

Tourmaline from porphyry copper belts as a proxy to assess boron budget in arc magmas

O.M. RABBIA AND L.B. HERNÁNDEZ

Instituto de Geología Económica Aplicada, Universidad de Concepción, Casilla 160c, Concepción, Chile
(rabbia@udec.cl, lahernan@udec.cl)

In the Andes, world-class porphyry Cu deposits are intimately associated to major changes in the subduction geometry (progressive flattening) resulting in episodes of intense deformation, crustal thickening, rapid uplift and erosion (major orogenic phases), accompanied by migration of the volcanic front and changes in the geochemistry of magmas (appearance of the adakitic signature). As consequence of these highly compressive events, volcanism tends to vanish leaving mostly plutonic rocks in the geologic record. Whole-rock analysis of these intrusive rocks offers no quantitative appraisal of the B content in their magmas if volatile exsolution has taken place. On the other hand, during these particular periods of the Andean orogen evolution, volatiles exsolved from magmas are the main source of B-bearing hydrothermal fluids from which tourmaline may precipitate in porphyry Cu deposits. Therefore, the assessment of the relative abundance of this borosilicate in copper deposit belts could cast some light on B abundance in the associated arc magmas during metallogenic periods.

Tourmaline breccia complexes, with up to ~20 vol% of tourmaline, are a characteristic feature of world-class porphyry Cu deposits from the ~370 km long, Late Miocene-Early Pliocene Cu belt from Central Chile, as well as, of prospects and deposits from the ~1500 km long, Paleocene-Early Eocene Cu belt from Northern Chile and Southern Peru. In contrast, tourmaline is rarely developed or relatively uncommon in most porphyry Cu deposits from the ~2000 km long, Late Eocene-Early Oligocene belt from Southern Peru and Northern Chile.

Considering that the amount of fluid involved in giant porphyry Cu deposits formation requires huge volumes of magma (up to ~2000 km³), the tourmaline-poor nature of the Late Eocene-Early Oligocene Cu belt, hosting giant Cu deposits (e.g.: Chuquicamata, La Escondida), suggests that the associated magmatism, and by extension its source, was fluid-bearing but B-poor. A possible explanation for the low B budget in these arc magmas could be related to a particular thermal configuration of the downgoing oceanic plate.

A high-resolution paleohydrological record of the Younger Dryas episode from Western Europe – Using lipid biomarker D/H ratios

OLIVER RACH^{1*}, ACHIM BRAUER², HEINZ WILKES²
AND DIRK SACHSE¹

¹University of Potsdam, Institute of Earth and Environmental Science, Karl-Liebknecht-Str. 24-25 14476 Potsdam-Golm (Germany) (*correspondence: rach@geo.uni-potsdam.de)
²GeoForschungsZentrum Potsdam, 14473 Potsdam

Despite the recognized importance of the hydrological cycle within the climate system it is difficult to predict hydrological consequences of current and future climatic changes on regional scales. However, regional climatic variations on the continents are often most dramatically expressed through hydrological changes. A key tool to better understand the underlying mechanisms is the reconstruction of the past climate changes from high-resolution lacustrine proxy data. We investigated how fast hydrological changes have taken place during abrupt climatic shifts, such as the Younger Dryas cold episode (YD) ca. 12 ky BP. We assessed this question with a novel proxy, the stable hydrogen isotope composition of higher-plant derived lipid biomarkers.

We analyzed sediments from Lake Meerfelder Maar (Germany), with a continuous annual varving during the YD, which provide an excellent archive to resolve this issue. We measured the hydrogen isotope ratios of higher plant lipid biomarkers (long-chain *n*-alkanes) and conducted X-Ray fluorescence analyses (XRF), with focus on catchment-typical allochthonous elements (K, Al, Ti) in high-resolution (8-33 years per sample). The average chain length of the *n*-alkanes shows short-term variabilities, suggesting changes in lake catchment ecology. While *n*-alkanes with the highest concentration are long-chain homologues (*n*C₂₅, *n*C₂₇, *n*C₂₉, *n*C₃₁) of terrestrial origin, an increase in *n*C₂₃ produced mainly by aquatic macrophytes suggests changes in the aquatic ecology during the early YD. XRF data show pronounced changes in sedimentary conditions with more allochthonous sediments in the later YD, probably related to hydrological variations. Indeed, the results from hydrogen isotope analysis, with a significant isotopic depletion in leaf-wax *n*-alkanes of about 20 ‰ during the initial part of the YD relative to Allerød, suggest colder conditions and/or enhanced precipitation. Furthermore, our data provide additional evidence for two hydrologically distinct periods within the YD interval. Through a combination of biomarker D/H ratios with XRF data our results deliver new insights into the timing and magnitude of regional hydrological changes as a consequence of abrupt global climatic variations.

Chemical weathering and erosion rates in Lesser Antilles: An overview in Guadeloupe, Martinique and Dominica

SÉTAREH RAD¹, KARINE RIVE², OLIVIER CERDAN¹,
VITTECOQ BENOIT¹ AND CLAUDE ALLÈGRE³

¹BRGM, 3, avenue Claude-Guillemin, Orléans, France

²CEGEO, 159 allée Chardin, Villeneuve d'Ascq, France

³IPGP, PRES Paris Cité, 75238 Paris Cedex 05, France

Guadeloupe, Martinique and Dominica Islands alike numerous tropical environment present extreme weathering regimes.

Physical denudation is mainly controlled by landside. This reflects the torrential dynamics of the rivers. For Guadeloupe, the mechanical weathering rates are 800-4000 t/km²/yr.

The lithology is very porous with high infiltration rates, which induces that most of the elements fluxes are produced on subsurface as the chemical erosion rates are 2 to 5 times higher than the rates from surface water. We show how kinetic of chemical weathering rates depends on the age of the lava and subsurface circulation.

In addition, timescale of erosion have been calculated from U-series analyses sediments from rivers. Our results show a large range: from 0 to 150 ka in Martinique and from 0 to 60 ka Guadeloupe. From analyses from the dissolved loads, we propose to evaluate residence times in the river water. It would appear that waters circulation is globally 3 times longer for subsurface water than for surficial water (Rad *et al.* 2011).

Moreover these islands are highly impacted by agriculture. It is therefore interesting to assess the impact of such influence on the weathering rates. Our result show that human activity brings no disturbance on Critical zone processes contrary to what one might think. Indeed, we show that among the combined impact of all parameters (climate, runoff, slopes, vegetation...), the basins age seems to be the control parameter on chemical weathering and land use: the younger the basin, the higher the weathering rate.

We could observe a combined effect between the higher erodibility and a higher climate erosivity of the younger reliefs.

Impact of a small downstream reservoir on metal cycling in acid mine drainage impacted waters

L.K. RADEMACHER^{1*}, K.L. FAUL² AND G. MCDANIEL¹

¹University of the Pacific, Stockton, CA 95211, USA

(*correspondence: lrademacher@pacific.edu)

²Mills College, Oakland, CA 94613, USA (kfaul@mills.edu)

The results of ongoing work in an acid mine drainage impacted watershed suggests downstream reservoirs play an important role in the cycling of metals and trace elements under variable flow conditions. The former Leona Heights Sulfur mine in Oakland, California produces acid mine drainage (AMD) that enters the Lion Creek watershed. These waters flow into the Lake Aliso reservoir, which is kept full during the dry summer months, thus contributing to the development of chemical gradients. Lake Aliso is drained during the wet winter months, allowing Lion Creek to flow freely across the lake bottom. The different flow regimes in Lake Aliso provide a wide range of geochemical conditions under which to study metal cycling in a single system.

Beginning in July 2009, monthly water samples were collected from Lion Creek and its two tributaries, Leona and Horseshoe Creeks, as well as from the inlet and outlet of Lake Aliso. Leona Creek is the source of AMD impacts within the watershed and Horseshoe Creek represents background watershed conditions. Lion Creek intergrades these two tributaries and discharges into Lake Aliso. Sediment cores collected from Lake Aliso provide a history of lake conditions and metals cycling.

Metals concentrations, including Pb, Cd, Fe, Ni, Cu, and Zn, in the AMD impacted Leona Creek tributary are significantly elevated above levels in the Horseshoe Creek tributary. After these tributaries mix in Lion Creek, measured concentrations of metals at the Lake Aliso inlet are lower than those measured in Leona Creek, due part to dilution by Horseshoe Creek waters. However, dilution alone cannot explain the reduction in metals concentration. Although all metal concentrations are lowered, only Cu (on most sampling dates), Fe, and Pb approach background levels. In addition, whether concentrations of metals at the Lake Aliso outlet are greater than or less than the lake inlet depends on whether the lake is full or empty, as well as the recent precipitation history. Depth profiles of lake temperature, pH, and dissolved oxygen suggest the chemical gradients that develop when the lake is full likely control the mobility of metals. Additionally, sediment cores from the lake exhibit fine scale (sub cm) oscillations in redox conditions.

Polar twins? Deglacial carbon and circulation records from the deep North Pacific and Southern oceans

J.W.B. RAE^{1*}, G.L. FOSTER², M. GUTJAHR¹,
M. SARNTHEIN³, L.C. SKINNER⁴, D.N. SCHMIDT¹
AND T. ELLIOTT¹

¹Bristol Isotope Group, Department of Earth Sciences,
University of Bristol, UK

(*correspondence: james.rae@bristol.ac.uk)

²School of Ocean and Earth Science, National Oceanography
Centre, University of Southampton, Southampton, UK

³Institut für Geowissenschaften, U. of Kiel, Kiel, Germany

⁴Godwin Laboratory, Department of Earth Sciences,
University of Cambridge, Downing St, Cambridge, UK

The cause of glacial – interglacial CO₂ transfer between the deep ocean and the atmosphere is one of the oldest puzzles in palaeoclimatology. The regularity of these cycles, and their strong coupling to a range of climate proxies, suggests a well-ordered set of controlling mechanisms [1]. The Southern Ocean is thought to play a key role by providing a (stemable) link for carbon and nutrients between the deep ocean and the atmosphere [2]. The North Pacific shares some of these nutrient and mixing characteristics; records from both locations may thus help us understand the fundamental processes driving glacial deep ocean CO₂ storage and release [3].

We present novel proxy data from the deep North Pacific and Southern oceans that provide new constraints on deep ocean chemistry and circulation changes during deglacial pCO₂ rise. Boron isotopes ($\delta^{11}\text{B}$) from benthic foraminifera are used to record the state of the deep ocean carbonate system, and are coupled with neodymium isotopes (ϵ_{Nd}) and benthic-planktic radiocarbon ($\Delta^{14}\text{C}$; [4]) to explore the influences of water mass mixing and ventilation age changes. Our $\delta^{11}\text{B}$ data show a pronounced pattern of millennial carbonate system variations that is consistent between two cores in the Southern Ocean and one in the North Pacific. In contrast, Southern Ocean ϵ_{Nd} shows a relatively smooth deglacial transition, suggesting that mixing of differently sourced water masses has minimal control on our millennial carbonate system variations. Rather, the $\delta^{11}\text{B}$ and $\Delta^{14}\text{C}$ data are best explained by increases in vertical mixing, consistent with the breakdown of glacial stratification in these high latitude oceans during the Heinrich Stadial 1 and Younger Dryas intervals of atmospheric CO₂ rise.

[1] Broecker & Henderson (1998) *Paleoceanogr.* **13**, 352–364. [2] Sigman *et al.* (2010) *Nature* **466**, 47–55. [3] Haug & Sigman. (2009) *Nature Geoscience* **2**, 91–92. [4] Gebhardt *et al.* (2008) *Paleoceanogr.* **23**, PA4212, 1–21.

