA,
94720, USA (*khwilliams@lbl.gov)

²Pacific Northwest National Laboratory, Richland, WA,
99352, USA (*michael.wilkins@pnl.gov)

The process of elemental sulfur (S⁰) reduction by a microorganism isolated from an acetate-stimulated aquifer at the Department of Energy's Rifle Integrated Field Research Challenge (IFRC) site in Rifle, Colorado (USA) was studied using a combination of transmission electron microscopy (TEM) and isotopic techniques. Results were compared to those obtained using the well-characterized S⁰ reducer *Geobacter sulfurreducens*. The site isolate was obtained from Rifle groundwater using acetate and S⁰ flowers as the electron donor and acceptor, respectively. Based on 16S rRNA analysis, the isolate was most closely related to the β -proteobacterium *Azospira orzyae* (syn *Dechlorosoma suillum*). TEM revealed the isolate to be a curved rod with a single polar flagellum. Finely particulate S⁰ granules (<5nm) were observed along the outer membrane as aqueous sulfide concentrations reached peak values of ca. 1200 μ M. Prolonged growth resulted in an abundance of aggregated filaments bound within a sulfur-rich matrix; their biogenesis and relation to cell growth remains unknown. Microbial reduction of S⁰ coupled to oxidation of acetate may lead to significant deviations in the δ^{34} S values of sulfide relative to δ^{34} S values of S⁰.

Such studies are critical for understanding the process of sulfur reduction in reduced environments, hypothesized to enable prolonged U(VI) immobilization at the Rifle IFRC site. Research at the site has identified significant accumulation of S⁰ accompanying oxidation of aqueous sulfide by Fe(III)-oxide minerals, with the process generating an abundant electron acceptor capable of supporting the activity strains implicated in enzymatic U(VI) reduction (e.g. *Geobacter*) following exhaustion of reactive Fe(III) minerals. These results will enable incorporation of rates of microbial S⁰ reduction and δ^{34} S fractionation within reactive transport models describing biogeochemical processes at the Rifle site and provide additional insights into sulfur cycling pathways.

Atomistic simulation of oxygen transport in actinide oxides and at their interfaces

N.R. WILLIAMS^{1*}, S.C. PARKER¹, A. DEVEY² AND M. READ²

¹Department of Chemistry, University of Bath, Bath BA2 7AY, United Kingdom
(*correspondence: n.r.williams@bath.ac.uk)

²AWE, Aldermaston, Reading, RG7 4PR
(mark.read@awe.co.uk, anthony.devey@awe.co.uk)

Actinides such as uranium and its oxides are receiving increasing attention because of the interest in nuclear fuels not least because of awareness of issues associated with CO₂ emissions, security of energy supply and waning fossil fuel reserves. This also has implications on the storage of these materials in both the long and short term. Computational methods provide a complementary route for studying the corrosion of nuclear fuels and transport through the environment.

We used computer simulation techniques, using both potential-based and electronic structure methodologies to investigate the structure and stability of the surfaces and interfaces, primarily of uranium dioxide as well as the factors controlling oxygen transport through the materials. The electronic structure simulations used the VASP code [1] using GGA+U method, but are further complicated by the magnetic contribution of the 5f electrons. The correct ground state and properties are obtained by correctly controlling the orbital occupation matrices [2]. The interatomic potentials were derived to reproduce the calculated and experimental properties and used to evaluate the grain boundary structures as a function of temperature using molecular dynamics with the DL_POLY code [3].

A number of grain boundary structures were investigated we found that at high temperatures but below the melting point that UO₂ undergoes a fast ion transition where oxygen becomes highly mobile. The grain boundaries showed enhanced diffusivity, displaying fast ionic conduction at significantly lower temperatures than observed in the bulk crystal.

In summary a number of computational techniques have been utilised to investigate actinides such as uranium and their oxides. Increased understanding of the intrinsic disorder present in these oxides and its effect on corrosion offers significant benefits for the safe storage and handling of nuclear fuel materials.

[1] Kresse & Furthmüller (1996), *Phys. Rev. B*, **54**, 11169-11186. [2] Devey (2011) *J. Nucl. Mater.* doi:10.1016/j.jnucmat.2011.03.012 [3] Smith and Forester (1996) *J. Mol. Graph* **14**, 136-141

Transitional oxygenation recorded in the Paleoproterozoic Turee Creek Group, Western Australia

KENNETH H. WILLIFORD^{1*}, MARTIN J. VAN KRANENDONK², TAKAYUKI USHIKUBO¹, REINHARD KOZDON¹ AND JOHN W. VALLEY¹

¹NASA Astrobiology Inst., WiscSIMS, Dept. of Geoscience, Univ. Wisconsin, Madison, WI 53706 USA,

(*correspondence: kwilliford@geology.wisc.edu)

²Geol. Surv. Western Australia, Perth, WA 6004, Australia

In situ, multiple sulfur isotope data from pyrite in the glaciomarine Meteorite Bore Member of the Paleoproterozoic Turee Creek Group, Western Australia, indicate deposition during a transitional stage in the rise of atmospheric oxygen. Abundant detrital pyrite in one diamictite layer exhibits a range of $\Delta^{33}\text{S}$ (-3.6 to 11.6‰) encompassing the entire known range for the Archean. Small, but significant, S-MIF ($\Delta^{33}\text{S}$ from -0.8 to 1.0‰) is preserved in authigenic pyrite throughout the section. A >90‰ range in $\delta^{34}\text{S}(\text{Py})$ (-45.5 to 46.4‰ VCDT) is strong evidence for vigorous microbial sulfate reduction under non-sulfate limited conditions, an indication that oxidative continental weathering of sulfides was sufficient before and during deposition to deliver a large quantity of sulfate to the ocean. Multiple generations of pyrite were observed, distinguished by their isotopic and minor element compositions. Sharp gradients in $\delta^{34}\text{S}$ (30‰ over <4 μm ; defined by 3 μm spots) constrain the degree of sulfur diffusion during metamorphism and thus the time-temperature history of the unit. This is the first observation of such a large range in $\delta^{34}\text{S}$ together with significant S-MIF, and it reveals a chapter in the history of atmospheric oxygenation heretofore unknown from similarly age-constrained glacial deposits in North America [1] and South Africa [2]. The new data highlight the critical role of microbial sulfate reduction in the oxidative transition and are consistent with the proposal by Zahnle *et al.* [3] that increasing seawater sulfate led to the shutdown of the Archean methane greenhouse, curtailing the preservation of S-MIF. However, the suggestion that S-MIF disappears completely before continental glaciation [3] is not supported by our data or those from North America [1] and South Africa [2], and details of the Great Oxidation Event remain to be elucidated.

[1] Papineau *et al.* (2007) *EPSL* **255**, 188-212. [2] Guo *et al.* (2009) *Geology* **37**, 399-402. [3] Zahnle *et al.* (2006) *Geobiology* **4**, 271-283.

High-resolution metabolomics reveals unusual *N*-methyl *lyso* phosphatidylethanolamines as abundant and strain-specific lipids in acid mine drainage biofilms

P. WILMES^{1*}, C.R. FISCHER², B.P. BOWEN³,
B.C. THOMAS⁴, R.S. MUELLER⁴, V.J. DENEFF⁴,
N.C. VERBERKMOES⁵, R.L. HETTICH⁵, T.R. NORTHEN³
AND J.F. BANFIELD⁶

¹Department of Earth and Planetary Science, University of California, Berkeley, CA 94720, USA; present address: Public Research Center – Gabriel Lippmann, Belvaux L-4422, Luxembourg
(*correspondence: wilmes@lippmann.lu)

²Department of Earth and Planetary Science, University of California, Berkeley, CA 94720, USA; present address: Ginkgo Bioworks, Boston, MA 02210, USA
(curt@ginkgobioworks.com)

³GTL Bioenergy Division and Life Sciences Division, Lawrence Berkeley National Laboratory, CA 94720, USA
(bpbowen@lbl.gov, trnorthen@lbl.gov)

⁴Department of Earth and Planetary Science, University of California, Berkeley, CA 94720, USA
(bcthomas@berkeley.edu, rmueller@berkeley.edu, vdenef@berkeley.edu)

⁵Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA (verberkmoesn@ornl.gov, hettichrl@ornl.gov)

⁶Department of Earth and Planetary Science, and Department of Environmental Science, Policy and Management, University of California, Berkeley, CA 94720, USA
(jbanfield@berkeley.edu)

High-resolution untargeted metabolomics was applied to 14 distinct biofilm samples retrieved from the air-solution interface of acid mine drainage (AMD) solutions within the Richmond Mine (Iron Mountain, Redding, CA). Among the detected metabolites, we identified and characterized a group of *lyso* phosphatidylethanolamine lipids which were highly abundant. The unusual polar head group structure of these molecules is similar to lipids found in phylogenetically unrelated acidophilic chemoautolithotrophs and may be related to the affinity of these lipids for iron and calcium ions. Correlations of *lyso* phospholipid and strain-resolved protein abundance patterns suggest a link between the *lyso* phospholipids and the UBA-type substrain of *Leptospirillum* group II. By combining high-resolution molecular “omic” technologies, we demonstrate focusing of upward fluid migration due to mineral grain size variation

the ability to identify cryptic but organism-specific small molecules that may be of paramount importance to biogeochemical processes occurring in mining impacted environments.

A spatial perspective on Nd isotope records from the Western Indian Ocean: Evidence for a ‘boundary exchange’ control?

D.J. WILSON*, A.M. PIOTROWSKI AND A. GALY

Department of Earth Sciences, University of Cambridge, Cambridge, CB2 3EQ

(*correspondence: david.wilson@esc.cam.ac.uk)

Reconstructing past water mass mixing using Nd isotopes relies upon the quasi-conservative behaviour of this tracer. In contrast, recent studies in the modern oceans have demonstrated that ‘boundary exchange’ [1] and/or reversible scavenging [2] may be important processes in the Nd cycle. ‘Boundary exchange’ in particular would complicate our interpretation of down core Nd isotope records, since any significant addition of Nd from sediments would make the proxy behave non-conservatively. However, modelling studies at a global scale [3, 4] have been unable to distinguish between advection and ‘boundary exchange’ as the dominant control on the Nd isotopic distribution of seawater.

In this study, using 10 sediment cores from the deep western Indian Ocean, we address the importance of ‘boundary exchange’ from the Madagascar and Mascarene Plateau margins. Deep water ϵ_{Nd} composition is reconstructed using foraminiferal coatings, which agree within error with bulk sediment leachates. Holocene core tops located along the south-to-north flow path of Circumpolar Deep Water (CDW) record different ϵ_{Nd} values. Cores nearest to the inflow record an ϵ_{Nd} of -8.6, which shifts to -11.3 near Madagascar and -7.1 near Mascarene. Comparison to detrital ϵ_{Nd} in the same cores suggests a control by local sedimentary inputs from Madagascar and the Mascarene Plateau. This allows a first attempt to quantify ‘boundary exchange’ along this margin and potentially to reconstruct past changes. Cores to the south of the Madagascan margin (i.e. upstream in deep water flow) appear to record the changing advected composition of CDW across Termination I, whereas marginal sites record offset ϵ_{Nd} values and reduced glacial-interglacial variability. This underlines the importance of deciphering ‘boundary exchange’ before inferring global ocean circulation changes from Nd isotope records. Additionally, it may provide insight into temporal changes in the inputs, and therefore budget, of REE’s and other particle-reactive elements in the oceans.

[1] Lacan & Jeandel (2005), *EPSL* **232**, 245-257. [2] Siddall *et al.* (2008), *EPSL* **274**, 448-461. [3] Arsouze *et al.* (2007), *Chem. Geol.* **239**, 165-177. [4] Jones *et al.* (2008), *EPSL* **272**, 610-619.

Tracing changes in the East Asian Monsoon using the Mg isotope record in a loess-paleosol sequence from Luochuan, China

JOSH WIMPENNY¹, QING-ZHU YIN^{1*},
DARREN TOLLSTRUP¹, LIE-WEN XIE² AND JIMIN SUN²

¹Department of Geology, University of California, Davis, CA

²Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China

We present Mg isotope data from a loess-paleosol sequence from Luochuan in the central Chinese Loess Plateau. The alternating loess-paleosol layers result from changes in climate and weathering intensity; loess layers representing cooler, drier periods when the winter monsoon was strong, while paleosol layers form during warmer, wetter periods with a stronger summer monsoon. Bulk $\delta^{26}\text{Mg}$ analyses show that both loess and paleosol layers are enriched in the light isotopes of Mg relative to the bulk continental crust. On average, loess layers contain lighter $\delta^{26}\text{Mg}$ values than the paleosol, with average values of $-0.57\text{‰} \pm 0.19$ (2σ), and $-0.37\text{‰} \pm 0.18$ (2σ) respectively. These light $\delta^{26}\text{Mg}$ values are a direct result of high amounts of carbonate in the sediment layers (up to $\sim 15\%$) and the fact that carbonate is enriched in light Mg relative to silicates. The higher chemical weathering intensity subjected to the paleosol layers means more carbonate has been leached away, hence the remaining sediment is isotopically heavier than the loess layers where more carbonate remains. The high amplitude changes in $\delta^{26}\text{Mg}$ related to alternating loess-paleosol layers at Luochuan closely match changes in other weathering tracers including magnetic susceptibility, grain size and Na/Ca ratios. This suggests that all of these proxies are controlled by the same process, i.e. changing climate related to changes in northern hemisphere circulation. In addition, our $\delta^{26}\text{Mg}$ analyses also record a longer term change in chemical weathering, manifested as a shift to more positive $\delta^{26}\text{Mg}$ values ~ 500 to 900Ka . This coincides with the approximate timing of a strengthening in the summer monsoon and a reduction in the seasonality of precipitation. Thus, Mg isotopes record weathering changes on two different timescales in Chinese loess, that have implications for our understanding of how the East Asian Monsoon may have behaved over the last 2.6Ma . We suggest that the sensitivity of Mg isotopes to the presence of carbonate, and to the formation of secondary silicates makes the Mg system a powerful tool that can be used to enhance our understanding of past weathering processes.

Carbon isotopes in DIC trace benthic and pelagic processes in tidal areas of the North Sea

VERA WINDE¹, PETER ESCHER¹, NICOLE KOWALSKI¹,
OLAF DELLWIG¹, BERND SCHNEIDER¹,
MATTHIAS SCHULTZ¹, PHILLIP BÖNING²,
JUSTUS E.E. VAN BEUSEKOM³, GERD LIEBEZEIT² AND
MICHAEL E. BÖTTCHER^{1*}

¹Leibniz IOW, D-18119 Warnemünde, Germany.

(*michael.boettcher@io-warnemuende.de)

²ICBM, CvO University of Oldenburg, D-26382

Wilhelmshaven/ D-26111 Oldenburg, Germany

³AWI Wadden Sea Station Sylt, D-25992 List, Germany

We investigate the spatial gradients and temporal dynamics of the dissolved inorganic carbonate system in tidal areas of the North Sea. We aim for an understanding of the impact of benthic processes on the production of alkalinity and its subsequent export to the open North Sea, as well as the role of benthic processes, e.g. the interaction (destruction, formation) of surface pore waters with sedimentary calcium carbonate. These processes in turn have the potential to modify the pore water and the bottom water composition that exchanges with the shallow North Sea. The benthic and pelagic processes may change in the future as the North Sea is facing increasing atmospheric CO_2 pressures, and decreasing pH and changes in nutrient inventories are expected.

Water column and pore water samples were taken at different seasons, during tidal cycles and on transects through different tidal basins of the German Wadden Sea (Jade Bay, Sylt, Spiekeroog) for measurements of alkalinity, DIC, pH, salinity, temperature, $\delta^{13}\text{C}(\text{DIC})$, besides major and trace elements. The carbonate system demonstrates significant tidal, and spatial, as well as seasonal variations in the water column. Such variabilities reflect mixing processes with freshwater via coastal tributaries and the influence of benthic and pelagic (e.g. primary production) processes, changing with season. Results from the East-Frisian Wadden Sea are compared to measurements in the North-Frisian Wadden Sea system. Locally, pore waters in sandy sediment, influenced by upward methane fluxes and AOM, reveal steep physico-chemical gradients. Low-tide drainage of anoxic pore waters leads to the liberation of ^{12}C -enriched DIC, TA, nutrients and (H_2S , CH_4).

Field data will be integrated in a modelling environment of the North Sea carbonate system. Research is supported by BMBF within the BIOACID project, IOW, AWI, and ICBM.

100-year record of $^{236}\text{U}/^{238}\text{U}$ in coral as a step towards establishing ^{236}U as oceanic tracer

S. WINKLER^{1*}, P. STEIER¹, J. CARILLI²

¹Faculty of Physics, University of Vienna, 1090 Wien Austria
(* correspondence: stephan.winkler@univie.ac.at)

²Institute for Environmental Research, Australian Nuclear Science and Technology Organisation

Since uranium is known to behave conservatively in ocean waters, ^{236}U has great potential in application as oceanic tracer. Approximately 600kg of ^{236}U ($t_{1/2}=23.4\text{Ma}$) were introduced into the oceans by atmospheric nuclear weapon testing [1]. A resulting initial average $^{236}\text{U}/^{238}\text{U}$ ratio of $5\cdot 10^{-9}$ is expected for the oceanic mixed layer. This ratio is significantly higher than the expected natural pre-nuclear background, which is expected to be at 10^{-14} levels [2].

In order to place first experimental constraints the input term from global stratospheric fall-out we established a year-by-year record of $^{236}\text{U}/^{238}\text{U}$ for a core from the Caribbean Sea. The selected core was taken in 2006. It has shown well-defined annual banding structure under X-ray and stretches back more than 100 years, therefore covering the interesting period of global stratospheric fall-out.

We used the exceptional sensitivity and ultra-low background for ^{236}U of the Vienna Environmental Research Accelerator's Accelerator Mass Spectrometry system for this measurement and find a $^{236}\text{U}/^{238}\text{U}$ signature of $(1.84\pm 0.08)\cdot 10^{-9}$ for the fall-out peak. Furthermore we set a first experimental upper limit of $4\cdot 10^{-12}$ on the pre-anthropogenic $^{236}\text{U}/^{238}\text{U}$ -ratio in ocean surface waters.

[1] Sakaguchi *et al.* (2009) *Science of the Total Environment* **407**(14), 4238-4242. [2] Steier *et al.* (2008) *NIM B* **266**(10), 2246-2250.

Aeolian iron flux in the South-Western Ross Sea, Antarctica

V.H.L. WINTON^{1,2*}, M.-A. MILLET³, N.A.N. BERTLER^{1,2}
G.B. DUNBAR¹, B. DELMONTE⁴ AND P. ANDERSSON⁵

¹Antarctic Research Centre, Victoria University of Wellington, PO Box 600, Wellington

(*correspondence: holly.winton@vuw.ac.nz)

²GNS Science Ltd, PO Box 31 321, Lower Hutt

³School of Geography, Environment and Earth Sciences, Victoria University of Wellington

⁴Dipartimento di Scienze dell'Ambiente e del Territorio Università degli Studi di Milano-Bicocca, Milano, Italy

⁵Laboratory for Isotope Geology, Swedish Museum of Natural History, PO Box 50 007, 104 05 Stockholm

Each summer the waters in the south-western Ross Sea experience vast phytoplankton blooms. This phenomenon is thought to be stimulated by the addition of bio-available Fe in an otherwise Fe-limited environment. Amongst all the potential Fe sources, input from aeolian dust, which has accumulated on sea ice and is released to the ocean in summer as the sea ice melts, is heavily underestimated. The south-western Ross Sea provides an excellent example to study this biogeochemical process.

The amount of bio-available Fe supplied to the ocean depends on a number of factors including, but not limited to; the dust flux into the ocean, particle size distribution and its Fe content. However, none of these parameters are well constrained in the south-western Ross Sea region and, as a result, the significance of this Fe source in the biogeochemical cycle of plankton growth remains to be quantified.

Dust is shown to be sourced locally based on: a) elevated regional dust flux for the region which is higher by orders of magnitude than predicted in global dust distribution models [1] and in the Antarctic Plateau [e.g. 2]; b) Sr and Nd isotopic signature matching local potential source rocks. The regional dust flux for particles $<10\ \mu\text{m}$ in size (the potentially bio-available fraction) is $\sim 0.08\ \text{g}/\text{m}^2/\text{yr}$. Fe-solubility measurements are currently being completed on the $0.4\text{-}10\ \mu\text{m}$ size fraction following the leaching protocol of Aguilar-Islas *et al.* [3]. This will allow us to quantify the amount and estimate its importance for aeolian Fe-fertilisation for bio-productivity in this region.

[1] Mahowald *et al.* (2005) *Global Biogeochem. Cycles* **19**, GB4025. [2] Delmonte *et al.* (2004) *Earth Planet. Rev.* **66**, 63-87. [3] Aguilar-Islas *et al.* (2010) *Marine Chem.* **120**, 25-33.

Quantification of H in olivine: Direct calibration of FTIR and SIMS by ERDA

A.C. WITHERS^{1*}, M.M. HIRSCHMANN¹, H. BUREAU² AND
C. RAEPSAET³

¹Department of Earth Sciences, University of Minnesota,
Minneapolis, MN 55455, USA (*correspondence:
withers@umn.edu)

²IMPMC, UMR CNRS 7590, Campus Jussieu, 4 place Jussieu,
75252 Paris, France

³Laboratoire Pierre Süe, CEA-CNRS, UMR9956, CEA
Saclay, 91191 Gif sur Yvette, France

Experimental studies show that varying the H content of olivine has a marked effect on rheology and electrical conductivity, such that the H content of olivine can be said to control tectonic processes and to affect the observable properties of the mantle [1,2]. In order to apply experimental results to the Earth, we need to be able to measure accurately the H content of olivines in experiments. Calibrations for the commonly used infrared (FTIR) and ion probe (SIMS) techniques rely on just a handful of truly independent measurements of natural olivines by ¹⁵N nuclear reaction analysis [3]. Moreover, it has been suggested, on the basis of comparative SIMS measurements, that the infrared absorption coefficient (k) for OH stretching bands in high pressure olivines could be greater by as much as a factor of 3 than that derived from natural samples [4], implying that H contents have been underestimated in many experimental studies.

We used elastic recoil detection analysis (ERDA) to determine k for OH bands in Fo₉₀ olivines with 240-2000 ppm H₂O, synthesised at 3-10 GPa in multi-anvil experiments that were optimised for growth of large, homogeneous crystals. On the basis of 20 ERDA and >200 FTIR analyses of olivines from 7 experiments, the H content (in ppm H₂O) is given by 0.120±0.008×total integral absorption, corresponding to an integral extinction coefficient of 45,000 L/(mol·cm²), i.e. k is ~35% smaller than the value previously derived for natural olivines. This implies that the H contents of experimental olivines have in fact been generally overestimated.

The samples that were analysed using ERDA are used as SIMS standards, thereby providing a direct calibration that avoids the baseline uncertainties that are inherent to FTIR. Direct calibration of SIMS using high pressure experimental samples allows for improved high accuracy analysis at high spatial resolution.

[1] Hirth & Kohlstedt (1996) *EPSL* **144**, 93-108 [2] Karato (1990) *Nature* **347**, 272-273 [3] Bell *et al.* (2003) *JGR* **108**, 2105 [4] Kovács *et al.* (2010) *Am Min* **95**, 292-299

W-Os isotope systematics in IVB iron meteorites

N. WITTIG AND M. HUMAYUN

National High Magnetic Field Laboratory & Dept. of Earth,
Ocean, & Atmospheric Science, Florida State University,
Tallahassee, FL 32310, USA. (wittig@magnet.fsu.edu)

¹⁸²Hf-¹⁸²W dating implies contemporaneous condensation of the earliest solar system solids (CAIs) and magmatic differentiation of planetesimals (i.e., iron meteorite groups) [1]. IVB iron meteorites exhibit ε¹⁸²W (-3.56±0.1) lower than CAIs (ε¹⁸²W -3.28±0.2). The initial W isotope signature of CAIs may have been reset by metamorphism of chondrites [2] while IVB irons need to be corrected for thermal neutron capture due to galactic cosmic ray (GCR) exposure. Although GCR corrections have become more sophisticated, determining the true ¹⁸²W deficit remains problematic [3].

Using Os isotopes as *in situ* neutron dosimeters [4], we re-evaluated the degree of GCR modification of ε¹⁸²W. Our IVB ε¹⁸²W data is derived from a more complete sampling of the IVB group (including Iquique, Weaver, Kokomo), but using smaller samples than [4-5]. MC-ICP-MS measurements (NEPTUNE™) of W isotopes were performed on 10-20ng aliquots using an Apex™ introduction system and Jet Ni sampler and X skimmer cones. The reproducibility of ε¹⁸²W for NIST SRM 3163 is ±0.14ε (2σ, n=142) and ±0.32ε (2σ, n=19, 10-25ng) if a smaller, random standard population is considered to capture the analytical uncertainty expected from our IVB set. Since Tlacotepec has systematically lower ε¹⁸²W, the average ε¹⁸²W (-3.31±0.22, 2σ) of IVBs is calculated for n=9 samples, excluding Tlacotepec. Our IVB average ε¹⁸²W is more radiogenic than previously reported [1-3,5-6] but with larger analytical uncertainty. Importantly, our ε¹⁸²W IVB average is identical to the most recent CAI value [1].

By using Tlacotepec with its large GCR-induced ¹⁸²W-¹⁹⁰Os shift as an anchor point, the Os-W isotope data of this group can be projected towards ε¹⁹⁰Os of 0 [4] to yield a pre-irradiation ε¹⁸²W of -2.95. This ε¹⁸²W allows for ~4 Myr of accretion and planetesimal differentiation for IVBs and reconciles current models of solar system formation with the W isotope record. A follow-up higher-precision W-Os isotope study from the same digestions is underway.

[1] Kleine *et al.* (2009), *GCA* **73**, 5150-5188. [2] Humayun *et al.* (2007), *GCA* **71**, 4609-4627. [3] Markowski *et al.* (2006), *EPSL* **250**, 104-115. [4] Huang & Humayun (2008), *LPSC XXXIX (1168)*. [5] Qin *et al.* (2008), *EPSL* **273** 94-104. [6] Markowski *et al.* (2006), *EPSL* **242** 1-15.

Analysis of As and Sb in samples from Turtle Pits hydrothermal field using new standard material

C.C. WOHLGEMUTH-UEBERWASSER^{1*}, S. SCHUTH²,
J. BERND³ AND F. VILJOEN¹

¹Paleoproterozoic Mineralization Research Group (PPM),
Department of Geology, University of Johannesburg, PO
Box 524, Auckland Park 2006, South Africa
(*correspondence: cora@geoinventio.de)

²Institut für Mineralogie, Leibniz Universität Hannover,
Callinstr. 3, 30167 Hannover, Germany
(s.schuth@mineralogie.uni-hannover.de)

³Institut für Mineralogie, Universität Münster, Corrensstr. 24,
48149 Münster, Germany (jberndt@uni-muenster.de)

New sulfide standard material was produced for the analysis of As, Sb, Se and Te in sulfides with LA-ICP-MS. The sulfide was synthesized from metal powders and elemental S. Trace metal concentrations are around 30 ppm and were added as chloride solutions. Reaction to sulfide powders proceeded in evacuated silica glass tubes at 973 K, then sintered in a piston-cylinder press for 4 hours at 2 GPa and 1373 K. About one third of the sulfide pellet was analysed with solution quadrupole ICP-MS for bulk trace metal concentrations. A part of the remainder was polished and analysed with an ArF excimer laser coupled to an Element 2 ICP-MS at the Universität Münster. Homogeneity given as 2-sigma relative standard deviation of 20 randomly distributed spot analyses is <7.6% for all trace elements.