Response of coralline alga *Lithothamnion glaciale* Kjellman to ocean acidification

F. RAGAZZOLA^{1*}, A. FORM¹, L. FOSTER², J. BÜSCHER¹,
T. HANSTEEN¹ AND J. FIETZKE¹

¹IFM-GEOMAR, Leibniz Institut für Meereswissenschaften
Wischhofstraße 1-3 , 24148 Kiel, Germany

(*correspondence: fragazzola@ifm-geomar.de)

²Dept. of Earth Sciences, University of Bristol, Wills
Memorial Building, Queen's Road, BS8 1RJ, UK

Since the industrial revolution, the partial pressure of carbon dioxide in the atmosphere has been rising. The increase of carbon dioxide in the atmosphere and the related uptake by the oceans [1] will result in a decrease in ocean pH by 0.2-0.4 units over the next century [2] and in a decline of calcium carbonate saturation states in the seawater surface. The potential for marine life to adapt to increasing CO₂ concentration are not well known, especially for the organisms living at high latitudes in waters which have naturally low saturation levels.

The effects of elevated pCO₂ were investigated in the high latitude coralline alga *L. glaciale*, an high Mg-Calcite calcifier. The algae were kept in the aquaria for 3 months at 8 ± 0.5 °C with 20 μmol photons m⁻² sec⁻¹ in 12 hours light/dark cycle at four different CO₂ concentrations: 410 ppm (control), 563 ppm, 838 ppm and 1120 ppm according to the IPCC prediction.

During this incubation period, *L. glaciale* showed a significant linear trend towards lower 'apical tip' growth rates (from 1.0 mm year⁻¹ to 0.8 mm year⁻¹) with increasing pCO₂ in the water. In water undersaturated with respect to aragonite (pCO₂ 1120 ppm- ΩAr = 0.9), the cell density of the newly grown thallus was 68 % less compared to the control together with a 56 % decrease in the cell walls thickness. Reduced growth rates and the weakening of the coralline thallus could have severe consequences for the biodiversity, growth and stabilization of carbonate reefs.

[1] Sabine *et al.* (2004) *Science* **305**, 367–371. [2] Caldeira & Wickett (2003) *Nature* **425**, 365.

Ba, Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ in Indian estuaries: Impact of submarine groundwater discharge

WALIUR RAHAMAN AND SUNIL K. SINGH

Physical Research Laboratory, Ahmedabad-380009, India
(waliur@prl.res.in, sunil@prl.res.in)

Dissolved Sr, Ba and $^{87}\text{Sr}/^{86}\text{Sr}$ were studied in three Indian estuaries linked to the Arabian Sea i.e. the Narmada, Tapi and the Mandovi. The concentration of dissolved Sr and Ba in the rivers show significant variations; ranges from 0.7-2.5 $\mu\text{mol}/\text{kg}$, 27-207 nmol/kg respectively whereas $^{87}\text{Sr}/^{86}\text{Sr}$ vary between 0.70875 and 0.71062 reflecting the lithologies they drain. The Sr/salinity profile in all these estuaries shows conservative mixing between river water and seawater end members whereas Ba shows nonconservative mixing with its gain in mid salinity region (10-15‰). The $^{87}\text{Sr}/^{86}\text{Sr}$ shows non-conservative behaviour; its distribution exhibits significant departures from the expected conservative mixing lines in all these estuaries. This difference in the behaviour between dissolved Sr and its $^{87}\text{Sr}/^{86}\text{Sr}$ is intriguing and suggests that there is supply of Sr from additional sources to these estuaries. Similarly, Ba gain could not be explained by Ba release from particles in the estuaries and river-seawater mixing and requires its additional source. The additional source seems to be submarine groundwater discharge (SGD). The non-conservative behaviour of $^{87}\text{Sr}/^{86}\text{Sr}$ provides a handle to estimate the quantum of SGD to these estuaries. Inverse model calculations have been used to characterize the Sr concentration, $^{87}\text{Sr}/^{86}\text{Sr}$ and salinity of the SGD and estimate its water fluxes to the Narmada estuary. The model derived SGD flow rates to the Narmada estuary are ~ 7 and 275 cm/day during nonmonsoon and monsoon respectively indicating large seasonal variability of SGD. This estimate is consistent with those reported from the south-west coast of India using dissolved ^{222}Rn [1] and other coastal regions of the world [2].

[1] Jacob *et al.* (2009) *Curr. Sci.* **97**, 1313–1320. [2] Burnett *et al.* (2003) *Spec Issue, Biogeochemistry* **66**, 202.

Constraints on the formation of a lunar core from metal-silicate partitioning of siderophile elements

NACHIKETA RAI AND WIM VAN WESTRENE

Faculty of Earth and Life Sciences, VU University
Amsterdam, The Netherlands (nachiketa.rai@falw.vu.nl)

Most models for the interior of the Moon include a small iron-rich core with a maximum diameter of several 100 km [1], but the composition and formation conditions of the lunar core are poorly constrained. One major consequence of core-mantle differentiation in planetary bodies is that the majority of the siderophile elements are strongly partitioned into the iron-rich core. Since the degree of extraction of these elements into the metallic phases is governed according to their metal/silicate partition coefficients (D) and the pressure-temperature-composition conditions during core formation, abundances of these elements in the silicate Moon can in principle be used to constrain lunar core formation and chemistry.

Estimates of siderophile element abundances in the lunar mantle have previously been used to argue for the presence of a small metallic core (0.1-5.5 wt%) [2-4], but recent improved approaches to terrestrial core formation models (including better thermodynamic models and the ability to model changing conditions through time) have not yet been applied to the Moon.

Here we re-examine whether a consistent set of conditions can be obtained to match observed siderophile element depletions in the silicate Moon. We combine new metal-silicate partitioning data for Ni, Co, Cr, Mn, Ga, P, Pb, W and V with literature data and characterize the dependence of the partition coefficients on temperature, pressure, oxygen fugacity and silicate melt structure and composition to derive equations of the following form: $\log D = \alpha + \beta (\Delta T) + \delta (1/T) + \epsilon (P/T) + \chi (\text{nbo}/t)$.

Initial results suggest that when using the proposed bulk Moon composition of [5] and siderophile element abundances from [6], data are consistent with the Moon possessing a small metallic core, with metal-silicate equilibration pressures close to the current core-mantle boundary, consistent with whole-Moon melting at the time of core formation.

[1] Weber *et al.* (2011) *Science* **331**, 309–312. [2] Righter & Drake (1996) *Icarus* **124**, 513–529. [3] O'Neill (1991) *GCA* **55**, 1135–1157. [4] Walter *et al.* (2000) In *Origin of the Earth & Moon*, U of A Press, Tucson, pp.265–289.

Geochemical and isotopic composition of quartzites near the MCT zone (Garhwal Himalaya, India): Implications to their provenance & deposition

SANTOSH K. RAI¹, SUNIL K. SINGH² AND H. K. SACHAN¹

¹Wadia Institute of Himalayan Geology, Dehradun (India)
(rksant@wihg.res.in, hksachan@wihg.res.in)

²Physical Research Laboratory, Navrangpura, Ahmedabad
(sunil@prl.res.in)

Quartzites are one of the major clastic sedimentary rocks in the Himalaya that had deposited in the Tethys Ocean basin and exhibit varying chemical composition, protoliths, age (pre-Himalaya) and depositional settings [1, 2, 3]. In this study, geochemical and isotopic composition were determined in the quartzite samples collected from the either side of MCT zone of the Garhwal Himalaya to determine their provenances and nature of the protoliths.

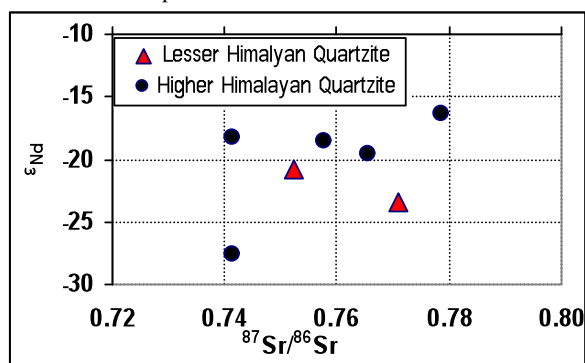


Figure 1: $^{87}\text{Sr}/^{86}\text{Sr}$ & ϵ_{Nd} of the Himalayan Quartzites near the MCT zone of the Garhwal Himalaya (India).

Major elements data of the Lesser Himalayan quartzites (Kaliasaud-Alaknanda region) demonstrate significant difference from those of the Higher Himalaya. For example, $\text{TiO}_2/\text{SiO}_2$, $\text{Al}_2\text{O}_3/\text{SiO}_2$, $\text{Fe}_2\text{O}_3/\text{SiO}_2$ are one to two order of magnitude higher for Higher Himalayan quartzites compared to those from the Lesser Himalaya. These differences could be related either to source variability or to mineralogical sorting during their weathering, transport and deposition. The limited samples measured in this study indicate overlapping Sr and Nd isotope composition between Higher (ϵ_{Nd} -16.5 to -27.7; $^{87}\text{Sr}/^{86}\text{Sr}$ 0.7414-0.7788) and the Lesser (ϵ_{Nd} -20.8 to -23.5; $^{87}\text{Sr}/^{86}\text{Sr}$ 0.7524-0.7714) Himalayan quartzites making it difficult to differentiate their sources. More work is underway to generate larger data set to study their protoliths.

[1] Ahmad, *et al.* (2000) *Geol. Soc. Am. Bull.* **112**, 467–477.

[2] Spencer, *et al.* (2011) *JAES* (in press). [3] Jain A.K. (1972) *Journ. Sed. Petrol.* **42**(4), 941–960.

Heat flow in the laser-heated diamond anvil cell and the thermal conductivity of the lower mantle

E.S. G. RAINEY^{1*}, A. KAVNER¹ AND J. HERNLUND²

¹Department of Earth and Space Sciences, University of California Los Angeles, Los Angeles, CA 90095

(*correspondence: erainey@ucla.edu)

²Department of Earth and Planetary Science, University of California Berkeley, Berkeley, CA 94720

The thermal conductivity of the lower mantle is a critical parameter for understanding the current heat budget and thermal evolution of the Earth. However, thermal conductivity measurements at high pressure and temperature are difficult due to the small sample volumes and large temperature gradients characteristic of the laser-heated diamond anvil cell (LHDAC) [1]. Temperature distributions in the LHDAC are determined by laser and sample geometry as well as physical properties such as sample absorbance and thermal conductivity [2]. During heating experiments, precise measurements of peak sample temperatures and 2-D hotspot intensity gradients can be made [3]. In order to infer physical properties of a sample using measured temperature distributions in the LHDAC, a quantitative understanding of heat flow in the LHDAC is needed.

We have developed a 3-D numerical model of steady-state heat conduction for continuous heating experiments in the LHDAC. The numerical model has been benchmarked against an existing 2-D analytic solution [2], yielding agreement in predictions of temperature distributions as a function of input laser power, sample geometry, and sample thermal conductivity. Model calculations show that peak temperature and hotspot width are strongly correlated and dependent on laser power, laser and sample geometry, and sample thermal conductivity. The rate of change of the peak temperature and hotspot width as a function of input laser power is especially dependent on sample thermal conductivity, all other variables being equal.

[1] Benedetti & Loubeyre (2004) *High Pressure Res.* **24**, 423–

445. [2] Panero & Jeanloz (2001) *J. Geophys. Res.* **106**, 6493–

6498. [3] Kavner & Nugent (2008) *Rev. Sci. Instr.* **79**, 024902.