The newly obtained standard material was used for the quantitative analysis of a pyrite sample from the Turtle Pits hydrothermal field by LA-ICP-MS. This allows for the spatial resolution of trace element distribution within the sample. Averages of 18 single spot analyses result in As concentrations of 140 – 2000 ppm and Sb contents of 1 – 60 ppm, with no obvious correlation of these two elements. In contrast, within single laser spectra from pyrite a strong correlation between As and Sb has been observed. As arsenic is assumed to be substituted non-stoichiometrically into the pyrite lattice, it seems obvious that in the sample under investigation, Sb is also substituted into the pyrite lattice and that it does not merely occur within inclusions as suggested in previous studies.

Analyses of coexisting sphalerite reveal higher Sb contents of up to 160 ppm, relative to pyrite. The ablation spectra are marked by abrupt elevations in the intensity of Sb which is probably caused by Sb-rich inclusion.

Primary phases in peridotites of the Ślęza ophiolite (SW Poland)

P. WOJTULEK¹, J. PUZIEWICZ^{1*} AND T. NTAFLÓS²

¹Univ. Wrocław, Poland

(*correspondence jacek.puziewicz@ing.uni.wroc.pl

²Univ. Wien, Austria (theodoros.ntaflos@univie.ac.at)

The peridotitic members of the Variscan Ślęza Ophiolite (SW Poland) are part of the complete ophiolitic sequence. WR trace element and REE patterns of gabbroic/basaltic ophiolite member show MORB affinity [1].

The peridotites are serpentinized but aggregates of olivine ± clinopyroxene ± spinel are preserved in the central part of the outcrop (Radunia Hill). Olivine (Fo_{91.8–92.6}) contains 0.2 – 0.4 wt % NiO. Clinopyroxene (mg# 0.92 – 0.94, Cr₂O₃ 0.9 – 1.2, Al₂O₃ 2.7 – 3.4, Na₂O <0.03 wt. %) is in places altered into clinopyroxene II (mg# 0.95 – 0.97), chromian magnetite (Cr usually between 0.10 and 0.80 atoms pfu, C=3). Isolated grains of olivine and chromian magnetite occurring in serpentine groundmass are less magnesian (Fo_{89.3–90.5}), and rich in Cr, respectively. The whole-rock REE contents are below detection limits of ICP-MS method.

The mineral composition of the aggregates suggests dunitic composition of the protolith. Highly magnesian content of olivine is probably the record of depletion typical for MORB mantle. Clinopyroxene possibly is the result of late melt infiltration. Serpentinization obviously decreases forsterite content in olivine, thus the chemical composition of phases occurring in relics may be not representative for the primary mineral composition.

[1] Pin *et al.* (1988) *Lithos* **21**, 195-209.

A fractal aggregate model of Early Earth organic hazes: UV shielding with minimal antigreenhouse cooling

E.T. WOLF^{1,2*}, F. TIAN¹ AND O.B. TOON^{1,2}

¹Laboratory for Atmospheric and Space Physics, University of Colorado, UCB 392, Boulder, CO 80309

(*correspondence: eric.wolf@colorado.edu)

²Department of Atmospheric and Oceanic Sciences, University of Colorado

The Archean Earth (3.8 to 2.5 billion years ago) was probably enshrouded by a Titan-like photochemical haze composed of fractal aggregate hydrocarbon aerosols. In this study a three-dimensional fractal aggregate model of the early Earth photochemical haze is explored and compared with the standard liquid drop haze model used in earlier studies [1]. Fractal aggregate microphysical processes are modeled using the method introduced by Cabane *et al.* [2]. The optical properties of the aerosols are determined using a mean-field approximation of multiple scattering by fractal aggregates composed of identical spheres [3]. Early Earth fractal hazes are found to be optically thick in the ultraviolet wavelengths while remaining relatively transparent in the mid-visible wavelengths. At an annual production rate of 10^{14} grams per year and an average monomer radius of 50 nanometers, the haze has global mean effective optical depths of $\tau_{uv} = 11.2$ and $\tau_{vis} = 0.5$. Such a haze would provide a strong shield against UV light while causing only minimal antigreenhouse cooling. Protected by a strong UV shield, photolytically unstable greenhouse gases such as CH_4 and NH_3 may have been able to build up to high concentrations helping warm the young Earth despite the faint young Sun. Our findings reopen the hypothesis of Sagan and Mullen [4] that the young Earth may have been home to a reducing atmosphere.

[1] J.D. Haqq-Misra *et al.* (2008) *Astrobiology* **8**(6), 1127. [2] M. Cabane *et al.* (1993) *Planet. Space Sci.* **41**(4), 257. [3] R. Botet *et al.* (1997) *Applied Optics* **36**(33), 8791 [4] C. Sagan, G. Mullen (1972) *Science* **177**, 52.

Magma physical properties affect isotope variations in volcanic rocks: The example of high-T rhyolites

J.A. WOLFF*¹, B.S. ELLIS¹ AND F.C. RAMOS²

¹School of Earth and Environmental Sciences, Washington State University, Pullman, WA 99164, USA

(*correspondence: jawolff@mail.wsu.edu)

²Dept. of Geological Sciences, New Mexico State University, Las Cruces, NM 88003, USA

Volcanic rocks often exhibit internal heterogeneity in radiogenic isotopes. Isotopic disequilibrium between co-existing phenocrysts, phenocrysts and matrix, and isotopic zoning within single crystals ("crystal isotope stratigraphy") has been demonstrated in basalts, andesites, dacites, rhyolites and alkaline magmas. High-temperature "Snake River type" rhyolites appear to be an exception. Despite the occurrence of Snake River Plain rhyolites in a region of isotopically highly variable crust and mantle, and significant differences from rhyolite unit to rhyolite unit, internally they are near-homogeneous in $^{87}Sr/^{86}Sr$. Little or no zoning is found within feldspar phenocrysts, and feldspars within a single unit are tightly grouped. Some units show minor contrasts between phenocrysts and matrix. In contrast, associated basalts and lower-T rhyolites in the same area represent different types of magmas that passed through the same crustal column, and have the relatively large internal $^{87}Sr/^{86}Sr$ variability exhibited by common volcanic rocks.

High temperature rhyolitic magmas possess a unique combination of temperature and melt viscosity. Although they are typically 200°C hotter than common rhyolites, the effect on viscosity is offset by lower water contents (~2 wt%), hence their melt viscosities are in the same range as common, water-rich, cool rhyolites ($10^5 - 10^6$ Pa s). However, the high magmatic temperatures dictate that cation diffusion rates are 2 – 3 orders of magnitude greater than in common rhyolites. We hypothesize that this combination of characteristics promotes Sr isotopic homogeneity: viscosities that are too high to permit crystal transfer and magma mixing on timescales shorter than those required for diffusive homogenization of Sr between phenocrysts and matrix (100 – 1000 years). This is untrue for the vast majority of magmas, in which either crystal transfer is rapid (\ll 100 years) due to low melt viscosities (basalts and intermediate magmas), or else Sr diffusion rates are so slow that the equilibration time is longer than the lifetime of the system (high-silica minimum melt rhyolites: $10^5 - 10^6$ years).

High-temperature hydrothermal activity in the lower oceanic crust: Petrological and geochemical evidence for fluid pathways in the Oman Ophiolite

P.E. WOLFF^{1*}, D. GARBE-SCHÖNBERG², J. KOEPKE¹ AND K. STREUFF²

¹Institute for Mineralogy, Leibniz University of Hannover, Callinstr. 3, 30167 Hannover, Germany
(*correspondance: e.wolff@mineralogie.uni-hannover.de)

²Institute of Geosciences, Christian-Albrecht-University of Kiel, Ludewig-Meyn-Str. 10, 24118 Kiel, Germany

The Oman ophiolite is regarded as best example for fast-spreading oceanic crust on land. Petrological findings indicate that multiple intrusions of gabbroic sills play a significant role for the formation of the deep plutonic crust at fast-spreading oceanic ridges [1], a model which requires a substantial cooling of the deep oceanic crust, probably by seawater-derived high-temperature hydrothermal circulation [e.g.,2]. In this study we present petrological and geochemical data for veins and zones formed by hydrothermal alteration within the lower layered gabbro sequence of the Samail ophiolite in Oman (Wariyah, Wadi Tayin Massiv).

Veins and alteration zones of mm to m scale within an unaltered olivine gabbro record high (>800°C), medium (~600°C), and low temperature (~350–500°C) hydrous alteration indicating possible fluid pathways for hydrothermal circulation. Petrological results show mineral assemblages typical for predicted interaction between olivine gabbro and seawater-derived fluid [3]. High temperature veins display mineral assemblage of olivine + plagioclase + pyroxenes + pargasitic amphibole ± oxides. Decreasing temperature result in a change in alteration paragenesis, where hydrous minerals become more abundant. The typical medium temperature mineral assemblage is plagioclase + clinopyroxene + chlorite + magnesiohornblende ± oxides followed by low temperature veins mainly consisting of epidote + prehnite + actinolite/tremolite.

Geochemical micro-analyses of sub-mm veinlets and adjacent host rocks show systematic enrichment of fluid mobile elements (e.g., LREE, Eu, Mo, W) in these veins and indicate possible element mobility during hydrothermal activity. These preliminary results suggest that hydrothermal circulation at very high temperatures exists.

[1] Kelemen (1997), *Earth Planet. Sci. Lett.* **146**, 475-488. [2] Bosch (2004), *J. Petr.* **45**, 1181-1208. [3] McCollom and Shock, *J. Geophys. Res.* **103**, 547-575.

Can seawater promote *in situ* mineral sequestration?

D. WOLFF-BOENISCH^{1*}, S. WENAU², E.H. OELKERS³ AND S.R. GISLASON¹

¹Institute of Earth Sciences, University of Iceland, Sturlugata 7, 101 Reykjavik, Iceland

(*correspondence: boenisch@raunvis.hi.is)

²MARUM – Centre for Marine Environmental Sciences, University of Bremen, Leobener Straße 28359 Bremen, Germany

³Géochimie et Biogéochimie Experimentale, GET/CNRS, Université de Toulouse, 14 Avenue Edouard Belin, 31400 Toulouse, France

Dissolution of mafic and ultramafic rocks in the presence of CO₂ is of great current interest due to the potential for carbon storage in basaltic and/or peridotitic rocks. This storage method involves converting gaseous or supercritical CO₂ into carbonate minerals for its safe, long-term storage. In-situ carbonatization of CO₂ faces a major challenge in that huge quantities of water are required to dissolve CO₂ to promote reactions. This challenge might be overcome by using seawater for the dissolution of CO₂ during its injection.

To assess the possible use of seawater during carbon storage efforts, steady-state silica release rates (r_{Si}) from basaltic glass and crystalline basalt of same chemical composition and dunitic peridotite have been determined in far-from-equilibrium dissolution experiments at 25°C and pH 3.6 in a) artificial seawater solutions under 4 bar pCO₂, b) varying ionic strength solutions, including acidified natural seawater, c) acidified natural seawater of varying fluoride concentrations, and d) acidified natural seawater of varying dissolved organic carbon concentrations. Glassy and crystalline basalts exhibit similar r_{Si} in solutions of varying ionic strength and cation concentrations. Rates of all solids increase by 0.3-0.5 log units in the presence of 4 bar pCO₂ compared to atmospheric CO₂ pressure. At atmospheric CO₂ pressure, basaltic glass r_{Si} were most increased by the addition of fluoride to solution whereas crystalline basalt rates were most enhanced by the addition of organic ligands. In contrast, peridotite rates are unaffected by either the addition of fluoride or organic acids. Most significantly, Si release rates from the basalts are found to be not more than 0.6 log units slower than corresponding peridotite rates at all conditions considered in this study. This rate difference becomes negligible in seawater suggesting that CO₂-charged seawater injected into basalt might be nearly as efficient for mineral sequestration as injection into peridotite.

Water structure at the structurally heterogeneous calcite surface

M. WOLTHERS^{1,2,*}, D. DI TOMMASO², Z. DU² AND N.H. DE LEEUW²

¹Department of Earth Sciences, Utrecht University, P.O. Box 80021, 3508 TA Utrecht, The Netherlands.

(*correspondence: wolthers@geo.uu.nl)

²Department of Chemistry, University College London, 20 Gordon Street, London WC1 H0AJ, United Kingdom.

The calcite surface has been subject of numerous simulation studies. These studies have generally focused on simulations of perfectly flat calcite surfaces, and in particular the dominant (10-14) face. In both natural environments and in experiments, the calcite surface is of course not atomically flat, and surface roughness is expected to have an effect on the reactivity of the surface sites. Indeed, it has been shown that trace elements differentially incorporate into the calcite surface depending on surface structure [1], while this differential reactivity is not at all captured in the current macroscopic surface chemical models [2,3]. The aim of this work is to obtain information on the interactions of water molecules with the different surface sites present in etch pits and on growth terraces at the calcite (10-14) surface. Results show that the local environment around the structurally distinct sites differs significantly, with the formation of more calcium-water bonds and H-bridges at less-coordinated sites, while the bond length of the metal-hydroxyl site does not vary with position at the surface. Temperature changes over the range of 300 to 340 K does not affect the local environment of the surface groups.

The information obtained in this study is crucial for the improvement of the existing macroscopic surface model for the reactivity of calcite [2]. This mineral surface structural model for calcite was developed using the Charge Distribution MUltiSite Ion Complexation (CD-MUSIC) modelling approach [4] to describe the chemical structure of carbonate mineral-aqueous solution interfaces. The high sensitivity of the model toward parameters describing hydrogen bridging and bond lengths at the mineral-water interface, currently limits the predictive application of the calcite CD-MUSIC model.

[1] Paquette and Reeder (1995) *Geochim. Cosmochim. Acta* 59, 735-749. [2] Wolthers M. *et al.* (2008) *Am. J. Sci.* 308, 905-941. [3] Villegas-Jiménez *et al.* (2009) *Geochim. Cosmochim. Acta*, 73, 4326-4345. [4] Hiemstra and Van Riemsdijk (1996) *J. Colloid Interf. Sci.* 179, 488-508.

Mass-independent Cd isotope fractionation during evaporation

FRANK WOMBACHER

Universität zu Köln, Institut für Geologie und Mineralogie, 50674 Köln, Germany (fwombach@uni-koeln.de)

Modern mass spectrometry is capable to reveal mass-independent isotope fractionations (MIF) for many heavy elements [1].

Here, we investigate mass-independent Cd isotope fractionations that result from the evaporation of liquid Cd into vacuum. Three residues from evaporation display large mass-dependent Cd isotope fractionations with $1000\ln\alpha$ ranging from -23.2 to -48.3 ‰ for $^{110}\text{Cd}/^{114}\text{Cd}$ relative to the starting material [2]. These samples were repeatedly analyzed at high precision using a Neptune MC-ICP-MS, with ion beam intensities typically larger than 20V for ^{114}Cd and analysis times of about 30 minutes. Deficits ranging from 8 to 28 ppm were well resolved for $^{111,113,116}\text{Cd}/^{114}\text{Cd}$. The accurate quantification of the MIF requires that the mass-dependence of the evaporation induced isotope fractionation is accurately corrected. This was facilitated using the generalized power law and normalization to $^{110}\text{Cd}/^{114}\text{Cd}$ of the starting material. Note, that the mass-dependence for evaporation was found to be intermediate between that expected to describe kinetic and equilibrium fractionation [2, 3].

MIF for ^{111}Cd , ^{113}Cd and ^{116}Cd scales with deviations from a trend between nuclide mass and mean-squared nuclear charge radii defined by the other five Cd isotopes, thus suggesting that the MIF is due to nuclear volume effects. The preferential evaporation of ^{111}Cd , ^{113}Cd and ^{116}Cd may result from their more tightly bound 5s electrons that are thus not as easily delocalized and hence form weaker metallic bonds in the liquid. Our results are in accord with previous work [4] on the evaporation of Hg, another group 12 element.

[1] Epov *et al.* (2011) *JAAS* advanced article. [2] Wombacher *et al.* (2004) *Geochim. Cosmochim. Acta* 68, 2349-2357. [3] Young *et al.* (2002) *Geochim. Cosmochim. Acta* 66, 1095-1104. [4] Estrade *et al.* (2009) *Geochim. Cosmochim. Acta* 73, 2693-2711.

Episodic estuarine hypoxic events: Integrating the biogeochemistry, hydrology and climate on a sub-tropical floodplain, Eastern Australia

V.N.L. WONG^{1*}, S.G. JOHNSTON¹, S. WALSH²,
S. MORRIS², E.D. BURTON¹, R.T. BUSH¹,
L.A. SULLIVAN¹, P.G. SLAVICH²

¹Southern Cross GeoScience, Southern Cross University,
Lismore, NSW 2480, Australia

(*correspondence: vanessa.wong@scu.edu.au)

²NSW Department of Trade and Investment, Regional
Infrastructure and Services, Wollongbar, NSW 2477,
Australia

Globally, the frequency, magnitude and spatial extent of anthropogenically-induced coastal hypoxic events is increasing [1]. Episodic hypoxia in riverine and estuarine systems can follow high-flow events such as floods or the release of environmental allocations. These events can result in complete deoxygenation of the water column and significant effects on aquatic organisms and ecosystem function. This study integrates the biogeochemical, hydrological and climatic processes from four flood events on two sub-tropical floodplains in eastern Australia [2,3].

We found that a key driver of hypoxia was the extensive modification of floodplain surface hydrology through the construction of drainage networks. Backswamp basins were originally natural storage basins for floodwaters, supporting large areas of wetland vegetation. Drier conditions, due to drainage, has shifted vegetation assemblages from wetland-dominant species to flood-intolerant species. When inundated, senescent vegetation provides a source of labile carbon which rapidly consumes oxygen from the overlying waters, producing anoxic water with high oxygen demand. Carbon metabolism during these events is strongly coupled with microbially-mediated reduction of accumulated Fe and Mn oxides commonly found on coastal floodplains. These redox sensitive species provide a geochemical signature to identify the sources and causes of estuarine hypoxic events. Whilst anoxic floodwaters were previously retained in backswamp wetland basins during the flood recession phase, these waters are now exported rapidly to the main channel.

Post-flood hypoxic events frequently occur in summer, especially when long, dry periods are followed by rapid, intensive rainfall. These events will most likely increase in frequency and magnitude as a result of climate change due to more frequent and hotter summer floods.

[1] Diaz & Rosenberg (2008) *Science* **321**, 926-929. [2] Johnston *et al.* (2003) *Mar. and Fresh. Res.* **54**, 781-795. [3] Wong *et al.* (2010) *Estuar. Coast. Shelf Sci.* **87**, 73-82.

Stable isotopes ratio in nitrate: A tool to unravel the biogeochemistry of nitrate in an estuarine environment

W.W. WONG^{1*}, P.M. COOK¹, M.R. GRACE¹ AND
I. CARTWRIGHT²

¹Water Studies Centre, Monash University, Clayton,
Melbourne 3800, Australia

(*correspondence: weiwen.wong@monash.edu)

²School of Geosciences, Monash University, Clayton,
Melbourne 3800, Australia

Port Philip Bay is a large coastal embayment in temperate south eastern Australia, with a population in excess of 4 million in the local catchment. Like other coastal waters, the bay is typically nitrogen limited and hence there is much interest in identifying sources and sinks of this nutrient within catchments and estuaries surrounding the bay.

This study was carried out in the Werribee estuary, one of the major estuarine systems within Port Philip Bay. Werribee estuary is eutrophic with nitrate concentrations exceeding 1mgN/L during base flow conditions. There are a number of potential sources of nitrogen to the estuary including treated sewage effluent, market gardens, groundwater and the Werribee River. We aimed to distinguish the sources and transformation processes of nitrate in this estuarine environment using a multidisciplinary approach, focussing on stable isotopes and radon measurements.

Monthly sampling of surface water and groundwater was carried out over a 12 month period. Our preliminary results showed that (i) there was a positive correlation between $\delta^{15}\text{N}-\text{NO}_3$ and $\delta^{18}\text{O}-\text{NO}_3$ with a 2:1 $\delta^{15}\text{N}:\delta^{18}\text{O}$ gradient in both surface and groundwaters suggesting that denitrification was occurring and led to considerable transformation of the isotope signatures from their sources values within groundwater and surface waters. (ii) There was a strong correlation between nitrate and radon concentrations ($R^2=0.79$) at a site in the upper estuary consistent with nitrate derived from groundwater. (iii) The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate were $+18\pm 4\%$ and $+11\pm 4\%$ respectively when nitrate concentrations in surface waters exceeded 0.2mgN/L, which was consistent with the signatures observed in ground water with high nitrate concentrations (>10mgN/L) beneath the market gardens.

Influence of cyanide on granite weathering

N. WONGFUN^{1*}, M. PLÖTZE², H. BRANDL³ AND G. FURRER¹

¹Inst. of Biogeochemistry and Pollutant Dynamics, ETH Zürich, Zürich 8092, Switzerland

(*correspondence: nuttakan.wongfun@env.ethz.ch)

²Inst. for Geotechnical Engineering, ETH Zürich, Zürich 8093, Switzerland

³Inst. of Evolutionary Biology and Environmental Studies, University of Zürich, Zürich 8057, Switzerland

Availability of nutrients in the glacier forefield is usually very low. Mobilization of nutrients from rock through weathering processes plays an important role to overcome this limitation [1]. Microorganisms and plants modify their local environment by various exudates including cyanide [2], which is a crucial agent during the initial period of colonization and soil formation.

To elucidate the effect of cyanide on dissolution of granite minerals, the samples were collected from the Damma glacier area (Central Alps, Switzerland) at approximately 2,500 m a.s.l. After crushing and sieving, materials with size fraction <63 μm (surface area=1.55 m^2/g) were selected for abiotic dissolution experiment. Batch experiments were carried out with a solid/liquid ratio of 10 g/L in the absence or presence of cyanide under oxic conditions at 22 ± 1 °C, $I=0.01$, pH range of 5-7 for 24 hours.

Among the elements released from granite, enhanced Fe concentrations were observed in presence of cyanide. This applies particularly with increasing pH, suggesting that deprotonated cyanide becomes more important for the formation of Fe complexes. Iron cyanide complexes presence at high concentrations in particular at pH above 6 [3] and allow high concentrations of dissolved Fe. The dissolved Al concentrations were considerably lower than those of Fe due to precipitation of secondary phases (e.g. gibbsite and kaolinite).

[1] Bernasconi *et al.* (2008) *MinMag* **72**, 19-22. [2] Frey *et al.* (2010) *AEM* **76**, 4788-4796. [3] Meeussen *et al.* (1992) *ES&T* **26**, 1832-1838.

Accretion and initial differentiation of the Earth

B.J. WOOD

Department of Earth Sciences, University of Oxford, South Parks Road, Oxford OX1 3AN, U.K.
(berniew@earth.ox.ac.uk)

A large number of moon- to Mars-sized planetary embryos with different metal/silicate/volatile ratios are believed to have formed around the young sun in ~ 1 M.yr. As Earth accreted from such embryos through a succession of impacts, the metallic core segregated and there was some loss of the most volatile elements. The chemical and isotopic composition of silicate Earth provides most evidence for these processes. Depletions of silicate Earth, relative to primitive meteorites, in elements known to have entered the core (e.g. Mo, W, Ni, Co) place constraints on the physical conditions of accretion. Short and long-lived chronometers (^{182}Hf - ^{182}W , $^{238,235}\text{U}$ - $^{206,207}\text{Pb}$, ^{205}Pb - ^{205}Tl , ^{107}Pd - ^{107}Ag) enable estimates of the timing of core formation, the influence of the moon-forming impact and the history of volatile accretion to the Earth. If we begin with the assumptions that core segregation was continuous during accretion and that metal and silicate fully equilibrated, simultaneous consideration of the depletion factors of a large number of elements in silicate Earth lead to the following general conclusions: (1) The average pressure of core segregation on Earth was high >30 GPa, implying depths of >800 km. (2) Earth began as a small, strongly reduced body and became more oxidised as it grew. (3) Si ($\sim 5\%$) and S ($\sim 2\%$) are major components of the "light" element in Earth's core. Relaxing the assumption of full equilibration (ie allowing for the addition of metal to the core without reaction with the mantle) and allowing for the influence of S and Si on partitioning does not significantly alter these conclusions.

The ^{182}Hf - ^{182}W age of Earth's core [1], may be used in combination with other short- and long-lived radioactive systems to show (1) Moderately volatile elements were predominantly added to Earth towards the end of accretion [2] and (2) The fractionation of U from Pb at ~ 100 M.yr after the origin of the solar system is consistent with Pb extraction in a small amount of core material added during the moon-forming giant impact.

[1] Kleine, T., Munker, C., Mezger, K., & Palme, H., Rapid accretion and early core formation on asteroids and the terrestrial planets from Hf-W chronometry. *Nature* **418** (6901), 952-955 (2002). [2] Schönbächler, M., Carlson, R.W., Horan, M.F., Mock, T.D., & Hauri, E.H., Heterogeneous accretion and the moderately volatile element budget of Earth. *Science* **328**, 884-887 (2010).

Core formation and volatile element addition to the Earth

B.J. WOOD¹ AND M. REHKÄMPER²

¹Dept of Earth Sciences, University of Oxford, South Parks Road, Oxford, OX1 3AN; U.K.

²Dept of Earth Science & Engineering, Imperial College, London SW7 3AZ; U.K.

It is well known that the Pb isotopic composition of the silicate Earth indicates a fractionation of U from Pb at ~100 M.yr after the origin of the solar system. This fractionation has recently been ascribed to entry of Pb into the core (e.g.[1]) on an Earth with low U/Pb, and to late addition of Pb and other moderately volatile elements to an Earth which initially had very high U/Pb [2]. Use of extinct radioactive systems, combined with an understanding of volatile element partitioning into the core can elucidate the relative timings of core formation and volatile addition [3]. We have determined the metal-silicate partitioning of moderately volatile elements Ag, Pb, Tl, Mn and Cr in order to use the extinct systems ¹⁰⁷Pd-¹⁰⁷Ag, ²⁰⁵Pb-²⁰⁵Tl and ⁵³Mn-⁵³Cr in conjunction with ¹⁸²Hf-¹⁸²W and ^{238,235}U-^{206,207}Pb to investigate core formation and volatile element addition to the growing Earth.

Tl, which is chalcophile but only weakly siderophile at low pressure is found to become as siderophile as Pb at pressures >20 GPa. This means that, given the high pressures of core formation indicated by refractory siderophile element (Ni, Co, Mo etc) abundances in the mantle, the ²⁰⁵Pb-²⁰⁵Tl system is consistent with core formation being the principal reason for the low Pb and Tl abundances (relative to lithophile elements of similar volatility) in silicate Earth. Ag is moderately siderophile at all pressures while Mn and Cr are similar to one another in having weak siderophile character. When considered together the 3 short-lived systems are consistent with addition of moderately volatile elements during the principal period of core formation with timescale constrained by the ¹⁸²Hf-¹⁸²W system. ⁵³Mn-⁵³Cr and ¹⁰⁷Pd-¹⁰⁷Ag indicate that accreted materials became more volatile rich as accretion progressed with major addition of volatiles during the last 30-60% of accretion.

[1] Wood, B.J. & Halliday, A.N., (2010) *Nature* **465**, 767-771.
[2] Albarède, F., (2009) *Nature* **461**, 1227-1233. [3] Schönbächler, M., Carlson, R.W., Horan, M.F., Mock, T.D., & Hauri, E.H., (2010) *Science* **328**, 884-887.

Controls on early biomineralisation: Oxygen and competition

R.A. WOOD^{1*}, A.R. PRAVE², K-H. HOFFMANN³,
S.W. POULTON⁴, J.W. LYNE¹, M.O. CLARKSON¹ AND
S. KASEMANN⁵

¹School of Geos., Univ. of Edinburgh, EH9 JW, UK

(*correspondence: Rachel.Wood@ed.ac.uk)

²Dept. of Earth Sci, Univ. of St Andrews, KY16 9AL, UK

³Geol. Survey of Namibia, Windhoek

⁴School of Civil Eng. and Geosciences, Newcastle Univ, NE1 7RU, UK

⁵Dept. of Geosciences, University of Bremen, 28334 Bremen, Germany.