***In situ* U-Pb dating of scheelite: Constraints on the age and genesis of the Felbertal tungsten deposit**

J.G. RAITH^{1*}, A. GERDES² AND D.H. CORNELL³

¹Chair of Resource Mineralogy, Montanuniversitaet Leoben, 8700 Leoben, Austria

(*correspondence: johann.raith@unileoben.ac.at)

²Institut für Geowissenschaften, Goethe Universität Frankfurt (gerdes@em.uni-frankfurt.de)

³Geovetarcentrum, Gothenburg Sweden (cornell@gvc.gu.se)

The Felbertal scheelite deposit, Salzburg province, Austria, is one of the biggest tungsten producers in the world. It has long been regarded as the type locality of stratiform-stratabound scheelite deposits. The deposit is situated in the Habach Complex, an Early Cambrian to Ordovician metavolcano-sedimentary ophiolitic to arc sequence. A chemically unusual W-bearing granite, the K1 orthogneiss, was emplaced in the Early Carboniferous into the western ore zone of the deposit. Several economic scheelite ore bodies are spatially associated with this orthogneiss. The ore deposit was overprinted during the Variscan (~330 Ma) and Alpine (~30 Ma) orogenies. Economic scheelite mineralisation is associated with SiO₂-rich lithologies including foliated fine-grained scheelite-quartz ores ('Scheelite-rich quartzite'), deformed quartz veins and stockwork like mineralisation. Trace element analyses using LA-ICP-MS techniques, controlled by cathodoluminescence (CL) images, confirmed the previously established classification of scheelite stages. Scheelite 1 is preserved as relict cores in fine-grained scheelite in the mylonitic scheelite-quartz ores. It preserves delicate oscillatory growth zoning, is characterised by flat wing-shaped REE patterns, and contains between 50 to 1120 ppm U. *In situ* U-Pb dating by LA-SF-ICP-MS of Scheelite 1 yielded a concordia age of 335.5 ± 4.6 (2 sigma). This new age constrains the timing of scheelite formation of this ore type for which a Cambrian age was previously assumed [1]. Within the uncertainty this new age is indistinguishable from the published 336 ± 19 Ma emplacement age of the K1 orthogneiss. The new scheelite age is inconsistent with previous genetic models, which proposed either syngenetic ore formation in the Cambrian or two stages of epigenetic ore formation, the first in the Cambrian and the second in the Early Carboniferous [1]. The Felbertal scheelite deposit is best interpreted as a metamorphosed granite-related magmatic-hydrothermal ore deposit of exclusively Early Carboniferous age.

[1] Eichhorn *et al.* (1999) *Int. J. Earth Sci.* **88**, 496–512.

Geochemical and mineralogical features of coal combustion wastes (CCW) of Angren Thermal Power Station (TPS) and possible ways of their recycling, Uzbekistan

SH.SH. RAKHMOKULOV A.* AND N.E. SHUKUROV

Institute of Geology and Geophysics Academy of Science of Uzbekistan, 49, Khodjibaeva Str. Tashkent, 100041, Republic of Uzbekistan

(*correspondence: rshakhnoza@yahoo.com)

The Angren TPS working on the basis of Angren lignite was found in 1958, during this 53 years functioning were generated 13 million tons of CCW and disposed in 3 coal ash dumps (203 acre). The physical and chemical characteristics of CCW have bearing on both its potential for use and its potential to present some level of risk to human health and the environment. Elemental and mineralogical content of samples from Angren CCW were checked by XRF and JEOL Superprobe microzond. The results of chemical and mineralogical analyses showed high content of metals and minerals with magnetic features (magnetite, haematite, titanomagnetite etc.), concentration of trace elements, as well as rare- earth elements etc. were elevated also. Subsamples were subjected to magnetic separation, results show that content of minerals with ferromagnetic feature is 65% of total mass. Investigations under the JEOL microanalyzer show that in spherical magnetic aggregates are containing Fe, Ti, Mn and W in high value.

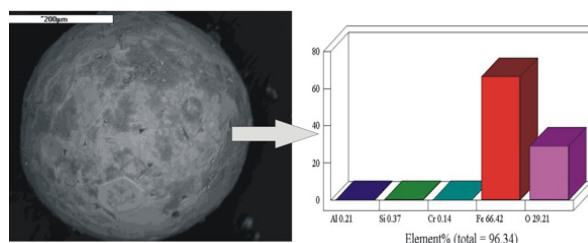


Figure 1: SEM image of magnetic particle and distribution ratio some magnetic elements.

High concentration of Fe and Mn in studied CCW samples showing their effective utilization and bright perspective for using as a raw material for producing several kinds of Ferroalloy for metallurgical industry.

Magnetic resonance imaging of pollutant mass transport in biofilms

B. RAMANAN^{1,2,3}, W.M. HOLMES², W.T. SLOAN³
AND V.R. PHOENIX^{1*}

¹School of Geographical and Earth Sciences, University of Glasgow, G12 8QQ, UK

(*correspondence: vernon.phoenix@glasgow.ac.uk)

²GEMRIC, Wellcome Surgical Institute, University of Glasgow (william.holmes@glasgow.ac.uk)

³School of Engineering, University of Glasgow (william.sloan@glasgow.ac.uk)

Introduction

Biofilms play a key role in immobilizing and degrading pollutants in both natural and engineered systems. Quantifying the mass transport of these pollutants in biofilms is critical for effective modelling of biofilm performance. Thus methods are needed which spatially image pollutant transport in a non-invasive manner. However, imaging inside biofilms thicker than several hundreds of microns becomes challenging for photon based methods such as CLSM due to attenuation of photon penetration and the fluorescent signal. These thicker biofilms, however, are by no means rare. For these, such as phototrophic biofilms in natural systems and those in granular waste-water treatment systems, alternative imaging methods must be sought.

Results and Discussion.

Here we report the use of Magnetic Resonance Imaging (MRI) for structural and mass transport imaging in a 2.5 mm thick phototrophic biofilm using a small (5 mm diameter), simple-to-construct RF coil. Notably, the RF coil is also far less expensive than similar commercially available coils.

Gd [DTPA] (molecular mass 547 g/mol) was chosen as a surrogate for an organic contaminant; the paramagnetic Gd making the molecule visible to MRI. The transport of Gd [DTPA] through the biofilm was imaged by acquiring a series of T_2 weighted images (T_2 being the spin-spin relaxation rate of ^1H nuclei in the water surrounding the Gd [DTPA]). Because T_2 is inversely proportional to the concentration of Gd [DTPA], fully quantitative maps of Gd [DTPA] transport inside the biofilm were constructed. MRI was also used to image structural heterogeneity and water diffusion within the biofilm. Biofilm structure, water diffusivity and Gd [DTPA] transport were clearly correlated. MRI is a valuable tool for imaging pollutant transport and fate in biofilms too thick for photon based imaging methods.

$\text{Au}_3(\text{Pb,Sb})_4$ mineral phase from Tetrem gold deposits, Ghana, West Africa

R.P. RAMDOHR¹ AND T.L. EVSTIGNEEVA²

¹High River Gold Exploration Burkina SARL 01 BP 4418

Ouagadougou Burkina Faso (reinramdohr@yahoo.com)

²IGEM RAS, 35, Satromonetny, 119017, Moscou, RF (evst@igem.ru)

The new Au-mineral phase with the composition $\sim\text{Au}_6\text{Pb}_5\text{Sb}_3$ [$\text{Au}_3(\text{Pb}, \text{Sb})_4$] and parameters (Å) of tetragonal cell $a=8.401$ (2), $c=8.239$ (1) is found in the gold deposit Tetrem, SW Ghana, Tarkwa area. The orebodies consist of a series of sedimentary Banket quartz reef conglomerates similar to those in the Witwatersrand Basin. Gold mineralization in Tetrem deposits is located in quartz veins, and appears to have formed during Eburnean II (2, 116-2, 080 Ma) within shear and fault networks developed during contraction deformation.

Gold minerals occur as free particles with an average size of 50-150 μm . The main gold mineral is native gold. There are only minor electrum and Au with 3-7% Ag. Gold is associated with sulphides: pyrite, sphalerite, galena, chalcopyrite, arsenopyrite, pyrrhotite, and molybdenite. Accessory oxides in the ore are magnetite, goethite, ilmenite, and rutile. The mineral proportions vary in gold occurrences of the area. Ore minerals occur in silicified and albitized (?) granite cut by numerous quartz veins and stringers.

The mineral $\text{Au}_6\text{Pb}_5\text{Sb}_3$ was found in quartz veins in association with: free gold containing up to 7.2 Wt% Ag, and up to 5.7 Wt% Hg, and hunchunite, Au_2Pb . Native Au in the sample contain also tiny, <5-10 μm grains of aurostibite, and altaite.

Data of study obtained using MRSA, SEM+EDD, and XRDA. show that by composition, physical properties, and crystallochemical characteristics $\text{Au}_6\text{Pb}_5\text{Sb}_3$ differs from other natural compounds of gold with metals and 'semi-metals': Au and Au-Ag tellurides; aurostibite, AuSb_2 ; maldonite, Au_2Bi ; hunchunite, Au_2Pb ; anyuinite, AuPb_2 ; and yuanjiangite, AuSn .

$\text{Au}_6\text{Pb}_5\text{Sb}_3$ analogue has been synthesized from the melt in multi-component Ag-Pb-Bi-Sb system for detail study of mineral properties and associations.

Financial support of Fundamental Researches Program n.5 of Dept.Earth.Sci. of Russian Academie of Sciences.

[1] Evstigneeva *et al.* http://geo.web.ru/conf/khitarjada/1-2003/informbul-1_2003/mineral-14e.pdf

Petrography and chemistry of zircons from the Chaltén Plutonic Complex and implication on the interpretation of U-Pb zircon ages

CRISTÓBAL RAMÍREZ DE ARELLANO¹,
BENITA PUTLITZ¹, OTHMAR MÜNTENER¹
AND MARÍA OVTCHAROVA²

¹Institute of Mineralogy and Geochemistry, University of
Lausanne, Switzerland. (ramirez.andes@gmail.com)

²Department of Mineralogy, University of Geneva,
Switzerland

The absolute geochronology of the Chaltén Plutonic Complex (CHPC), located in the Southernmost Andes, has a strong influence on the geodynamic interpretation of Patagonia. In addition, the textural and chemical features of zircons from the different plutonic units of this composite intrusion provide important constraints for understanding the growth of zircons in magmas with variable degree of differentiation. These features should be taken into account for the interpretation of zircon ages, since increasing precision of ages is obtained thanks to the development of the U-Pb CA-TIMS dating techniques during the last decades.

The CHPC is a calc-alkaline (arc related) intrusion, which was emplaced at upper crustal levels (3.5 to 2 kbar). The zircon ages (16.90 ± 0.05 to 16.37 ± 0.02 Ma) are consistent with the relative geochronology inferred from field relationships. Where undulated ductile contacts are observed, the age difference cannot be resolved. In the case of brecciated contacts a minimum age difference of 80ky was obtained, which is at the limit of the obtained precision (± 40 ky).

The petrographic textures of zircons from mafic rocks indicate crystallization in isolated pockets, i.e. interstitial. The application of the Ti-in-zircon thermometer yield consistently low temperatures ($\sim 760^\circ\text{C}$). This indicates that most zircons from these samples might have crystallize near solidus temperatures and consequently post-date the emplacement. In contrast, the textures of zircons from granitic rocks indicate a more protracted crystallization. The chemistry (LA-ICP-MS analysis) of zircons from granitic rocks displays systematic variation of U/Th and U/Ta ratios between core and rim. This pattern can be correlated with the observed variations of calculated temperatures and $\text{Ce}^{\text{III}}/\text{Ce}^{\text{IV}}$ ratios. These features suggest that in granitic melts there could be several episodes of zircon crystallization at different temperatures. These temperatures are 100° to 200° higher than the solidus, which implies that many zircons might have crystallize prior to the emplacement (antecryst).