Animals require oxygen, and so the first appearance of metazoans during the Ediacaran (580-543 Ma) has been linked to the widespread development of oxygenated oceanic conditions [1, 2, 3]. However, the nature of ocean redox chemistry through this period is complex, with deeper water anoxia persisting in certain areas [4]. In addition, few studies have directly documented the nature of ocean chemistry at locations that coincide with palaeontological evidence for major biological innovation [3]. Thus, the precise environmental context for early animal evolution, particularly the rise of biomineralisation, remains unclear. Here, we present a high resolution reconstruction of carbon isotope and ocean redox dynamics, as recorded in sedimentary rocks deposited from ~553-549 million years ago in the Zaris Sub-Basin of the Nama Group, Namibia. The succession spans deep distal to shallow proximal carbonate settings, and coincides with the first appearance of skeletal metazoans. Iron-sulphur systematics demonstrate that oxic conditions developed only intermittently in the shallowest waters where the first skeletal metazoans are preserved, while deeper waters remained consistently anoxic and iron-rich (ferruginous). Thus, late Ediacaran surface-water oxygenation was unstable, inferring that the first skeletal metazoans developed in short-lived habitats. The opportunistic ecologies and characteristically simple biomineralisation styles of Ediacaran taxa are likely to be a direct consequence of these dynamic redox conditions.

[1] Knoll et al. (1999) *Science*, 284, 2129-2137 [2] Fike *et al.* (2006) *Nature*, **444**, 744-747 [3] Canfield *et al.* (2007) *Science*, **315**, 95-99 [4] Canfield *et al.* (2008) *Science*, **321**, 949-952.

Testing boundary exchange of Nd isotopes in the Eastern tropical Pacific Ocean

STELLA WOODARD^{1*}, FRANCO MARCANTONIO²,
DEBORAH THOMAS¹ AND MITCHELL LYLE¹

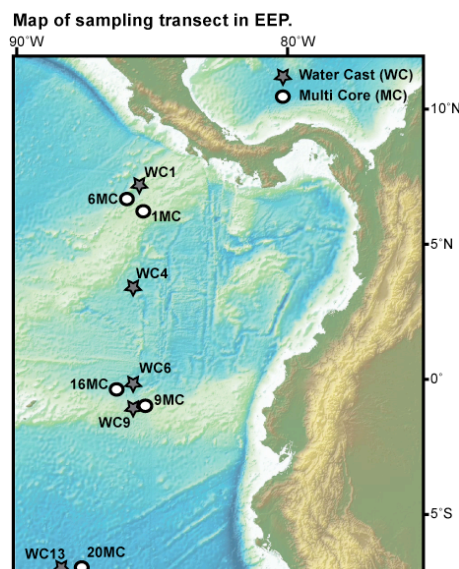
¹Department of Oceanography, Texas A&M University,
College Station, TX 77843, USA

(*correspondence: swoodard@ocean.tamu.edu)

²Department of Geology & Geophysics, Texas A&M
University, College Station, TX 77843, USA

We investigate the possibility of boundary exchange as a mechanism for altering the Nd isotopic composition of seawater along the eastern margin of the equatorial Pacific Ocean by analyzing Nd isotopes and concentrations in seawater and sediment collected along a transect in the Panama and Peru Basins during the Fall of 2010. The region plays an important role in the global carbon cycle due to enhanced productivity, upwelling and venting of CO₂ rich waters and is affected by enhanced precipitation and riverine runoff. In addition, the area is interesting in terms of intermediate water circulation with the confluence of NPIW and AAIW near the equator at depths of ~500-1000m.

Seawater dissolved ¹⁴³Nd/¹⁴⁴Nd and [Nd] profiles were determined for five locations (see map) and compared with the Nd isotopic composition of biogenic apatite (thought to reflect bottom water εNd) and lithogenic material isolated from the tops of five multi-cores (see map). Preliminary data from seawater collected at site WC13 show a decrease in εNd from -2.1 at 500m to -3.4 at 2750m water depth.



Minor effect of physical size sorting on iron solubility of transported mineral dust

M.T. WOODHOUSE, Z.B. SHI, K.S. CARSLAW,
M.D. KROM, G.W. MANN AND L.G. BENNING

School of Earth and Environment, University of Leeds, Leeds,
United Kingdom (m.woodhouse@see.leeds.ac.uk)

Observations show that the fractional solubility of Fe (FS-Fe, defined as the ratio of dissolved to total Fe) in dust aerosol increases from ~0.1% in regions of high dust mass concentration and up to 80% in remote oceanic regions where concentrations are lowest [1, 2]. Here, we combined laboratory geochemical measurements with global aerosol model simulations to test the hypothesis that the increase in FS-Fe is due to physical size sorting during dust transport. We determined the FS-Fe in size-fractionated dust generated from two representative Saharan dust source samples using a customized dust re-suspension and collection system. The results show that the FS-Fe is size-dependent and ranges from 0.1-0.8%. The size-resolved FS-Fe data were then combined with simulated (size-resolved) dust mass concentration data from a global aerosol model, GLOMAP, to calculate the FS-Fe of dust aerosol over the tropical and subtropical North Atlantic Ocean. We found that the calculated FS-Fe in the dust aerosol increased from ~0.1% at high dust mass concentrations (e.g., >100 μg m⁻³) to ~0.2% at low concentrations (<1 μg m⁻³) due to physical size sorting alone. These values are one to two orders of magnitude smaller than those observed on cruises across the tropical and sub-tropical North Atlantic Ocean [1, 3] under an important pathway of Saharan dust plumes for similar dust mass concentrations. Even when the FS-Fe of the sub-micrometer size fractions (0.18-0.32 μm, 0.32-0.56 μm, and 0.56-1.0 μm) in the model were increased by a factor of 10 over the measured values, the calculated FS-Fe of the dust was still more than an order of magnitude lower than that measured in the field. Therefore, the physical sorting of dust particles alone is unlikely to be an important factor in the observed inverse relationship between the FS-Fe and the atmospheric mineral dust mass concentrations. These results suggest that processes such as chemical reactions and/or mixing with combustion particles are the main mechanisms to cause the increased FS-Fe in long-range transported dust aerosols.

[1] Baker, A., Jickells, T., (2006) *Geophys Res Lett*, **33**, L17608; [2] Mahowald N. *et al.*, (2005) *Global Biogeochem Cycle*, **19**, GB4025; [3] Buck, C. *et al.*, (2010) *Mar Chem*, **120**, 14-24.

Structural systematics of Mg-Fe²⁺-bearing spinels and spinelloids

A.B. WOODLAND^{1*}, R.J. ANGEL² AND M. KOCH³

¹Inst. für Geowissenschaften, Universität Frankfurt, Altenhöferallee 1, 60438 Frankfurt, Germany

(*correspondence: woodland@em.uni-frankfurt.de)

²Dept. of Geosciences, Virginia Tech, Blacksburg, VA, 24060, U.S.A.

³Inst. für Geowissenschaften, Universität Heidelberg, Im Neuenheimer Feld 234-6, 69120 Heidelberg, Germany

Spinel and structurally related spinelloids have been synthesised in the geologically relevant system M_2SiO_4 - $MFe^{3+}_2O_4$, where $M = Mg$ and Fe^{2+} at 1100-1200°C and 3 to 16 GPa. Starting materials were mixtures of Fe_3O_4 and pre-synthesised olivine solid solutions. Unit-cell parameters were determined by Rietveld refinement of powder diffraction patterns containing Si as an internal standard.

Spinel exhibits a range in composition, which requires consideration of four endmembers: ringwoodite, Fe-ringwoodite, magnetite and magnesioferrite. As expected, the cell parameter decreases with increasing M_2SiO_4 content. A least squares fit to the dataset ($n=53$) suggests ideal or near ideal behaviour in this quaternary system. The derived molar volume for $MgFe_2O_4$ ($V^\circ = 44.51(12) \text{ cm}^3$) implies a degree of inversion of $x = 0.78$ [1], although this was not explicitly accounted for in the fit.

Spinelloid II exhibits only a limited compositional range with $nMg \leq 0.26$ c.p.f.u. Molar volumes decrease with increasing Mg content. Single-crystal refinements indicate that Mg preferentially resides on the M3 site, which is the octahedral site containing the bridging oxygen of the T_3O_{10} tetrahedral group.

Compared with Mg-free [2] spinelloid III, the incorporation of Mg causes a systematic reduction in volume. A weighted least squares fit yields $V^\circ_{Fe_3O_4} = 45.04(6) \text{ cm}^3$, $V^\circ_{Fe_2SiO_4} = 42.89(10) \text{ cm}^3$ and $V^\circ_{Mg_2SiO_4} = 40.9(4) \text{ cm}^3$, assuming ideal mixing (non-ideality is not statistically significant). Mg prefers the M2 site, which is attached to the bridging oxygen of the T_2O_7 group.

The volume behaviour of spinelloid V is similar to the other spinelloids, except that the volume reduction from Mg addition is not so clearly defined. This could be due to changing ordering of i) Fe^{3+} and Si on the TO_4 and T_2O_7 sites, and/or ii) Mg, Fe^{2+} and Fe^{3+} across the octahedral sites. A weighted least squares fit yields $V^\circ_{Fe_3O_4} = 44.96(4) \text{ cm}^3$, $V^\circ_{Fe_2SiO_4} = 42.53(8) \text{ cm}^3$ and $V^\circ_{Mg_2SiO_4} = 40.3(3) \text{ cm}^3$ for the theoretical endmembers, assuming ideal mixing.

[1] O'Neill *et al.* (1992) *Am Min* **77**, 725-40, [2] Woodland, Angel (2000) *Contrib Mineral Petrol* **139**, 734-47.

F, Cl and S contents of olivine-hosted melt inclusions from picritic dike rocks, Etendeka, NW Namibia

L. WORGARD^{1*}, R.B. TRUMBULL², J. K. KEIDING², I.V. VEKSLER^{2,3}, M. WIEDENBECK², T. WENZEL¹ AND G. MARKL¹

¹Universität Tübingen, Wilhelmstr. 56, D-72074 Tübingen, Germany

(*correspondence: linda.worgard@uni-tuebingen.de)

²GeoForschungsZentrum Potsdam, Telegrafenberg, D-14473 Potsdam, Germany

³Technical University Berlin, Department of Mineralogy and Petrology, Ackerstrasse, 71-76, D-13355 Berlin, Germany

Volatile contents and their evolution during magma differentiation are important to understand for better assessment of their role during volcanic eruptions and for estimation of atmospheric loading. Furthermore volatiles have shown potential to be used to put constraints on different mantle sources. Here we present for the first time F, Cl and S concentrations of olivine-hosted melt inclusions analyzed by SIMS from picritic dikes from the southern Etendeka region, NW Namibia.

The analyzed host olivines are Mg-rich ($F_{O_{84,93}}$) and their re-homogenized (and post-entrapment corrected) melt inclusions contain between 10 and 18 wt.% MgO and show SiO_2 contents of 45-52 wt.% and thus range from basalt to komatiite in composition.

F concentrations in the analyzed melt inclusions vary from 200 to 450 ppm, Cl varies from 5 to 40 ppm and S from 10 to 1100 ppm. F and S concentrations increase with decreasing forsterite content of the host olivine, whilst Cl does not. F/Cl ratios are variable and range from 4 to 45, with the highest values presumably being influenced by degassing prior to melt inclusion entrapment and/or post entrapment leaking. Most F/Cl ratios and low Cl/K ratios (≤ 0.3) indicate a depleted mantle source for these picritic dikes [1-3], which is consistent with earlier Sr and Nd isotope work of [4]. We plan to compare the volatile contents of the melt inclusions with that of the corresponding whole rocks (analyzed by pyrohydrolysis) in order to further constrain the significance of potential degassing processes.

[1] Stroncik & Haase (2004), *Geology* **32**, 945-948. [2] Michael & Cornell (1998), *Journal of Geophysical Research* **103**, 18, 325-18, 356. [3] Pyle & Mather (2009), *Chemical Geology* **263**, 110-121. [4] Thompson *et al* (2001), *Journal of Petrology* **42**, 2049-2081.

Computational modelling of water and amino acid adsorption at corundum structured oxide surfaces

L. WORONCZ^{1*}, T.V. SHAPLEY¹, C. ARROUVEL²,
D. COSTA³ AND S.C. PARKER¹

¹Department of Chemistry, University of Bath, Bath,
Somerset, BA2 7AY, United Kingdom
(*correspondence: L.Woronczyk@bath.ac.uk)

²Universidade Federal de Sergipe, São Cristóvão, SE 49.100-
000 Brazil

³LPCS, ENSCP Chimie Paris Tech, Paris, France.

The interactions between biomolecules and inorganic surfaces play an important role in many natural environments and hence it is essential to understand the nature of the chemical interaction between the biomolecule and the surface, the resulting biomolecule conformation and the influence of other surface species notably water. This can be achieved by using atomistic simulation techniques and we have focused on the corundum structured oxide α -Cr₂O₃ and compared with the structural analogues of α -Fe₂O₃ and α -Al₂O₃.

We have used a combination of simulation techniques to investigate the surfaces and surface adsorption. These include potential-model based techniques using the static lattice code METADISE [1] for generating the initial structures of the surfaces and the molecular dynamics code: DL_POLY [2] on incorporation of water. The interatomic potentials were then tested with DFT using VASP [3].

The results from both interatomic potentials and DFT show that the {10.2} and {00.1} surfaces are the most stable and energetically prefer dissociative adsorption. The adsorption energies are in reasonable accord, for example DFT predicts -0.75 eV on the {10.0} surface compared to -0.84 eV. The DFT studies on the different forms (neutral, anionic and cationic) of glycine (Gly) 1, lysine (Lys) and glutamic acid (Glu) have been used to test and develop the potential models. The results show that the neutral amino acid molecules become anionic on adsorption at low coverage on anhydrous Al₂O₃ and Cr₂O₃. An oxido-amino acid complex is formed with the creation of an ionic-covalent bond M-O(C). Finally, the results show that hydroxylation of the surfaces clearly modify amino acid adsorption.

[1] Watson *et al.* (1996), *J. Chem. Soc. Farad. Trans.*, **92**, 433-438. [2] Smith and Forester (1996) *J. Mol Graph* **14**, 136-141 [3] Kresse & Furthmuller (1996), *Phys. Rev. B*, **54**, 11169-11186.

Magnesium isotope fractionation in a hardwood forest of Southern Québec, Canada

S. WORSHAM^{1*}, C. HOLMDEN¹ AND N. BÉLANGER²

¹Saskatchewan Isotope Laboratory, University of
Saskatchewan, Saskatoon, Canada
(*correspondence: srw039@mail.usask.ca,
ceh933@mail.usask.ca)

²Université du Québec à Montréal, Montréal, Canada
(belanger.nicolas@teluq.uqam.ca)

Magnesium (Mg) is an essential macronutrient for plants, acting as the coordinating cation for chlorophyll as well as serving other important metabolic functions. Recent laboratory studies have demonstrated mass dependent fractionation of Mg within plants [1,2], while there is only one confirmation of plant fractionation in the field to date [3]. Our study builds on previous work through an investigation of Mg isotope fractionation in a forested ecosystem. Broader questions motivating this work include the potential impact of forest Mg cycling on the signature of the continental weathering flux of Mg delivered to the oceans by river flow.

Mg isotope fractionation is being examined in a forested first order catchment in southern Québec, Canada, dominated by sugar maple (*Acer saccharum*) and characterized by soils developed from granite, mangerite and anorthosite. Thus far, we observe fractionation coupled with the uptake of Mg into maple trees from the soil pool as well as significant internal plant fractionation. Preliminary $\delta^{26}\text{Mg}$ ($^{26}\text{Mg}/^{24}\text{Mg}$) values for the study plot exhibit an overall fractionation range of 1.15‰ (23% of reported terrestrial variation). Most interesting is considerable fractionation associated with the degradation of chlorophyll during leaf senescence. We believe translocation of light chlorophyll-bound Mg back into the tree accounts for this finding, driving whole leaf $\delta^{26}\text{Mg}$ to higher values prior to litter fall. Measured $\delta^{26}\text{Mg}$ values of senescent leaves and litter range from $-0.88 \pm 0.10\text{‰}$ to $-1.32 \pm 0.09\text{‰}$. Analyses of soil water and stream water samples during low and high flow indicate that Mg isotope values in the stream may be influenced by fractionation during plant uptake; however, a lithology driven (particularly silicate weathering [4]) control is still under investigation. With this presentation, we will review the progress made to date on factors influencing Mg isotope fractionation in a forested catchment.

[1] Black *et al.* (2008) *Environ. Sci. Technol.* **42**, 7831-7836. [2] Bolou-Bi *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 2523-2537. [3] Tipper *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 3883-3896. [4] Tipper *et al.* (2006) *EPSL* **250**, 241-253.

Carbonate-associated sulfate: A seawater proxy with potential and weaknesses

T. WOTTE^{1*}, H. STRAUSS¹ AND G.A. SHIELDS²

¹Institut für Geologie und Paläontologie, WWU Münster, D-48149 Münster, Germany

(*correspondence: thomas.wotte@uni-muenster.de)

²Department of Earth Sciences, University College London, London WC1E 6BT, UK

It is generally considered that the sulfate ion is incorporated into the carbonate lattice during precipitation, consequently called carbonate-associated sulfate (CAS). Even if the mechanism of incorporation as well as the potential effects that diagenesis might have on the sulfur isotopic composition of CAS are not completely understood, it is regarded as a powerful proxy for reconstructing the primary seawater sulfate sulfur composition. Both, analytical and diagenetic aspects can affect the isotopic composition of CAS and have to be carefully considered when talking about carbonate-associated sulfate in the context of primary seawater composition. Bacterial sulfate reduction, particularly under sulfate limiting conditions in the pore water realm, causes ³⁴S-enrichment in the residual dissolved sulfate. On the other hand, sulfide oxidation results in ³⁴S-depleted sulfate. If incorporated, both would alter $\delta^{34}\text{S}_{\text{CAS}}$.

When extracting the original CAS signal it is essential that any other sulfates, which could influence this primary information, are removed. Otherwise, a mixed $\delta^{34}\text{S}$ signal is generated, composed of primary and secondary sulfate sulfur, that does not represent the sulfate sulfur isotopic composition of the paleo-seawater. Various methods of CAS extraction were developed, using different chemicals (e.g., NaCl, NaOCl, H₂O₂) or only deionised water to exclude non-CAS, organic sulfur, and metastable sulfides. These different methods result in variations in $\delta^{34}\text{S}_{\text{CAS}}$, but, no thorough calibration or comparison between the methods is presently available.

Based on comprehensive leaching procedures and detailed data sets comparing several extraction methods for CAS, we are able to identify the sources of secondary sulfate which has the potential to affect the primary CAS isotopic signal during extraction. Further, we determined the effect of pyrite oxidation on CAS by using $\delta^{34}\text{S}$ data generated from chromium-reducible sulfur (CRS). The aim of our research is to establish a rigid protocol for CAS extraction that enables the interpretation of sulfur isotope data from carbonate-associated sulfate as a true seawater proxy.

Petrologic significance of high- precision zircon U-Pb dates from the Skaergaard intrusive complex

J.F. WOTZLAW^{1*}, I.N. BINDEMAN², U. SCHALTEGGER¹,
C.K. BROOKS³ AND H.R. NASLUND⁴

¹Earth Sciences, University of Geneva, Switzerland

(*correspondence: joern.wotzlaw@unige.ch)

²Geological Sciences, University of Oregon, Eugene, USA

³Natural History Museum, Univ. Copenhagen, Denmark

⁴Geological Sciences, SUNY, Binghamton, USA

The Skaergaard intrusion (East Greenland) has long been regarded as a type example of a layered intrusion that essentially evolved by closed-system fractional crystallization. Late-stage ferrodiorites, however, are depleted with respect to ¹⁸O ($\delta^{18}\text{O}_{\text{magma}} \sim 3\text{-}4\%$), recording incorporation of meteoric water derived oxygen into the magma prior to final solidification [1]. Incorporation of meteoric water into these late-stage differentiates requires either devolatilization of hydrated stopped blocks or remelting after subsolidus hydrothermal alteration. Such processes probably operated on timescales of ~ 100 ka and are thus potentially resolvable by high-precision ID-TIMS U-Pb geochronology.

We present high-precision zircon U-Pb dates for low- $\delta^{18}\text{O}$ ferrodiorites from the Sandwich Horizon (SH), a normal- $\delta^{18}\text{O}$ pegmatite from the lower zone of the layered series and the tholeiitic Basistoppen sill, that was emplaced ~ 200 m above the SH shortly after solidification of the Skaergaard magma [2]. Weighted mean ²⁰⁶Pb/²³⁸U zircon dates of statistically equivalent clusters yield precise crystallization ages for the normal- $\delta^{18}\text{O}$ pegmatite and the Basistoppen sill that overlap within subpermil uncertainty. In contrast, ²⁰⁶Pb/²³⁸U zircon dates from the SH do not form a statistically equivalent cluster. We interpret the observed scatter to reflect 321 ± 182 ka of crystallization. Notably, the youngest zircon from the SH is 125 ± 84 ka younger than the age of intrusion of the Basistoppen sill. This requires that either the SH was still molten or was remelted after emplacement of the Basistoppen sill. If the latter interpretation is correct, it would support models for the generation of late-stage low- $\delta^{18}\text{O}$ magmas that involve remelting induced by intrusion of the Basistoppen sill. These results demonstrate the potential of high-precision U-Pb geochronology for resolving complex histories of Cenozoic intrusions.

[1] Bindeman, I.N., Brooks, C.K., McBirney, A.R. & Taylor, H.P. (2008), *J. Geol.* **116**, 571-586. [2] Naslund, H.R. (1986), *Contrib. Mineral. Petrol.* **93**, 359-367.

Extracellular electron transport by the Gram-positive species *Thermincola potens*

K. WRIGHTON¹, H. CARLSON, R. MELNYK¹,
K. BYRNE-BAILEY¹, J. THRASH¹, J. BIGI^{2,3}, J. REMIS⁴,
D. SCHICHNES⁵, M. AUER⁴, C. CHANG^{2,3}
AND J. COATES^{1*}

¹Department of Plant and Microbial Biology, University of California, Berkeley CA

(*correspondance: jdcoates@berkeley.edu)

²Department of Chemistry, University of California, Berkeley

³Howard Hughes Medical Institute, University of California, Berkeley

⁴Life Sciences Division, Lawrence Berkeley National Laboratory

⁵College of Natural Resources Biological Imaging Facility, University of California, Berkeley

Despite their importance in iron redox cycles and bioenergy production, the underlying physiological, biochemical, and genetic mechanisms of extracellular electron transfer by Gram-positive bacteria remain insufficiently understood. We investigated respiration by *Thermincola potens* strain JR of the insoluble electron acceptors Fe(III) oxyhydroxide and anode surface. This isolate, a member of the Firmicutes, was obtained from the anode surface of a microbial fuel cell [1]. We found no evidence for soluble redox-active components secreted into the surrounding medium based on cyclic voltammetry measurements in conjunction with medium replacement experiments. Confocal microscopy revealed highly stratified biofilms in which cells contacting the electrode surface were disproportionately viable relative to the rest of the biofilm. There was also no correlation between biofilm thickness and power production, suggesting cells in contact with the electrode were primarily responsible for current generation. These data, along with cryo-electron microscopy experiments, support contact-dependent electron transfer by *T. potens* strain JR from the cell membrane across the 37 nm cell envelope to the cell surface. Furthermore, we present physiological and genomic evidence that direct extracellular electron transfer is mediated by *c*-type cytochromes. Taken together, our findings provide the first evidence to implicate direct extracellular electron transfer by Gram-positive bacteria and identify *c*-type cytochromes as a potential molecular conduit for charge transport.

[1]. Wrighton, K.C., Agbo, P., Warnecke, F., Weber, K.A., Brodie, E.L., DeSantis, T.Z., Hugenholtz, P., Andersen, G.L., & Coates, J.D. (2008). *ISME Journal* 2, 1146-1156.

Fluid inclusion study of Haojiahe sandstone-type copper deposit, Yunnan province, China

HAI-ZHI WU, RUN-SHENG HAN AND PENG WU

Kunming University of Science and Technology, Southwest Institute of Geological Survey, Geological Survey Center for Non-ferrous Mineral Resources, Kunming, 650093, China (*correspondence: haizhiwu664@yahoo.com.cn)

Haojiahe sandstone-type copper deposit is located in the Chuxiong red bed basin, Yunnan province, China. Two dominant stages of fluid, rock-forming period and reworked mineralization period, are recorded in the gangue minerals of different types of ore.

The rock-forming period of fluid inclusions, mainly aqueous inclusions, can be observed in calcite and quartz cement and secondary enlargement of quartz in disseminated and lamellar ores. The homogenization temperatures range from 84.1 to 162.3°C, with peak values between 122 and 146°C; and the salinities are from 3.3 to 14wt%NaCl_{eq}, with peak values between 5.5 and 7.5wt%NaCl_{eq}. The analytic results got by Laser Raman Spectroscopy, show that the gas components were mainly H₂O, SO₂ and CO₂, suggesting a relative oxidizing environment.

The reworked mineralization period of fluid inclusions, including aqueous inclusions and some hydrocarbon inclusions, can be observed in quartz paragenetic with copper minerals in banding or vein ores. The homogenization temperatures range from 145.5 to 227.2°C, with peak values between 170 and 200°C; and the salinities are from 4.5 to 15.2wt% NaCl_{eq}, with peak values between 7 and 9.5wt%NaCl_{eq}. The gas components were H₂O, CH₄, C₂H₆, CO and CO₂, suggesting a relative reducing environment.

Results of this study show the fluid evolution have experienced increased temperature, increased salinity and an environmental change from oxidizing to reducing.

Granted jointly by the project of State Crisis Mine (20089943) and the Distinguishing Discipline of KUST (2008).

Fluorine partitioning between hydrous minerals and aqueous fluid at 1 GPa and 770 – 850 °C

J. WU* AND K.T. KOGA

Laboratoire Magmas et Volcans, Clermont Université, BP 10448, Université Blaise Pascal, CNRS, IRD, Clermont-Ferrand, France
(*correspondence: j.wu@opgc.univ-bpclermont.fr)

Mechanisms of volatile transfer from subducting slab to melting region beneath arc volcanoes are probably the least understood process of arc magma genesis. Fluorine, which suffers minimum degassing in arc primitive melt inclusions, retains the information of magma genesis at the depths. It is our interest to understand geochemical behavior of F along with other trace element, and to characterize volatile transfer from the slab to the mantle. Experimentally determined solubility of F in aqueous fluid, and partition coefficients of F between fluid and minerals provide first order information about the character of the volatile-transporting agent. Here, we report experimentally determined the solubility of F in aqueous fluid. The solid starting materials contain 5% or 1.9% F, and an approximately same amount of pure water was added right before an experiment. The experiments are conducted at 1GPa and from 770 to 850°C, for the duration of 3 to 13 days, in gold capsule, with Ni/NiO buffer, using piston cylinder high-pressure apparatus. After quenching, the liquid part is retrieved into a known volume of deionized water for the liquid analysis and the solid part is measured by an electron microprobe. We also calculate the fluid composition with mass-balance.