Predicting the character of future eruptions: Insights from single crystal analyses

F.C. RAMOS^{1*}, J.B. GILL², J.A. WOLFF³, C.A. DIMOND¹
AND D.L. TOLLSTRUP⁴

¹Dept. of Geological Sciences, New Mexico State University,
Las Cruces, NM, 88003, USA

(*correspondence: f Ramos@nmsu.edu)

²Dept. of Earth and Marine Sciences, UC Santa Cruz, Santa
Cruz, CA, 95064, USA

³School of Earth and Environmental Sciences, Washington
State University, Pullman, WA, 99164, USA

⁴Thermo Fisher Scientific, 1400 N. Pointe PWKY, West Palm
Beach, FL, 33407, USA

While the science of predicting volcanic eruptions is becoming a viable practice, few constraints exist as to the chemical nature of future eruptions, especially regarding the composition and character of the magma or magmas to be erupted. Usually compositional assessments can only be undertaken post-eruption. However, volcanoes characterized by a variety of volcanic products (i.e. a variety of erupted rock compositions) that erupt in short geological time periods (e.g. <10 ky), may allow for assessing magma composition/character prior to when an eruption actually occurs. Baitoushan volcano, located along the China/North Korean border, is known for the largest rhyolitic, caldera forming eruption in the last 2000 years and has shown signs of recent seismic activity. Baitoushan is characterized by at least three recent eruptions (<5000 ka) involving at least four distinctive highly evolved magma compositions. Following a detailed approach involving Sr and Pb isotopes of single mineral crystals, we have identified specific mineral populations that cannot have originated from host magmas, but rather, must have originated from magmas seen only in later eruptions. These populations become more common in subsequent eruptions until they become the dominant mineral population in the latest-erupted magmas. Results suggest the presence of crystals in older erupted materials up to 5000 years prior to eruptions where these crystals are the dominant population. Results are consistent with a magma residence age of ~ 10 ky and document the first time in which crystals associated with future magmatic activity are observed in materials from earlier eruptions. In addition, isotope variations in selected crystals suggest open system processes occurring ~ 3000 years prior to eruption in highly viscous, high-silica rhyolites. Ultimately, detailed crystal evaluations offer compositional constraints of magmas resident under volcanoes 1000s of years prior to their eventual eruption.

Li-O-Pb-Nd-Hf isotope and trace element systematics and S in residual peridotites: Evidences for ancient hydrothermal fluid-rock interactions at mid-ocean ridges

L.V. RANAWEERA, T. MORIGUTI, R. TANAKA, A. MAKISHIMA AND E. NAKAMURA*

The Pheasant Memorial Laboratory (PML), Institute for Study of the Earth's Interior, Okayama University at Misasa, Tottori-Ken, 682-0193, Japan
(*correspondence: eizonak@misasa.okayama-u.ac.jp)

Massive plagioclase lherzolite (MSPL) from the Horoman orogenic massif, Japan, which formed at ~ 1 Ga at a mid-ocean ridge (MOR), represents the most unradiogenic Pb reservoir ever found in the mantle [1]. New data for O and Li isotopes of these MSPL combined with previously published trace element, S contents, and Pb, Nd and Hf isotope data reveal evidences for ancient hydrothermal fluid-rock interaction (HFRI) at mid-ocean ridges.

The trace element patterns of MSPL show element enrichment and depletion in variably melt extracted residues. They show 2-43 times lower U/Pb and 3-11 times lower Ce/Pb than those of the depleted MORB mantle or DMM indicating Pb enrichment. Several MSPLs show bulk rock S elemental abundance (146-273 ppm) higher than those of the DMM (116 ppm) and primitive mantle (250 ppm) also suggesting S enrichment. In addition, S positively correlates with Pb. $\delta^{18}\text{O}$ (5.11-5.49 ‰) and $\delta^7\text{Li}$ (-0.83-3.96 ‰) compositions of MSPL suggest a mixing between DMM and a light Li and O isotope source. These oxygen isotope values negatively and positively correlate with age corrected Pb and Nd and Hf, respectively at ~ 1 Ga.

The correlation in O-Li isotope system indicates hydrothermal fluid and MSPL interaction. Hydrothermal fluids can react with residual peridotites at MORs giving rise to sulfide which can sequester Pb and increase S. The correlation of O with Pb, Nd and Hf indicates that HFRI of MSPLs occurring around 1 Ga. Thus, our data reveal evidences for hydrothermal fluid alteration of peridotites occurred at ancient time at MORs and account for origin of highly unradiogenic Pb reservoirs in the mantle.

[1] Malaviarachchi *et al.* (2008) *Nature Geosci.* **1**, 859-863.

Variation in contribution of Bay of Bengal moisture source derived from stable isotopic composition of cave carbonates in Meghalaya, India

R. RANGARAJAN¹, J. ROUTH², P. GHOSH¹, A. MANGINI³, J. FOHLMEISTER³, S. BASKAR⁴, R. BASKAR⁴ AND S. HOLZKÄMPER⁵

¹Center for Earth Sciences, IISc, India

(ravi@ceas.iisc.ernet.in. pghosh@ceas.iisc.ernet.in)

²Department of Earth Sciences, IISER, India

³Heidelberger Akademie der Wissenschaften, Germany

⁴Guru Jambheshwar University, India

⁵Johannes Gutenberg University Mainz, Germany

Stable isotope (SI) ratio of calcites in stalagmite samples collected from 3 different caves in the Jaintia (Krem Syndai and Rupasor; N25°09' and E92°00') and Khasi Hills (Krem Mawmluh; N25°20' and E42°45') of Meghalaya in northeast Himalayas reveals change in rainfall intensity during the last 21 ka BP. Analysis of stalagmite collected from Mawmluh Cave (6.95 – 21.6 ± 0.5 ka) revealed signature of the glacial maxima registered as an abrupt drop in $\delta^{18}\text{O}$ values by $\sim 7\text{‰}$. This is the first observation documenting large variability in isotopic ratio. The Syndai stalagmite (1.8 ± 0.05 ka – 4.69 ± 0.15 ka) captures climatic amelioration across 2.5 to 5 ka. The actively growing Rupasor stalagmite covers the period 0.42 ± 0.14 ka – 2.5 ± 0.03 ka. The late Holocene events, like the Medieval Warm Period (MWP) and Little Ice Age (LIA) have also been captured. Comparing the seasonal variability of present day average rainwater SI record from the Shillong region and wind speed observation from the nearest meteorological observatory allows defining an empirical relationship for predicting the contribution of BoB moisture. The estimates suggests more than 60% drop in the Wind speed (WS) vector corresponding to the $\sim 7\text{‰}$ difference observed between glacial and non-glacial times.

Geospeedometry applied to El'gygytgyn impact glass

U. RANTZSCH^{1*}, T. HABER¹, D. KLIMM² AND G. KLOESS¹

¹Institute for Mineralogy, Crystallography and Materials Science, University of Leipzig, Germany

(*correspondence: rantzsch@uni-leipzig.de)

²Leibniz Institute for Crystal Growth, Berlin, Germany

The El'gygytgyn impact glass has been investigated with the method of relaxation geospeedometry. The sibirian impactite was found in the 3.6 Myr old El'gygytgyn impact structure in lacustrine terraces.

The aim of this research was to determine the natural cooling rate of the El'gygytgyn rhyolitic glass (71.3 % SiO₂, 14.9 % Al₂O₃, 4.1 % K₂O, 2.8 % CaO, 2.8 % Na₂O₃, 2.7 % FeO, 1.1 % MgO, 0.3 % TiO₂, in wt-% by 20 EMPA analysis).

The method of geospeedometry based on the structural relaxation in silicate melts was first applied to natural glasses by [1]. The procedure is referred to the Tool-Narayanaswamy approach [2]. The cooling history of the impactite is frozen in its structure. The temperature-dependent reheating across the glass transformation was used to obtain the original cooling history. The relaxation of the enthalpy was achieved by measurements of the heat capacity.

Therefore, differential scanning calorimetry (DSC) measurements with certain heating and cooling rates were performed. The impact glass was heated above the glass transition (T_g) to ensure the complete relaxation of the glass structure. Thereupon, the kinetic parameters were adjusted for each thermal cycle.

We can deduce that the cooling rate for the impact glass is between 0.15-0.85 K/min. The cooling rate is comparable to the data determined for phonolite obsidian flows on Tenerife [3] but significantly slower than for tektites reported in literature. Hence, we present that the final cooling of the El'gygytgyn impact glass originated within the hot impact structure.

[1] Wilding, M.C. Webb, S.L. Dingwell, D.B. (1995) *Chem. Geol.* **125**, 137–148. [2] Narayanaswamy, O.S. (1971) *J. Am. Ceram. Soc.* **54**, 491–498. [3] Gottsmann, J. Dingwell, D. B. (2001) *J. Volcanol. Geotherm. Res.* **105**, 323–342.

The influence of physically-induced porewater advection, benthic photosynthesis and respiration on CaCO₃ dynamics in reef sands

ALEXANDRA RAO^{1,2,3*}, LUBOS POLERECKY³, DANNY IONESCU³, FILIP MEYSMAN^{1,2} AND DIRK DE BEER³

¹Laboratory of Analytical and Environmental Chemistry, Earth System Science Research Unit, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium

²Centre for Estuarine and Marine Ecology, Netherlands Institute of Ecology, PO Box 140, 4400 AC Yerseke, The Netherlands (*correspondence: a.rao@nioo.knaw.nl)

³Microsensor Group, Max Planck Institute for Marine Microbiology, Celsiusstr. 1, 28359 Bremen, Germany

Reduced net calcification owing to increasing pCO₂ from the burning of fossil fuels suggests a potential reduction in carbonate accumulation in continental margins, where a large fraction of global carbonate accumulation occurs. This feedback in the ocean carbonate cycle lends particular importance to understanding the factors controlling carbonate accumulation and dissolution in coastal and shelf deposits. Permeable biogenic carbonate sediments in reef environments are poised to play a crucial role in the response of ocean margin environments to ocean acidification, because of the interplay between porewater exchange, benthic community metabolism and CaCO₃ dynamics in these deposits.

Sediment oxygen consumption rates, porewater profiles and benthic fluxes of oxygen, pH, calcium, alkalinity, and dissolved inorganic carbon were determined in reef sands (Heron Island, Australia) of different permeability across a range of hydrodynamic conditions. In these biogenic deposits, porewater advection and light stimulate rates of benthic photosynthesis, which, in turn, fuels calcification in surface sediments. Furthermore, our results indicate an important damping effect of porewater advection on the efficiency of respiration-driven carbonate dissolution in sediments. Therefore, we argue that the synergistic effects of porewater advection, benthic respiration, photosynthesis, calcification and carbonate dissolution promote carbonate preservation in permeable ocean margin deposits, and have a direct bearing on past, present and future changes in the ocean carbonate cycle.

The impact of sea level rise on salt water intrusion into coastal aquifers

JOHN RAPAGLIA¹, HENRY BOKUNIEWICZ²,
ATHANASIOS VAFEIDIS³ AND TSVI PICK⁴

¹The Future Ocean Excellence Cluster, Institute of Geography,
Christian Albrechts University, Kiel, Germany 24098
(rapaglia@geographie.uni-kiel.de)

²School of Marine and Atmospheric Science, Stony Brook
University, Stony Brook, NY 11794
(hbokuniewicz@notes.cc.sunysb.edu)

³The Future Ocean Excellence Cluster, Institute of Geography,
Christian Albrechts University, Kiel, Germany 24098
(vafeidis@geographie.uni-kiel.de)

⁴School of Marine and Atmospheric Science, Stony Brook
University, Stony Brook, NY 11794
(tpick@ic.sunysb.edu)

According to the IPCC (2007) sea level rise is one of the more certain consequences of climate change. Salt water intrusion into coastal aquifers is an important impact of sea level rise, which has received some attention among the coastal scientific community in recent years (e.g. [1]).