All samples are equilibrated with hornblende, a humite group mineral, and fluid. With mass-balance calculation a range of partition coefficients are determined: $D(\text{fluid}/\text{hornblende}) = 0.13\text{-}0.42$; $D(\text{fluid}/\text{norbergite}) = 0.02\text{-}0.04$; $D(\text{hornblendes}/\text{norbergite}) = 0.13\text{-}0.17$. The D_F are constant over the temperature range within their uncertainties. Furthermore, F anions are preferentially incorporated into the humite group minerals than hornblende, and nearly all OH site of nobergite are occupied by F in our system. The concentration of F in the fluid is 0.22-0.78 wt% based on mass-balance, and direct analyses of fluids are under way. The F/H_2O values are 10-100 times larger for primitive arc melt inclusions (0.05-0.81) than for ours (0.0024-0.0085). This suggests either 1) drastic water loss in arc melt incusions, or 2) presence of fractionation phases other than ones in this study.

Advances and challenges in the study of mechanisms on salinization and contamination of deep groundwater in the North China Plain

J. F. WU*, Y. YANG, Y. ZHANG AND X. B. ZHU

Department of Hydrosciences, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210093, China
(*correspondence: jfwu@nju.edu.cn)

Groundwater in deep aquifers is the main water source of households, industry and agriculture in the North China Plain (NCP). However, information on degradation of groundwater quality is often seen in this region, which poses a great threat to the interests of society or ecosystems. This presentation reviews the recent advances in the study on mechanism of deep groundwater quality degradation over the last several decades in the NCP: salinization due to shallow saline groundwater intrusion and contamination by man-made sources. In general, degradation and deterioration of deep groundwater quality found in the NCP was deductively explained by groundwater over-exploitation and mismanagement, but the mechanism of groundwater quality degradation is largely unknown so far. As a consequence, further investigation is needed to uncover the mechanism of salinization and contamination of deep groundwater resource. Due to the complexity of the aquifers, some techniques developed for fractured rock systems [1, 2] may be used as a reference in highly heterogeneous porous aquifers, and the confronting issues and challenges can be summarized as: (i) how to address the heterogeneity of alluvial deposits including aquifers and aquitards [3]; (ii) how to characterize the spatial and temporal extent and intensity of downward salinity intrusion of shallow saline groundwater [4]; (iii) how to delineate the chemical and biochemical processes of man-made sources in aquifers [5]; and (iv) how to understand the apparent scale-effects on different hydrogeological parameters at a regional scale under field conditions [6, 7]. (Grant Nos. 2010CB428803 and 41072175)

[1] Zhou *et al.* (2004) *Int. J. Rock Mech. Min. Sci.* **41**(3), 402-402. [2] Qian *et al.* (2006) *Hydrogeol. J.* **14**, 1192-1205. [3] Rojas *et al.* (2010) *Water Resour. Res.* **46**, W08520. [4] Song *et al.* (2007) *Hydrogeol. Eng. Geol.* **34**(1): 44-46. [5] Singhal & Islam (2008) *J. Contam. Hydrol.* **96**, 32-47. [6] Qian *et al.* (2007) *J. Hydrol.* **339**, 206-215. [7] Chen *et al.* (2009) *Journal of Hydrodynamics* **21**(6): 820-825.

Geochemical anomaly pattern in the Haojiahe sandstone-type copper deposit, Yunnan, China

PENG WU*, RUNSHENG HAN AND JING LI

Kunming University of Science and Technology; Southwest Institute of Geological Survey, Geological Survey Center for Non-ferrous Mineral Resources, Kunming 650093, China (*correspondence: wupeng8104@yahoo.com.cn)

Haojiahe deposit controlled by the Upper Cretaceous (K_2mx_2) is the typical one of sandstone-type copper deposits in the Chuxiong Basin. Ore-bodies (average grade: Cu 1.5%) are located in the interface between purple bed and grey bed. From purple bed to grey bed, the ore mineral zonality is hematite, chalcocite, bornite, chalcopyrite and pyrite.

Ore-forming elements association is Cu, Ag, As, Hg. The average contents of copper ores $\Sigma REE=119.19 \times 10^{-6}$, $LREE/HREE=8.93$, $\delta Eu=0.74$, $\delta Ce=0.95$. Chondrite-normalized REE distribution patterns show oblique to the HREE side with the poor Eu and enrichment in LREE. From oxidized zone to transitional zone (purple bed \rightarrow copper ore \rightarrow grey bed), ΣREE and δCe decrease gradually with the increase of δEu . The geochemical characteristics well indicate the change of oxidation and reducing environment [1, 2]. These are probably related to the water-rock interaction or infiltration metasomatism.

The vertical zonation of indicator elements in K_2mx_2 from the top to the bottom is Zn, Cs \rightarrow Pb, Tl, Mo \rightarrow Cu, Ag, As \rightarrow Sb, Hg, Co and the transversal zonation from grey belt to purple belt is Mo, Pb \rightarrow Cu, Hg, Ag \rightarrow Cu, Ag, As, Sb, Hg.

Geochemical anomaly pattern has been established, that is, the anomaly of Zn, Pb, Mo appears above the orebodies (average distance: Zn 30m, Mo 10m), and the anomaly of Sb, Hg, Co under the orebodies. The anomaly of Cu, Ag and the ratio of $Cu/Ag > 170$, $Cu/(Pb+Zn) > 10$, $Cu/(As+Sb+Hg) > 180$ are concomitant with rich orebodies; the anomaly of Pb, Zn, Co, (Ni) and $Cu/Ag < 128$, $Cu/(Pb+Zn) < 9$, $Cu/(As+Sb+Hg) < 8$ implies barren. The contents of Cu, Ag, As, Hg and the ratio of dual elements increase longitudinally, and it shows that the copper mineralization is enhanced gradually. This pattern provides an important basis for the depth ore-forming prognosis.

Granted jointly by the Basic Applied Research Foundation of Yunnan Province (2010ZC013) and the Distinguishing Discipline of KUST (2008).

[1] Alex C. Brown (2006). *Journal of Geochemical Exploration* **89**, 23-26. [2] El Desouky (2008). *Ore Geology Reviews* **34**, 561-579.

Origins and sources of CO₂ in natural gas in Eastern Sichuan Basin, China

XIAOQI WU

PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China
(wuxiaoqi@petrochina.com.cn)

The eastern Sichuan Basin in China is well-known for the development of H₂S-bearing gas fields such as Puguang, and the natural gas generally contains CO₂. High-content CO₂ was thought to accompany high-content H₂S, and this might be one of the proofs of TSR (Thermochemical Sulfate Reduction) [1]. The CO₂ contents of natural gas from eastern Sichuan Basin vary from 0% to 32.04%, and gas samples with low-content (<2%) and 6%-10% CO₂ account for 61.6% and 20.0% of the total respectively.

The $\delta^{13}C_{CO_2}$ values vary from -23.4‰ to 3.3‰, and 34.4% of the samples have low $\delta^{13}C_{CO_2}$ values (<-12‰) which are in accordance with those of typical organic CO₂ [2], and they are mainly with low contents of CO₂ (<3%). The corresponding H₂S contents are very low or zero. This type of CO₂ was derived from the oxidation of organic matters. However, the other type of CO₂ displays large $\delta^{13}C$ values (>-8.3‰) and shares similar carbon isotopic characteristics with inorganic CO₂ [2] and reservoir carbonates [1], and differs dramatically from that of TSR origin [3]. In this case, no obvious relation exists between the CO₂ and H₂S contents, so it does between the CO₂ and TSR as study by Huang *et al.* [4]. Under the precipitation in the deep-burial period, CO₂ generated during the TSR was mainly transformed into secondary calcite, which demonstrated low $\delta^{13}C$ values (-18.2‰~-10.3‰) [1].

Inorganic CO₂ can be divided into mantle-derived origin and decomposition or dissolution of carbonates [2]. The helium in the natural gas was crustal derived due to the low R/Ra ratios (<0.036) without significant contribution from the mantle. The temperature required for decomposition of carbonates was too high to reach for the deep-buried carbonate reservoirs. In consideration of substantial uplift in late Jurassic, CO₂ with large $\delta^{13}C$ values was mainly derived from the dissolution of reservoir carbonates under the effect of acidic fluid.

[1] Zhu *et al.* (2005) *Sci China -Earth Sci* **48**, 1960-1971. [2] Dai *et al.* (1996) *AAPG Bull* **80**, 1615-1626. [3] Worden *et al.* (1995) *AAPG Bull* **79**, 854-863. [4] Huang *et al.* (2010) *Sci China-Earth Sci* **53**, 642-648.

The distribution of biomarkers and the geological significance of the severely biodegraded crude oil in Gudao reservoir

YINGQIN WU^{1,2}, YONGLI WANG¹, TIANZHU LEI¹,
JIANG CHANG¹, YOUXIAO WANG¹ AND YANQING XIA^{1*}

¹Key Laboratory of Petroleum Resources Research, Institute of Geology and Geophysics, Chinese Academy of Science, Lanzhou 730000, China
(*correspondence: yqxia@lzb.ac.cn)

²Graduate School of the Chinese Academy of Sciences, Beijing 100049, China (wuyingqin001@163.com)

Biodegraded crude oil in China are distributed widely and make up a certain portion of heavy-oil resources. An unresolved complex mixture (UCM) of hydrocarbons isolated from a biodegraded crude oil of the Gudao reservoir in the Shengli Oilfield, China. Some of the hydrocarbons were identified using GC-MS. The result showed that the hydrocarbons expect for tricyclic terpanes, steranes, hopanes, 25-norhopanes, were completely depleted in saturated fraction, as well as hydrocarbons expect for triaromatic steranes and few methylnaphthalenes, methylphenanthrenes, chrysene series in the aromatic fraction, which indicate that severe biodegradation occurred in this reservoir. Relatively abundant pentacyclic terpane characterized by high concentration of norhopane and gammacerane, low content of Ts and Tm, the "L"-type and asymmetrical "V"-type distribution of regular steranes and 4-methylsteranes, and high maturity as revealed by sterane and terpane parameters, suggesting aerobic depositional environment with a salt and stratified water body. Furthermore, The results also showed that the magnitude of "UCM" hump existed in the aromatic fraction is apparently larger than that of "UCM" hump existed in the saturated fraction, which implied that the biodegradation rate for aromatic hydrocarbons is parallel or even exceed that of saturated hydrocarbons and the alteration occurred in this reservoir was associated with biodegradation with water-washing.

Supported by grants No. KZCX2-YW-Q05-05, XDA05120204, KZCX2-EW -104(2), NSFC No.40672123 and 2005CB422001.

Determination on nitrate use capacity in plants via isotope tracer

YANYOU WU* AND KUAN ZHAO

IAE, Jiangsu University, Zhenjiang, 212013, China
(*correspondence: yanyouwu@ujs.edu.cn)

Materials and Treatments

Broussonetia papyrifera (BP) and *Morus alba* (MA) seedlings were cultured in the modified Hoagland nutrient solution adding different concentrations (0, 20, 60 g L⁻¹) of polyethylene glycol (PEG, simulating drought) (pH5.5). *Orychophragmus violaceus* (OV) seedlings were cultured in the modified Hoagland nutrient solution adding different concentrations (0, 2.5, 10 mM) of NaHCO₃ (BC) (pH 8.2). The sole nitrate N was potassium nitrate with 16.99‰ of the δ¹⁵N. The sole ammonium N was NH₄H₂PO₄ with -1.21‰ of the δ¹⁵N. The δ¹⁵N, net photosynthetic rate (Pn, μmol m⁻²s⁻¹) and N content (Cn, mg g⁻¹) of the third or fourth fully expanded leaf were measured. The proportion (f_B) of nitrate to total inorganic N was calculated by a two-component mixing model. The nitrate use capacity (NUC, mg m⁻²h⁻¹) in plants was calculated by the formula: NUC= 90CnPn/f_B.

Results and discussion

From Table 1, we can found that OV under high concentration BC had the greatest NUC, MA under drought stress the least. Even under drought stress, BP had a great NUC. The great NUC of BP and OV under the Karst drought or high concentration bicarbonate resulted in their adaptability to Karst environment, partly. The plants of the adaptability to Karst environment alternately use nitrate and ammonium N under Karst environment.

PS-T	δ ¹⁵ N	Pn	f _B	NUC
MA-PEG/0	-2.41	6.3	0.11	1.59
MA-PEG/20	-1.51	1.0	0.15	0.40
MA-PEG/60	-1.53	0.1	0.15	0.03
BP-PEG/0	-1.25	2.8	0.17	1.04
BP-PEG/20	3.19	2.9	0.38	2.39
BP-PEG/60	2.91	3.9	0.37	3.10
OV-BC/0	12.73	3.9	0.84	6.28
OV-BC/2.5	15.95	2.1	0.99	4.77
OV-BC/10	16.08	3.3	1.00	7.10

Table 1: NUC of several species of plants under different treatment (PS=plant species, T=treatment).

This work was supported by NSFC (No. 40973060, No.31070365).

Tectonic evolution of the Qinling-Tongbai-Dabie orogenic belt

YUAN-BAO WU¹ AND YONG-FEI ZHENG²

¹State Key Laboratory of Geological Processes and Mineral Resources, Faculty of Earth Sciences, China University of Geosciences, Wuhan 430074, China (*correspondence: yuanbaowu@cug.edu.cn)

²CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China

The Qinling-Tongbai-Dabie-Sulu orogenic belt marks the suture between the North and South China Blocks in Central China, forming one of the most important orogens in the eastern Asia. Although it has been extensively studied for more than 20 years, there are hot controversies about the location and number of sutures and the timing of arc-continent and continent-continent collisions during the convergence between the North and South China Blocks. The Dabie-Sulu orogenic belt is characterized by the occurrence of Triassic UHP eclogite-facies metamorphic rocks. On the other hand, there are Paleozoic events of arc-continent collision in the Qinling-Tongbai orogenic belts that were subsequently followed by the Triassic process of continental collision. Rifting occurred at the northern part of the Yangtze Block, synchronous with the middle Paleozoic collision, and was followed by the opening of the Paleo-Tethyan ocean during the Late Paleozoic. These indicate that the Qinling-Dabie-Sulu orogen is a typical multiple evolution orogen, including the Early to Middle Paleozoic continental subduction and collision, the Silurian extension and rifting in relation to the opening of the Paleo-Tethyan ocean during the Late Paleozoic, and the Triassic continental material subduction, HP-UHP metamorphism and subsequent exhumation. Therefore, it is a complex orogenic belt on the time and location of arc-continent and continent-continent collisions between the North and South China blocks, and the amalgamation of the two continental blocks along the Qinling-Tongbai-Dabie-Sulu orogenic belt is a multistage process that spans about 300 Ma.