Several studies have produced global scale salt water intrusion maps, both these maps are at a coarse spatial resolution, which limits their use. We contend that there remains a need to investigate how future changes in climate will affect freshwater-seawater interactions in coastal aquifers both in terms of seawater intrusion as well as groundwater discharge.

We present a first order, global model intended to predict change in the salt water intrusion length into coastal aquifers under different sea level rise scenarios. Forecasts are made up to a pixel resolution of 30 arc-seconds. This model is based on existing sea level rise scenarios, the Bruun Rule and assumptions concerning the relation between surface topology and the hydraulic head which is expected to be a function of aquifer recharge and public consumption. Saltwater intrusion lengths in water stressed areas are likely to increase with sea level rise but that the effect of changing consumption rates due to population change is often greater than the effect of sea level rise alone.

Several limitations remain regarding the utility of the analysis based on data quality; however the model remains a useful first step towards understanding future salt water intrusion at a global level.

[1] Döll, P. (2009) Vulnerability to the impact of climate change on renewable groundwater resources: a global-scale assessment. *Environmental Research Letters* 4(3), 12pp.

Exploring geoengineering using climate and detailed modelling strategies

PHILIP J. RASCH*, HAILONG WANG, JIN-HO YOON,
DILIP GANGULY, PO-LUN MA AND VINOJ VELU

Pacific Northwest National Laboratory (PNNL)

(*correspondence: philip.rasch@pnl.gov)

Geoengineering (the deliberate perturbation of the planet to counteract some of the effects of increasing CO₂ concentrations) has received increasing attention in scientific and policy communities due to concern about the difficulty of transforming the planet's energy infrastructure and the scientific consensus that reductions in emissions must take place soon to avoid the risk of undesirable impacts and dangerous climate change. Due to the difficulty of energy transformation, societies have been slow to respond, in spite of the risks.

As a stopgap measure, a number of geoengineering strategies have been suggested that introduce aerosols into the atmosphere to increase the planetary albedo, or to reduce the opacity of the atmosphere to longwave energy to cool the planet. The conflation of aerosols, energy, and climate make these strategies a natural topic for this Goldschmidt session. I will describe some modeling studies that explore three geoengineering strategies: 1) introducing sources of stratospheric aerosols; 2) introducing sea salt aerosols to brighten marine stratocumulus clouds; 3) introducing aerosols that act as ice nuclei to reduce the opacity of cirrus clouds.

Geoengineering is complex, and it is important to consider a variety of issues in considering this topic:

1. What are the consequences of particular geoengineering strategies to climate, ecosystems, and society?
2. How do these geoengineering strategies compare to each other?
3. How well do we understand the fundamental physics and chemistry of the processes employed by each strategy? Are climate models providing an adequate representation of these processes so that they may be used for studying geoengineering consequences?

Climate models can be used to explore the planetary response to geoengineering. Process models can be used to better understand the fundamental physics and chemistry that the strategies depend upon. I will describe a number of studies performed by our group using both types of models and identify some of the remaining challenges.

Secondary origin for 'primary' mineral inclusions in detrital zircons from Jack Hills, Western Australia

B. RASMUSSEN^{1*}, I.R. FLETCHER¹, J.R. MUHLING²,
C.J. GREGORY¹ AND S.A.W. WILDE¹

¹Dept Applied Geology, Curtin Univ., Bentley, 6102, Australia (*correspondence: B.Rasmussen@curtin.edu.au, I.Fletcher@curtin.edu.au, C.Gregory@curtin.edu.au, S.Wilde@curtin.edu.au)

²CMCA, Univ. Western Australia, Crawley, 6009, Australia (janet.muhring@uwa.edu.au)

The Hadean crust has long been regarded to comprise mainly primitive mafic and ultramafic rocks. However, detrital zircons up to 4.4 Ga from Jack Hills, Australia, have been used to infer the existence of extensive granitic crust during the Hadean. Mineral inclusions in these zircons have been interpreted to be primary and magmatic, and therefore to provide important clues about the chemistry of the early crust.

In situ U-Pb dating of monazite and xenotime inclusions in detrital zircon grains from Jack Hills, shows that the inclusions are much younger than their zircon host, and formed during episodes of regional metamorphism at 2.68 Ga or 0.8 Ga. Monazite-xenotime thermometry of intergrowths in the inclusions and the quartz-muscovite rock matrix constrain temperatures to ~450°C, corresponding with conditions during peak metamorphism. Evidence from inclusions in zircon from other localities indicates that the replacement of primary inclusions may commence in the granite host-rock and continue after deposition through to high-grade metamorphism. In metasedimentary rocks, the inclusion assemblage in detrital zircon may increasingly resemble the composition of the rock matrix. In Jack Hills, the most abundant minerals filling inclusions are also the main matrix minerals (quartz and muscovite), consistent with their formation during metamorphism.

Our results show that detrital zircon is not impermeable to post-depositional fluids. We suggest that many of the primary inclusions were replaced by secondary minerals during metamorphism, raising doubts about the use of mineral inclusions in zircon to infer magma chemistry.

Integrating climate and landscape controls on regolith depth, chemistry and mineral assemblage

CRAIG RASMUSSEN^{1*}, REBECCA LYBRAND¹,
ANGIE JARDINE², JON PELLETIER³, PETER TROCH²
AND JON CHOROVER¹

¹Dept. of Soil, Water, and Environmental Science, Univ. of Arizona, AZ-85721, USA

(*correspondence: crasmuss@cals.arizona.edu)

²Dept. of Hydrology and Water Resources, Univ. of Arizona, AZ-85721, USA

³Dept. of Geosciences, Univ. of Arizona, AZ-85721, USA.

Linkages among climate, erosion and mineral weathering are central to pedogenesis and critical zone evolution. We approach these linkages through synthesis of climate, erosion and regolith geochemical data for upland terrain, coupled with detailed studies on climate and landscape position controls on pedon-scale regolith weathering patterns across the steep semiarid climate gradient encompassed by the Santa Catalina Mountain (SCM) Critical Zone Observatory in southern Arizona, USA. Climate forcing was quantified in terms of effective energy and mass transfer (*EEMT*), that includes energy flux to the subsurface critical zone in the form of primary production and effective precipitation, whereas chemical depletion and mineral transformation were quantified using a combination of geochemical, isotopic and mineralogical analyses. The regional synthesis indicated regolith chemical depletion increased exponentially with water availability and *EEMT* for sites with annual temperature greater than 5°C and erosion rates greater than 10 g/m²/yr, suggesting first order control of climate on chemical depletion, and second order control of temperature and erosion. SCM geochemical and mineralogical data indicated strong linkages among *EEMT*, physical erosion, regolith depth, chemical depletion and mineral assemblage. Specifically, divergent landscape positions demonstrated a pattern similar to that in the regional synthesis of increasing chemical depletion with increasing *EEMT*. In contrast, convergent landscape positions demonstrated minimal mineral mass loss and relatively greater content of neogenic secondary mineral phases. Solution chemistry data suggest the convergent positions concentrate soluble weathering products from adjacent divergent positions, thus resulting in locally reduced mineral-solution weathering gradients and promotion of neogenic mineral precipitation. The coupled datasets indicate that timing and amount of available water is a central control on regolith weathering with strong local-scale modification related to landscape position.

Behaviour of Zr/Hf and Y/Ho ratios during transition between seawater column and deep-sea brines

M. RASO¹, F. SAIANO², E. OLIVERI³, M. YAKIMOV⁴
AND P. CENSI^{1,3}

¹Dipartimento DiSTeM, Università di Palermo, Via Archirafi, 36 90123 - Palermo (Italy)

²Dipartimento S.A.G.A., Università di Palermo, Viale delle Scienze, ed.4, 90128 Palermo, Italy

³I.A.M.C.-CNR –UOS di Capo Granitola, Via del mare, 3 - 91026 Torretta Granitola, C.bello di Mazara (Italy)

⁴I.A.M.C.-CNR –UOS di Messina, Spianata S. Raineri, 86 - 98122 Messina (Italy)

During the oceanic cruise Mamba 2011 in the Eastern Mediterranean Sea seawater, biogeochemistry of the oxic layers and of the underlying anoxic deep-sea brines was studied. In order to extend the knowledge of processes occurring at oxic-anoxic interface in seawater, Zr/Hf ratio, coupled for the first time with Y/Ho and lanthanide behaviour, was investigated. Lanthanides and especially Y/Ho ratio are considered powerful probes of geochemical processes and a coherent behaviour with respect to Y/Ho was shown by the Zr/Hf ratio in several geochemical systems [1]. Observed covariance of Zr/Hf ratio with respect to dissolved Mn and Fe in anoxic brine, suggest that Zr was preferentially scavenged on MnO₂ surfaces under oxic conditions and the same process occurred for Hf onto FeOOH. These data confirm the observed behaviour in pore water studies [2] and extend the knowledge of Zr and Hf reactivity also onto Mn-oxides.

Different is the Y/Ho behaviour that correlates with dissolved Fe content, especially in brine from Tyro basin but not with Mn content, neither in brines, nor in oxic seawater. The observed lack of correlation observed among Y/Ho and Zr/Hf with respect Fe and Mn contents in seawater is probably due to the delivery of detrital materials in shallowest water layers.

[1] Bau (1996) *Contrib. Miner. Petrol* **123**, 323–333.

[2] McKelvey (1994) *PhD Thesis*, Univ. British Columbia.

The role of multicomponent diffusion and electromigration for reactive transport in porous media

PEJMAN RASOULI^{1*}, K. ULRICH MAYER¹
AND SERGIO A. BEA^{1,2}

¹Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, BC, Canada (umayer@eos.ubc.ca) (*correspondence: prasouli@eos.ubc.ca)

²now at: Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA (sabea@lbl.gov)

Aqueous diffusion is the dominant mass transport process in low permeability formations or in the absence of significant advection. There are systems in which electrostatic interactions between diffusing molecules strongly affect the apparent diffusion coefficients. Neglecting electromigration may lead to the inability of reactive transport models to adequately simulate diffusion dominated transport and to properly reproduce key phenomena such as mineral dissolution and precipitation [1]. An application for which electrochemical migration plays a significant role is the electrokinetic remediation of contaminated groundwater. Electrokinetic remediation is based on controlled application of low intensity direct current through the soil between electrodes. The change of redox condition induced near the electrodes shifts the thermodynamic conditions and ionic mobility with the goal to decontaminate the soil.

The formulation for numerical modeling of reactive transport including multicomponent diffusion and electromigration will be presented and preliminary results from simulations of electrokinetic remediation of metal contaminated soils will be discussed.

This modelling effort evaluates the importance of feedback mechanisms between electromigration, applied electric current, and homogenous and heterogeneous reactions in the aqueous phase and attempts to integrate the simulated response with observed geochemical data.

[1] Galíndez, J. M. & Molinero, J. (2010) On the relevance of electrochemical diffusion for the modeling of degradation of cementitious materials. *Cement & Concrete Composites* **32**, 351–359.

Mineral compositions indicate magma recharge processes in the Ilímaussaq Complex, Greenland

B. RATSCHBACHER*, M. MARKS, K. PFAFF
AND G. MARKL

Eberhard Karls Universität Tübingen, 72072 Tübingen,
Germany

(*correspondence: barbara.ratschbacher@yahoo.de)

The peralkaline Ilímaussaq intrusion, South Greenland, exhibits various types of syenites and nepheline syenites. The latest magma pulse represents the most evolved rocks (lujavrites), which mainly consist of eudialyte group minerals (EGM), feldspar, Na-pyroxene (aegirine) and sodic amphibole (arfvedsonite). Based on varying proportions of aegirine or arfvedsonite the lujavrites are subdivided into several units (Fig. 1). Our investigated samples cover the whole sequence of these rocks, including the upper part of the underlying cumulates (kakortokites). We analyzed early magmatic EGM to track the geochemical evolution of their parental melt. Textures (change from poikilitic to dispersed amphibole) and compositional variations (Fe/Mn and Ca/REE ratio systematics) imply that aegirine lujavrites I & IIA continuously evolved from the underlying kakortokites (Fig. 1). Data for arfvedsonite lujavrite A shift back to similar element ratios as aegirine lujavrite I and evolve further on a comparable trend. In contrast, aegirine lujavrite IIB and arfvedsonite lujavrite B data seem to evolve differently. We take these data as indication for the presence of three melts batches responsible for the formation of the lujavrite sequence, which is in contrast to earlier interpretations, who suggested that the kakortokite-lujavrite sequence formed from one single magma batch [1].

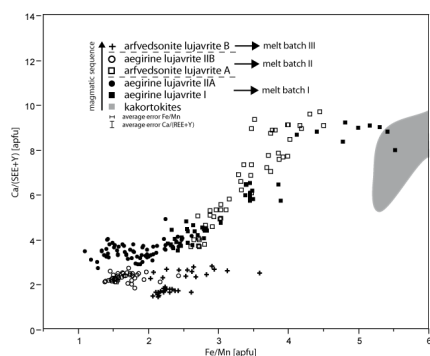


Figure 1: Element ratios in eudialyte; combined with data from [2].

[1] Sørensen *et al.* (2006) *Lithos* **91**, 286. [2] Pfaff *et al.* (2008) *Lithos* **106**, 280.

Electrochemical enhancement of carbonate and silicate weathering for CO₂ mitigation

GREG H. RAU^{1,2*} AND SUSAN A. CARROLL²

¹Inst. Marine Sciences, Univ. Calif., Santa Cruz, CA 95064

²Carbon Management Program, Lawrence Livermore Nat.

Lab., Livermore, CA 94550, USA

(*correspondence: rau4@llnl.gov)

Given the urgent need to stabilize if not reduce atmospheric CO₂ levels, might it be possible to safely and cost-effectively accelerate the consumption and storage of CO₂ via mineral weathering? Exposure of silicate and especially carbonate minerals to elevated CO₂ (e.g. flue gas) can effectively increase the reaction rates leading to CO₂ capture and storage via bicarbonate and/or carbonate formation (1). However, the slow kinetics of the silicate/CO₂ reactions appear to require additional chemical and/or physical treatment, especially in consuming more dilute CO₂ such as found in air. Because of the sensitivity of carbonate and silicate mineral dissolution to acids, and given the ability of saline water electrolysis to generate strong acids, it has been previously shown that electrochemistry can be used to accelerate mineral weathering for purposes of air CO₂ mitigation (2, 3). To explore this further, powdered wollastonite or ultramafic rock standard (UM-4) was encased around the acidic anode of a saline water electrolysis cell composed of graphite electrodes and a 0.25M Na₂SO₄ electrolyte solution. After 0.5 to 1.5 hrs of electricity application (3.5V_{dc}, 5-10mA), the electrolyte pH rose to as much as 11.1 (initial and blank pH's <6.6). Subsequent bubbling of these basic solutions with air lowered pH by at least 2 units and increased dissolve carbon content (primarily bicarbonate) by as much as 50X that of the blanks. While Ca²⁺ and Mg²⁺ concentrations were elevated, these were insufficient to balance the majority of the bicarbonate anions in solution. We suggest that in these experiments the silicate minerals acted as acid absorbers, forming mostly insoluble CaSO₄ and MgSO₄ at the anode, thus allowing NaOH formation at the cathode to accumulate in solution, in turn reacting with air CO₂ to form NaHCO₃. Longer electrolysis times and/or alternative electrolyte solutions might allow formation and precipitation of Ca or Mg carbonates. Such electrochemistry might ultimately provide a safe, efficient way to harness the planet's: i) large, off-peak or off-grid renewable electricity potential, ii) abundant basic minerals, and iii) vast natural brine electrolytes for air CO₂ mitigation and carbon-negative H₂ production.

[1] Rau, G.H. (2011) *Environ Sci. Technol.* **45**, 1088–.

[2] House, K.Z. *et al.* (2007) *Environ Sci. Technol.* **41**, 8464–.

[3] Rau, G.H. (2008) *Environ Sci. Technol.* **42**, 8935–.

Calcium carbonate veins in ocean crust record a threefold increase of seawater Mg/Ca and Sr/Ca in the past 30 Million years

SVENJA RAUSCH¹, FLORIAN BÖHM²,
ANTON EISENHAEUER², ANDREAS KLÜGEL¹
AND WOLFGANG BACH¹

¹Geoscience Department, University of Bremen, Germany
(srausch@uni-bremen.de)

²IfM-GEOMAR, 24148 Kiel, Germany

Carbonates in the basaltic ocean crust form during low-temperature alteration and provide a significant sink of CO₂ in the global carbon cycle. Coggon *et al.* [1] calculated ancient seawater Mg/Ca and Sr/Ca ratios based on the record of calcium carbonate veins in the ocean crust and proposed that these ratios were quite uniform throughout the period between 170 and 24 Ma, but then suddenly increased by a factor of 4 to present-day seawater composition. This increase, although delayed by tens of millions of years, is interpreted as an effect of decreasing ridge flank hydrothermal activity, which may be related to a decrease in ocean crust production rate in the late Cretaceous. The goal of this study was to use calcium carbonate veins in reconstructing seawater Mg/Ca and Sr/Ca ratios with a specific emphasis on young sites (≤ 57 Ma) in cold ridge flanks. While our data fill gaps in the critical interval of compositional change in the past 30 Ma, they strongly corroborate the results of Coggon *et al.* [1] in showing simultaneous increases in Mg/Ca and Sr/Ca. Our data also indicate that the Mg/Sr ratio of seawater did not change in the Neogene. We find this to be at odds with a hydrothermal driver of seawater compositional change which should not leave Mg/Sr unchanged. We suggest that a scenario first proposed by Wallmann [2], can explain both the observed trends and the time lag between the late-Cretaceous and the Neogene compositional changes of seawater. The late Cenozoic decrease in ocean crust production rate led to an increase in the average age of the crust and thus to a sea level drop. Lower sea level caused a shift of carbonate deposition from the shelves to the pelagic ocean. Finally, subduction-recycle delayed transfer of CO₂ from deep-sea carbonates to volcanic arcs in combination with accelerated erosion increased the carbonate alkalinity input to the oceans and boosted the Ca sink flux by carbonate formation.

[1] Coggon *et al.* (2010) *Science* **327**, 1114–1117.

[2] Wallmann (2001) *Geochim. Cosmochim. Acta* **65**, 3005–3025.

How Jupiter's two-phase gas-driven migration shaped the inner Solar System

SEAN N. RAYMOND¹, KEVIN J. WALSH²,
ALESSANDRO MORBIDELLI², DAVID P. O'BRIEN³
AND AVI M. MANDELL⁴

¹Laboratoire d'Astrophysique de Bordeaux, BP 89, 33271 Floirac, France (rayray.sean@gmail.com)

²Observatoire de la Côte d'Azur, Nice

(kwalsh@boulder.swri.edu, morby@oca.eu)

³Planetary Science Institute, Tucson, AZ, USA

⁴NASA Goddard Space Flight Center, MD, USA

Accretion simulations cannot adequately reproduce the terrestrial planets, in particular Mars' small mass [1]. Currently, the best solution to this problem assumes that the terrestrial building blocks were initially concentrated in a narrow annulus from 0.7-1 AU [2]. These initial conditions could have been sculpted by Jupiter's two-phase migration in the gaseous Solar Nebula: Jupiter first migrated inward due to standard type 2 torques, then back outward once Saturn grew and was trapped in 2:3 resonance [3]. If the turnaround point or "tack" occurred when Jupiter was at 1.5 AU then the inner disk of material would be truncated at 1 AU, forming a small Mars (Figure 1). In this scenario, the asteroid belt was first emptied and then re-filled by Jupiter: S-type asteroids (red in Figure 1) originated between 1-3 AU and C-types (blue) originated between the giant planets and beyond Neptune [4].

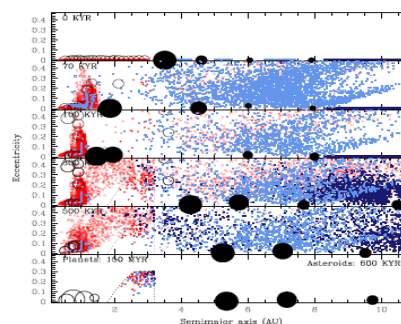


Figure 1: illustrates this evolution.

In the absence of migration, primitive C-type asteroids represent a plausible source for Earth's water [5]. In the context of the 'grand tack' model [4], this same population may still deliver water to the growing Earth: for every C-type planetesimal injected into the asteroid belt, ~10 were scattered onto eccentric orbits that intersect the terrestrial planet-forming region. These scattered C-types can deliver several oceans of water to the growing Earth.

[1] Raymond *et al.* (2009) *Icarus* **203**, 644–662. [2] Hansen (2009) *ApJ* **703**, 1131–1140. [3] Masset & Snellgrove (2001) *MNRAS* **320**, L55–L59. [4] Walsh *et al.* (2011, in press) *Nature*. [5] Morbidelli *et al.* (2000) *M&PS* **35**, 1309–1320.

Juvenile glass fragments in phreatic explosion debris from Turrialba Volcano, Costa Rica

MARK K. REAGAN¹, MICHAEL C. ROWE²,
ELIECER DUARTE³ AND ERICK FERNANDEZ³

¹U. Iowa, Iowa City IA, 52242 USA,
(mark-reagan@uiowa.edu)

²Washington State U., Pullman WA, 99164 USA

³OVSICORI, UNA, Costa Rica

After several years of increasing fumarolic activity, Turrialba volcano experienced small phreatic explosions on January 5-6, 2010, leaving a 55x20 m crater with an incandescent floor. Ash and lapilli from the explosions consists mostly of crystal-rich and altered material originally erupted in 1864-1866 and earlier. Nevertheless, careful examination of the tephra revealed that ~1% of the medium to coarse ash-sized particles consists of fresh glass. The freshness of the glass and its unusual chemical traits suggest that this glass is juvenile. EMP analysis of the glass fragments showed them to be calcalkaline andesites, whose major element compositions were largely consistent with derivation by low-P crystal fractionation of basaltic parental magmas. Na₂O, however, is depleted in most glass fragments (1.1-2.8 wt. %) compared to Turrialba's basaltic lavas (2.8-3.8). Incompatible trace element compositions determined by LA-ICPMS are broadly similar to those of the 1864-1866 basalts. REE element patterns are strongly light enriched and most fragments have the elevated Ba/Ce and La/Nb ratios (8-16 and 1.8-2.2 respectively, which is commonplace for calcalkaline lavas. However, one fragment had Ba/Ce and La/Nb ratios (5 and 1.1) more typical of an ocean island basalt, but was otherwise similar in composition to the other fragments.

The concentrations of S in all fragments were near the EMP detection limit, and Cl in most samples were also unusually low for a Turrialba basalt. The concentrations of F, however, were highly variable, ranging from 0.03 to 0.6 wt. %. High F was associated lower concentrations of Na, REE and HFS elements. We speculate the F was enriched by interaction with high-T fumarolic gasses which also leached highly-charged cations and Na.

Important findings are: (1) phreatic explosion debris can contain juvenile glass fragments that provide compositional information about the magma triggering the unrest; (2) magmas intruding into Turrialba's upper edifice at present are basalts or basaltic andesites with varying La/Nb; and (3) gas streaming can affect compositions of apparently fresh glass, particularly Na concentrations.