Composition and structure of the 3.65 Å phase: A DHMS with exclusively six-fold coordinated Si

B. WUNDER*, R. WIRTH, M. KOCH-MÜLLER AND S. JAHN

GFZ German Research Centre for Geosciences, Section 3.3, Telegrafenberg, 14474 Potsdam, Germany (*correspondence: wunder@gfz-potsdam.de)

Dense Hydrous Magnesium Silicates (DHMS) are suggested to be important hosts and carriers of water under hydrous conditions of the Earth's mantle and in subduction zones. Therefore, their study is central to the understanding of the Earth's deep water cycle. The so-called 3.65 Å phase, named after the *d*-value of its prominent X-ray reflection, is the least well-characterized phase of the DHMS family, as neither its chemical composition nor its structure are well constrained.

In our recent study [1], the 3.65 Å phase was synthesized in the system MgO-SiO₂-H₂O at 10 GPa and 425 °C for 77 hours run duration in a multi-anvil press from a gel plus excess water. The composition of the 3.65 Å phase was determined to be MgSi(OH)₆ by combining results from SEM-, TEM-, EMP-, IR- and Raman-analysis. Powder XRD combined with Rietveld refinement revealed the 3.65 Å phase to be isostructural with δ-Al(OH)₃. Its structure can be described as an A-site vacant perovskite with probably long-range random distribution of Si and Mg at octahedral sites. The 3.65 Å phase represents beside phase D the second DHMS with exclusively six-fold coordinated Si.

The H-positions could not be determined by the powder XRD Rietveld refinement. Therefore, the apparent orthorhombic space group – either *Pnam* with protons in unordered configuration, or *P2₁2₁2₁* with ordered H-positions – was ambiguous. Preliminary first-principles DFT-calculations predict the structure with *P2₁2₁2₁* or monoclinic *P2₁* symmetry with ordered Mg and Si as the most stable structure at ambient conditions.

The 3.65 Å phase is stable at pressures above about 9.0 GPa and decomposes above about 500 °C due to the reaction 3.65 Å phase = high-clinoenstatite + water. This limited P-T stability together with its high water content of 35 wt.% makes it a rather unrealistic phase in the Earth's mantle. If at all, the 3.65 Å phase might only exist under hydrous conditions in very limited areas, i.e., in the coldest parts of old and extremely fast subducted slabs, e.g., Tonga.

[1] Wunder *et al.* (2011) *Am. Mineral.*, in press, DOI: 10.2138/am.2011.3782.

Exploring carbonate aquifers and their susceptibility for metal release during CO₂ leakage

A. WUNSCH^{1*}, A.K. NAVARRE-SITCHLER¹,
R.M. MAXWELL² AND J.E. MCCRAY¹

¹Environmental Science and Engineering Division, Colorado School of Mines, Golden, CO 80401, USA
(*correspondence: awunsch@mines.edu)

²Geology and Geological Engineering Department, Colorado School of Mines, Golden, CO 80401, USA

Metal transport resulting from potential CO₂ leakage into freshwater aquifers is a major concern accompanying carbon sequestration operations. Acidity resulting from dissolution of leaked CO₂ into aquifer waters may result in release of metals from aquifer minerals. Carbonate aquifers have the ability to buffer increased acidity through calcite and dolomite dissolution, and are therefore theoretically “safer” than non-buffering aquifers. However, carbonate minerals are rarely found as pure phases in nature, often containing impurities in the solid phase. These impurities substitute for either calcium or carbonate in the crystal lattice. Buffering of acidity requires dissolution of carbonate minerals, resulting in potential release of trace elements. Whole-rock analysis of natural carbonate rock samples show solid-phase concentrations of Pb and Cr on the order of several ppm, and of Ba, Co, Ni, Rb, Sc and Zn on the order of tens or hundreds of ppm. Prediction of the behavior of these metals through modeling is difficult, as there are several models of co-precipitation and dissolution in solid solutions. Simple stoichiometric dissolution predicts very different release behavior of these metals from calcite dissolution at various CO₂ partial-pressures. For example, at low P_{CO₂}, cobalt concentrations in solution are as high as 776 ppb, and decrease with increasing P_{CO₂}, whereas barium concentrations in solution increase with increasing P_{CO₂}, following a trend similar to that of calcium. In this work, batch dissolution experiments are combined with SEM and electron microprobe analyses, to investigate dissolution rates and equilibrium release of metals from carbonate rocks and to determine their solid-phase source.

Uncovering the key processes involved in manganese biogeochemical cycling in the Ocean

K. WUTTIG¹, M. HELLER¹ AND P. CROOT²

¹IFM-Geomar, Kiel, Germany (kwuttig@ifm-geomar.de, mheller@ifm-geomar.de)

²Plymouth Marine Laboratory, Plymouth, United Kingdom (pecr@pml.ac.uk)

Mn forms a critical part of many redox enzymes most notably for photosynthesis, where as part of Photosystem II it converts H₂O to O₂. Many marine organisms also contain Mn superoxide dismutases (SOD), that act as part of the intracellular defences against reactive oxygen species (ROS) and in particular rapidly convert superoxide (O₂⁻) into O₂ and H₂O₂. While laboratory studies have shown that the growth of marine phytoplankton is reduced for some species at the low Mn concentrations found in open ocean seawater, currently there is little evidence from fieldwork to suggest Mn limitation occurs, but this possibility remains, particularly for the Southern Ocean.

The supply of Mn to the open ocean is predominantly via the deposition of aeolian dust and subsequent dissolution of Mn(II) from the particles. The released Mn(II) is slowly oxidized (via biota or chemically) to insoluble MnO₂ which precipitates out of the water column. In the sunlit ocean, H₂O₂ can reduce MnO₂ back to Mn(II) completing a redox cycle. New work by a number of groups suggest that transient Mn(III) species, intermediate in the cycling between Mn(II) and MnO₂ may play an important role in both the Mn and Fe biogeochemical cycles in surface waters. In coastal waters Mn(II) can diffuse from reducing sediments with subsequent mixing into the photic zone.

In this presentation we will present data for Mn concentrations, speciation and kinetic reactivity from two research cruises in the Tropical Atlantic (M83-1 and MSM17-04) and from a dust deposition experiment performed in trace metal clean mesocosms in the Mediterranean (DUNE2). We will use our combined dataset to determine the predominant source of Mn to shelf waters in the Mauritanian upwelling region and the adjacent open ocean in the Tropical Atlantic, which are impacted by both Saharan dust and potentially coastal sedimentary sources that are advected offshore by the upwelling waters. Finally we will examine the evidence for Mn(III) in the euphotic zone of the open ocean and the implications this had for Mn biogeochemical cycling in the ocean.

XANES investigation of selenium speciation in silicate glasses

JEREMY L. WYKES, HUGH ST. C. O'NEILL AND
JOHN A. MAVROGENES

Research School of Earth Sciences, Australian National
University, Acton, ACT, 0200, Australia

The speciation of sulfur in silicate melts as a function of oxygen fugacity is an important factor in volcanic degassing and ore deposition. Due to the large number of electrons involved in the 2- to 6+ transition, sulfur changes from 2- to 6+ over a very narrow fO_2 interval, <2 log units. The 4+ valence state of sulfur does not appear to be an important species in silicate melts. Selenium lies directly below sulfur in group 16 of the periodic table and is considered to display similar geochemical behavior. However, differences in redox speciation between sulfur and selenium, either in the fO_2 of Se^{2-} to Se^{6+} relative to S^{2-} to S^{6+} transitions, or the existence of a Se^{4+} stability field will result in fractionation of Se from S in magmatic systems [1].

We have conducted high pressure, high temperature experiments under controlled fO_2 conditions to investigate the speciation of Se in silicate melts. Oxide mixes of basaltic composition were doped with 500 to 2500 ppm Se and equilibrated in Pt or graphite-Pt capsules at 1400°C for 36 hours. Chemical potential of oxygen was controlled by the addition of Ru-RuO₂, PtO₂ and the presence of graphite, to produce experiments reflecting reduced (graphite \approx FMQ-2.2; [2]), oxidising (Ru-RuO₂ \approx hematite-magnetite at 1400°C) and very oxidising conditions (PtO₂ produces O₂ gas phase).

Quenched glasses were recovered from the piston-cylinder experiments and the selenium K-edge XANES (X-Ray Absorption Near Edge Structure) spectra were collected in fluorescence mode at the Australian National Beamline Facility at the Photon Factory, Tsukuba, Japan.

Glasses from each redox condition produced a distinct Se K-edge spectra, with the absorption edge energy increasing with increasing fO_2 . The spectra are interpreted to represent Se^{2-} , Se^{4+} and Se^{6+} . Thus, at moderate to high fO_2 , selenium exhibits distinct redox speciation to sulfur, with the existence of a significant stability field for Se^{4+} , and the Se^{2-} to Se^{4+} transition will occur over a larger fO_2 range than S^{2-} to S^{6+} . We suggest that Se^{6+} is not an important species in silicate melts at geologically relevant oxygen fugacities.

[1] Jenner, O'Neill, Arculus, Mavrogenes (2010) *Journal of Petrology* **51**, 2445-2464. [2] Médard, McCammon, Barr, Grove (2008) *American Mineralogist* **93**, 1838-1844.

Geochemical evidence of source and process controls on Mid-Miocene silicic volcanism in the Idaho-Oregon-Nevada Region, USA

A. WYPYCH* AND W.K. HART

Geology Dept., Miami University, Oxford, OH 45056, USA
(*correspondence: wpycha@muohio.edu)

In this study we report results of a geochemical and petrological investigation of Mid-Miocene silicic volcanism in the Idaho-Oregon-Nevada (ION) region aimed at examining models of continental crust formation and modification in the northwestern US. In the late Oligocene to Miocene portions of the northwestern US underwent extension accompanied by bimodal (mafic and silicic) volcanism [1,2]. The ION region resides in the northernmost Basin and Range Province on a "transitional" lithosphere between Mesozoic accreted lithosphere to the west and Precambrian Wyoming Craton to the east as marked by Sr isotopic composition (0.704 and $>$ 0.706 respectively). It is characterized by bimodal, silicic (~16 to ~13 Ma) and mafic (~17 to 15 Ma) volcanism temporally related to the main volumes of Columbia River flood basalt activity to the north. Mantle upwelling behind an active magmatic arc, mafic magma intrusion into crust, melting of heterogeneous lithosphere and mixing of the melts from heterogeneous sources are contributing to the ION region bimodal volcanism and its continuation in time and space to the NE (Snake River Plain-Yellowstone) and the NW (High Lava Plains-Newberry) [1,3,4].

To investigate the heterogeneity and spatial and temporal relationships between off craton, "transitional", and on craton sources and reservoirs five ION volcanic centers are investigated. We conducted petrological, geochemical and Sr, Nd and Pb isotopic analyses on 23 whole rock-glass separate pairs and Hf isotopic analyses on the glass separates [3]. In addition to the influence of spatial and temporally heterogeneous source regions open system behavior in crustal storage chambers plays an important role in ION area silicic magma evolution. This is evident from feldspar dissolution textures and differences in trace element and isotopic compositions between whole rock and glass separate pairs.

[1] Brueseke et al. (2008) *Bull. Volc.* **70**, 343-360. [2] Scarberry et al. (2010) *Tectonophysics*. **488**, 71-86. [3] Nash et al. (2006) *Earth Planet. Sci. Lett.* **247**, 143-156. [4] Christiansen and McCurry (2008) *Bull. Volc.*, **70**, 251-267.

Generating Kermadec Arc SMS deposits: Roles of magmatic volatiles

R.J. WYSOCZANSKI^{1*}, M.R. HANDLER², C.I. SCHIPPER³,
J. CREECH², M.D. ROTELLA², C.J.N. WILSON² AND
R.B. STEWART³

¹NIWA, PO Box 14901, Wellington, New Zealand

(*correspondence: r.wysoczanski@niwa.co.nz)

²SGEES, Victoria University, Wellington, New Zealand

³INR, Massey University, Palmerston North, New Zealand

Seafloor massive sulphide (SMS) deposits in oceanic subduction zones, such as the Kermadec Arc/Havre Trough (KAHT), are a valuable commodity and may be viable as a precious metal source. The ultimate source, however, of S and metals in SMS deposits is unknown. Here, we present elemental data, including volatiles (H, C, S, Cl) of basalts from along the southern KAHT to address the relationship between magmatic composition and hydrothermal venting. The findings are as follow:

1. Back-arc melt inclusion (MI) water contents (~2.5 wt. %) are similar to the hydrothermally active arc, implying that the lack of back-arc hydrothermal activity is not due to lower magmatic water contents. Slab-derived fluid components do not differ between the southern and middle portions of the Kermadec Arc, implying that subduction of the thick Hikurangi Plateau crust in the south (cf. normal oceanic crust in the north) does not enrich the mantle in fluids.

2. SO₃ contents do not correlate with slab-derived components, suggesting that little S is added to the mantle source from the slab. S degasses as sulphate, resulting in more reduced rock compositions, which then interact with hydrothermal fluids. Pressures from H₂O contents of MIs imply that the magma chambers of arc front volcanoes that are hydrothermally inactive are deeper than for hydrothermally active volcanoes.

3. Basalt compositions from hydrothermally active arc front volcanoes do not significantly differ from those with no activity. This implies that factors other than magmatic composition determine the location and extent of hydrothermal activity.

4. Concentrations/ratios of metals in basalt magmas require metal enrichment over magmatic compositions to produce SMS deposits in the order Pb>Zn>>Cu. This may occur via crustal scavenging or magmatic fluid additions. Elemental ratios in chalcopyrite-bearing chimneys can, however, be achieved from basalt magmas by fractionation to evolved compositions.