Glass composition impact on water reactivity at the glass surface

D. REBISCOUL^{1*}, F. BRUGUIER¹, V. MAGNIN²
AND S. GIN¹

¹CEA Marcoule,CEA/LCLT, BP 17171, 30207 Bagnols-sur-Ceze BP 17171, 30207 Bagnols sur FRANCE

(*correspondence: diane.rebiscoul@cea.fr,
florence.bruguier@cea.fr, stephane.gin@cea.fr)

²ICSM/LDD, BP 17171, 30207 Bagnols-sur-Ceze, FRANCE
(valerie.magnin@cea.fr)

Understanding the interactions of water with glass surface is of great interest to improve glass alteration models. In this study, the impacts of soda-lime borosilicate glass composition [1] and particularly the effect of network formers such Si and Zr, and of charge compensators such Ca and Na, on water penetration and water structure at the first time of alteration were investigated. Two surface characterizations were used: X-ray reflectometry to determine the thickness and density of the modified glass zone and attenuated total reflection infrared spectroscopy to precise the predominant alteration mechanisms (water diffusion through glass network or hydrolysis) resolving the O-H stretching band into four components corresponding to different types of water in glass (hydroxyl group, free, network and ion bounded water). The results of glass alteration at pH=3 and 30°C have shown that hydrolysis was the predominant mechanism after few seconds for glass having a low ZrO₂/SiO₂ ratio. This phenomenon can be explained by the high amount of NBO content. For the other glasses, the diffusion was the limiting reaction characterized by a modified zone having a density close to the hydrated glass and a high amount of free water. The calculated water diffusion coefficients highlighted a decrease of the water diffusion with an increase of Ca content in glass probably due to the compaction of the network by incorporation of divalent cations [2].

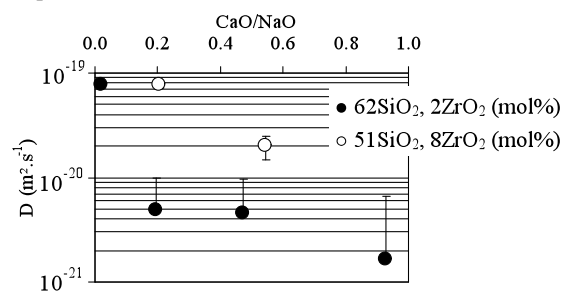


Figure 1: Diffusion coefficients of water through the glasses at pH=3 and 30°C calculated from the first Fick law.

[1] Angéli *et al.* (2010) *J. Am. Ceram. Soc.* **93**, 2693–2704.

[2] Indris *et al.* (2005) *Phys. Rev. B* **71**, 064205.

The combined use of CALIOP, MODIS and OMI aerosol and cloud products for calculating direct aerosol radiative effects

JENS REDEMANN¹, M. VAUGHAN², Y. SHINOZUKA¹,
P. RUSSELL³, J. LIVINGSTON⁴ AND L. REMER⁵

¹BAER Institute/NASA Ames, 290 Maple Ct. Ste. 268,
Ventura, CA 93003, USA

(*correspondence: Jens.Redemann-1@nasa.gov)

²NASA Langley Research Center, Hampton, VA 23681, USA

³NASA Ames Research Center, MS 245-5, Bldg. 245, P.O.
Box 1, Moffett Field, CA 94035, USA

⁴SRI, International, G-179, 333 Ravenswood Ave., Menlo
Park, CA 94025, USA

⁵NASA Goddard Space Flight Center, code 613.2, Bldg. 33,
Greenbelt, MD 20771, USA

We describe a technique for combining CALIOP aerosol backscatter, MODIS spectral AOD (aerosol optical depth), and OMI AAOD (absorption aerosol optical depth) measurements for the purpose of estimating full spectral sets of aerosol radiative properties, and ultimately for calculating direct aerosol radiative effects. We will present first results using 1-month of collocated CALIOP V3, MODIS and OMI data collected in October 2007, as well as a test of our methodology using airborne observations in the ARCTAS field experiment. As a prerequisite for the application of our methodology to the actual satellite observations, we assessed the consistency between comparable measurement quantities from the different A-Train sensors. For eight months in 2007 and 2009, comparisons of the standard MODIS-Aqua AOD data to AOD calculated from CALIOP aerosol extinction profile data show differences in global, monthly mean, over-ocean AOD (532nm) between CALIOP and MODIS ranging between 0.025 and 0.04 for CALIOP V3, with CALIOP generally biased low. Differences for CALIOP V2 are often smaller, but correlation with MODIS AOD is significantly lower.

Anelastic processes in minerals at high temperature: Examples of quartz and spinel

S. REDFERN*, Z. PENG, J. WALSH
AND M. DARAKTCHIEV

Department of Earth Sciences, University of Cambridge,
Downing Street, Cambridge, CB4 2BD, UK
(*correspondence: satr@cam.ac.uk)

Features of recent mechanical spectroscopic studies in Cambridge will be reviewed. The first measurements of higher-order harmonic responses of coelastic materials at displacive phase transitions are reported: Second and third harmonics of strain have been measured by forced torsion pendulum for quartz at the high-low transition. The incommensurate phase and the highly non-linear thermal expansion of quartz at this transition may play a role in controlling higher order elastic moduli. Jerky elastic and strain responses to applied stress also reveal themselves in such experimental arrangements, and we have seen the development of power law distributions of such elastic noise in a number of systems. Self-induced defects appear to lead to such crackling microstructures.

As a contrasting example, the high temperature behaviour of MgAl₂O₄ spinel is known to be dominated by kinetic rearrangements of Mg and Al cations as the system undergoes non-convergent order-disorder. We have measured the anelastic loss associated with such order-disorder processes in crystals and ceramics of spinel at ambient and high pressure. The loss is revealed as a strong anelastic relaxation, with well-defined activation energy and relaxation time, in the seismic frequency range. Finally, the implications for seismic damping in ringwoodite spinel are considered.

Methane geochemistry's 'stealth' process: Microbial oxidation

WILLIAM S. REEBURGH

Earth System Science, University of California Irvine, Irvine, CA, 92697, USA (reeburgh@uci.edu)

For the purposes of this presentation, I consider a 'stealth' process as one that cannot be directly measured. Microbial methane oxidation, aerobic and anaerobic, are examples. Most of the fluxes used to assemble the global methane budget are net fluxes, the difference between production and consumption, so direct measurements of production and consumption require tracer measurements. Several recent high-profile climate modeling papers have fallen into the 'stealth process' trap by failing to explicitly consider microbial oxidation.

This talk reviews recent developments in quantifying methane oxidation in the oxic ocean and estimates the global importance of both aerobic and anaerobic oxidation in a range of environments as controls on global change induced production. New methods are discussed and remaining challenges are enumerated.

Phase separation, degassing and anomalous methane at the Menez Gwen hydrothermal field

EOGHAN P. REEVES¹, X. PRIETO¹, M. HENTSCHER¹,
M. ROSNER², J. SEEWALD³, K.-U. HINRICHS¹
AND W. BACH¹

¹MARUM Center for Marine Environmental Sciences, Universität Bremen, Bremen 28359, Germany (*correspondence: reeves@uni-bremen.de)

²Fachbereich Geowissenschaften, Freie Universität Berlin, Berlin 12249, Germany

³Woods Hole Oceanographic Institution, Woods Hole MA 02543, USA

The Menez Gwen neovolcanic dome, lying at ~800m depth, hosts one of the shallowest basalt-hosted hydrothermal systems on the Mid-Atlantic Ridge and vent fluids there have unusually high CH₄/H₂ ratios relative to ultramafic- and other basalt-hosted systems [1]. To further constrain the origin of this CH₄, fluids were sampled in 2010 from vents on the dome's eastern flank, and from a newly discovered vent field, Bubbylon, 5km to the south of the Menez Gwen dome.

Maximum vent temperatures (270–298°C) in the eastern Hot Sands and AzorAna areas are near the 2-phase boundary and near-seafloor subcritical phase separation (boiling) is pervasive. Endmember CH₄ (0.37–3.6mmol/kg) and CO₂ (11–78mmol/kg) concentrations are high, but H₂ (0.06–0.57mmol/kg) is low, and only a narrow Cl range (202–368mmol/kg) is evident. Two volatile-rich diffuse fluids (91–117°C) sampled appear to have formed by subsurface mixing of near zero salinity vapor phases with entrained seawater, with apparent CH₄ and CO₂ end-member concentrations of ~30 and ~600mmol/kg, respectively. Such extreme volatile enrichments due to boiling are likely responsible for the ubiquitous gas bubble exsolution evident at the seafloor, releasing substantial CO₂ and CH₄ to the water column. Despite boiling-related variability, endmember CH₄/H₂ ratios (2.5–18) remain anomalously high in 2010. Trace NH₄⁺ concentrations (<5µmol/kg) and δ¹³C_{CH₄} values (-16.6‰ to -19.9‰) within the typical range of unsedimented systems preclude any subsurface sedimentary source of thermogenic CH₄ [2]. Thermodynamic considerations also exclude abiotic CO₂ reduction to CH₄ at the conditions encountered by fluids. This suggests a deeper source of CH₄, such as the volatile-rich fluid inclusions found in oceanic crust Layer 3 [3]. CH₄ radiocarbon and C₂₊ hydrocarbon analyses are ongoing.

[1] Charlou *et al.* (2000) *Chem. Geol.* **171**, 49–75. [2] Lilley *et al.* (1993) *Nature* **364**, 45–47. [3] Kelley & Früh-Green (1999) *J. Geophys. Res.* **104**, 10439–10460.

Oceanic basalts provide a biased view of mantle composition

MARCEL REGELOUS, KARSTEN M. HAASE
AND PHILIPP A. BRANDL

GeoZentrum Nordbayern, Universität Erlangen-Nürnberg,
Erlangen, Germany (regelous@geol.uni-erlangen.de)

Chemical and isotopic variations in oceanic basalts are commonly used to infer the chemical structure and evolution of the Earth's mantle. The mantle source of intraplate oceanic basalts is thought to be more 'enriched' than that which melts beneath spreading ridges, due to a greater contribution from recycled oceanic crust or sediment, which can be identified using incompatible trace element and isotope ratios. This approach assumes that mantle melts inherit the incompatible trace element and isotope ratios of their mantle source, an assumption which is also inherent in many geochemical models for melting at spreading ridges and ocean islands.

We will present geochemical data for lavas erupted during slowdown and after the end of active spreading on the fossil Galapagos Rise spreading centre, which show that many oceanic basalts probably do not faithfully record the average composition of the volume of mantle that is melted. Galapagos Rise lavas were generated by variable degrees of melting from 'normal' depleted upper mantle, yet display an enormous range of compositions. At 9.2 Ma, before spreading ceased, incompatible element depleted NMORB (0.75 ppm Nb, Nb/Zr 0.011, $^{87}\text{Sr}/^{86}\text{Sr}$ 0.70251) were erupted. Younger post spreading lavas, dated at between 7.5 and 5.7 Ma, were produced by smaller degrees of melting and are increasingly enriched. The youngest basalts are trace element enriched EMORB with 77.9 ppm Nb, Nb/Zr 0.256, $^{87}\text{Sr}/^{86}\text{Sr}$ 0.70311.

The correlated trace element and isotope variations in Galapagos Rise lavas are inconsistent with simple mixing of endmember melt compositions, and also cannot be explained by melting of variably heterogeneous mantle in which enriched and depleted materials contribute equally to melting. Instead, our data can be explained by variable degrees of melting of heterogeneous mantle, within which incompatible element enriched lithologies melt to a greater extent than the more depleted 'matrix'. Our results have implications for the way in which oceanic basalts can be used to infer mantle melting processes and source compositions. For example, the 'garnet signatures' inferred from rare earth element and Nd isotope compositions in MORB may be more sensitive to variations in mantle composition, than to the average depth of melting. Melts of heterogeneous mantle will be biased towards the compositions of more fertile, enriched lithologies, so that the mantle may be significantly more depleted than is often assumed.

Monitoring fluid properties in a geothermal plant

SIMONA REGENSPURG*, HARALD MILSCH,
RONNY GIESE AND MATHIAS POSER

Helmholtz-Centre Potsdam, German Research Centre for
Geosciences (GFZ) Potsdam, Germany
(*correspondence: regens@gfz-potsdam.de)

Measuring chemical properties of geothermal fluids, processed in a geothermal plant is challenging due to high temperatures, salinities and change of conditions resulting in chemical reactions such as corrosion or scaling (=mineral precipitation). At the geothermal *in situ* research laboratory Groß Schönebeck (Germany) chemical reactions of a fluid produced from a Permian sandstone at ~ 4300 m depth, are investigated by a newly developed, fluid-chemical monitoring unit. The apparatus can be connected to different locations at the above ground installations. At these adapters, part of the fluid from the main pipe, would flow through a bypass containing a small heat exchanger. On both sites of the heat exchanger a sampling unit as well as probes to measure pH value and redox potential are installed which can be operated at 150 and 70°C, respectively. Besides high temperatures, the sensors need to be corrosion resistant due to the high chloride concentration typically found in geothermal brines (up to 5 M).

The device simulates processes occurring at heat exchangers which are typically installed in geothermal plants to transfer the heat of the fluid for electric energy production. The chemical informations obtained from this monitoring unit describe not only the compositional variability of the produced fluid over time, but also chemical processes and their kinetics potentially occurring within the plant due to temperature decrease, which could result in corrosion or clogging of the pipes and components. In Groß Schönebeck, chemical equilibrium calculations indicated oversaturation of sulfate-, silicate-, iron- and lead minerals due to temperature drop. The monitoring validates modeled reactions and thus gives evidence on these reactions and might finally predict plant failures.

The ^{129}I isotopic composition of supergene iodine minerals in Chile and Australia

MARTIN REICH^{1,2}, FERNANDA ALVAREZ¹, ALIDA PÉREZ¹, GLEN T. SNYDER³, C. PALACIOS¹, G. VARGAS¹, Y. MURAMATSU⁴, EION M. CAMERON⁵ AND UDO FEHN⁶

¹Department of Geology, Universidad de Chile, Santiago Chile (mreich@ing.uchile.cl)

²Andean Geothermal Center of Excellence, Universidad de Chile, Santiago, Chile

³Department of Earth Sciences, Rice University, Houston, TX

⁴Department of Chemistry, Gakushuin University, Tokyo, Japan

⁵Eion Cameron Geochemical Inc., Carp, ON, Canada

⁶Department of Earth and Environmental Sciences, University of Rochester, Rochester, NY

Because of its large ionic radius, iodine (I) is rarely incorporated into minerals and remains in the aqueous phase much longer than other halogens. Naturally-formed I minerals are very rare, but are found in the nitrate ore fields of the Atacama Desert in Chile and the supergene zones of base and precious ore deposits in extremely arid environments (Chile, Australia). The presence of I in Cu deposits in northern Chile has not been investigated previously, but provides the opportunity to apply the ^{129}I system for the study of the tectonic history of the area and of climatic changes, particularly the desiccation of the Atacama region.

Here, we report the first ^{129}I data of iodide minerals from supergene zones of Cu and Ag deposits from the hyperarid Atacama Desert. Two marshite (CuI) samples from the supergene zone of the Chuquicamata Cu deposit show $^{129}\text{I}/\text{I}$ ratios of 218 ± 72 and 562 ± 77 ($\times 10^{-15}$ at-at⁻¹), similar to the ^{129}I isotopic signature of a geochemically anomalous, iodine-rich soil sampled above the Spence porphyry Cu deposit (473 ± 75). Therefore, mineral and soil samples range between typical volcanic arc fluids ($^{129}\text{I}/\text{I} \sim 700\text{-}1000$) and forearc fluids ($^{129}\text{I}/\text{I} \sim 100\text{-}250$). In contrast, marshites and iodargyrites (AgI) from the Broken Hill Pb-Zn-Ag deposit in Australia and the Chañarcillo Ag deposit in Chile show a wider dispersion of $^{129}\text{I}/\text{I}$ ratios, ranging from ~ 100 to 2000, indicating a significant meteoric influence.

We suggest that I-rich fluids were involved in supergene enrichment and recycling of Cu in the Atacama region, revealing a complex link between multiple sources of fluids, active tectonics and climate change.

Melting conditions associated with the Colorado Plateau, USA

M.R. REID^{1*}, ROMAIN A. BOUCHET²
AND J. Blichert-Toft²

¹School of Earth Sciences and Environmental Sustainability, Northern Arizona University, Flagstaff, AZ 86011-4099 USA (mary.reid@nau.edu)

²Ecole Normale Supérieure de Lyon, 69007 Lyon, France

Continental foundering occurs by lithospheric detachments associated with gravitational instabilities as well as by shear-related thinning. Volcanic activity is progressively encroaching on the otherwise tectonically stable Colorado Plateau in the southwestern U.S. We show that decompression melting of local ambient enriched mantle lithosphere - rather than compression melting of lithospheric mantle drips or delaminations, or decompression melting of the asthenospheric mantle return flow - is likely responsible for this volcanism. New Hf and Nd isotope data (>120 analyses) significantly expand evidence for heterogeneous enriched mantle sources beneath the Colorado Plateau. $^{206}\text{Pb}/^{204}\text{Pb}$ values <18.5 and as low as 17, characterize those samples with Hf-Nd isotope signatures that are evocative of mantle enrichment by mixing with pelagic \pm terrigenous sediments: values >18.5 would be expected if Cordilleran and other sediments had been incorporated into their sources during Laramide-aged (80–40 Ma) shallow subduction. Relative abundances of minor and trace elements further show that the more volumetrically significant melts are sourced dominantly in peridotite rather than in pyroxenite or eclogite. Silica- and MgO-based thermobarometry supports evidence from trace element fractionation that melting locally transcends the garnet-spinel transition (~ 75 km), with shallower melts characterized by higher degrees of partial melting. Low P- and S-wave velocity domains, pronounced thinning of the lithosphere beneath the margins of the Colorado Plateau, and possible evidence for lithospheric delamination [1] may be further evidence that localized mantle upwelling is responsible for Colorado Plateau volcanism.

[1] Levander *et al.* (in press) *Nature*.

Biogeochemistry as a regional mineral exploration tool: Northeast Yilgarn Craton, Western Australia

N. REID^{1*}, M.J. LINTERN¹, R.R.P. NOBLE¹,
R.R. ANAND¹, D.J. GRAY¹, G. SUTTON²
AND R. JARRETT²

¹CSIRO Earth Science and Resource Engineering, Kensington WA 6151, Australia

(*correspondence: nathan.reid@csiro.au)

²CSIRO Mathematics, Informatics and Statistics, Urrbrae SA 5064, Australia

Regional biogeochemical surveys can potentially be of great use for mineral exploration where access problems and the hindrance of transported overburden make other techniques problematic. A large area of the north Yilgarn Craton hosting numerous Ni, Au, U and VMS deposits was selected for this proof of concept study. *Acacia aneura* (mulga) was sampled approximately every 8 km in this region as it is one of the most widespread plant species across Australia. Mulga samples were collected at water wells and bores corresponding to a regional hydrogeochemistry sampling program. Vegetation samples were dried, split, milled, digested in aqua regia then analysed using ICP-MS/OES. A large, robust, statistically verified geochemical data set was generated which provides the ability to detect lithological signatures using geochemical indices and multivariate statistics (with around 20% error of prediction). Uranium in mulga was the only distinct target element for secondary U deposits, and was successful for most known prospects. Gold exploration potential was improved by the use of multi-element indices. Nickel prospects were identified where the samples were close to the prospects (<2 km) or where supergene mineralisation was dispersed. The Leinster and Murrin Murrin areas were highlighted by elevated Ni, Co, Cr and Fe concentrations compared to background with haloes up to 20 km wide. Detection of VMS style deposits is hampered by Zn and Cu being essential plant nutrients however, high Zn values seen on the regional scale may warrant further investigation. Little correlation exists between hydrogeochemistry and biogeochemistry, meaning one cannot be used as a surrogate for the other; however, both are useful tools in detecting mineralisation and lithological signatures using different chemical properties for a regional setting. Also, mulga can be sampled without the need for drilling to access groundwater.

Sensitivity and feedback in the oceanic molybdenum cycle

C.T. REINHARD^{1*}, C.T. SCOTT² AND T.W. LYONS¹

¹Dept. of Earth Sciences, Univ. of California, Riverside, Riverside, CA 92521 (timothy1@ucr.edu)

(*correspondence: christopher.reinhard@ucr.edu)

²Dept. of Earth and Planetary Sciences, McGill Univ., Montreal, QC H3A 2A7 (clinton.scott@mcgill.ca)

The oceanic inventories of trace elements have fluctuated markedly during Earth's history as a function of prevailing Earth surface redox conditions. Given the importance of many trace elements in a wide variety of enzymatic processes, such changes may have had significant downstream effects on the global biogeochemical cycling of carbon, nitrogen, and oxygen [1]. Molybdenum (Mo) is particularly important in this regard, being a crucial catalytic component of enzymes involved in biological N₂ fixation, assimilation of NO₃⁻, and oxygen atom transfer reactions.

Here, we explore the response of the oceanic Mo reservoir to perturbations in marine redox in a one-box ocean model in which Mo enrichment and burial are first-order with respect to the ambient Mo reservoir. Despite imposing this negative feedback, we find that relatively small changes in ocean redox can have significant effects on the concentration of Mo in seawater ([Mo]_{sw}) at steady state, and that relaxation to steady state following perturbation occurs relatively quickly. In addition, although it is possible to draw down [Mo]_{sw} to levels that would have been likely to exert negative effects on some biological processes, the muted enrichments seen in many Proterozoic black shales [2] are likely not compatible with global-scale sulfidic conditions.

In order to further explore the feasibility of attaining varying degrees of expanded anoxia we employ a simple oxygen budget for the modern North Atlantic. This exercise corroborates that of [3], and suggests that the redox state of the deep ocean could have been severely impacted purely by air-sea gas exchange limitations at presumed Proterozoic atmospheric oxygen levels. Further, a simple regional budget of sulfide and highly reactive iron (Fe_{HR}) fluxes to marine sediments suggests that were the ocean to become anoxic due to limited O₂ supply (as in the Proterozoic) the deep ocean would most likely have become ferruginous (anoxic and Fe-rich) [4] while marginal environments would likely have been prone to sulfidic conditions.

[1] Anbar & Knoll (2002) *Science* **297**, 1137–1142. [2] Scott *et al.* (2008) *Nature* **452**, 456–459. [3] Canfield (1998) *Nature* **396**, 450–453. [4] Poulton & Canfield (2011) *Elements* **7**, 107–112.

Transformations of silver nanoparticles in environmental systems

B.C. REINSCH^{1,2}, R MA^{1,2}, C. LEVARD^{2,3}, N. KABENGI^{2,4}, G.E. BROWN JR.^{2,3}, C.S. KIM⁵ AND G.V. LOWRY^{1,2*}

¹Carnegie Mellon University, Pittsburgh, PA 15213, USA

(*correspondence: glowry@cmu.edu)

²Center for the Environmental Implications of Nanotechnology (CEINT)

³Stanford University, Stanford, CA 94305, USA

⁴University of Kentucky, KY 40546, USA

⁵Chapman University, Orange, CA 92866, USA

The persistence, toxicity, and effects of silver nanoparticles (AgNPs) released to the environment depends on their eventual speciation. Reduced sulfur-silver species are predicted to dominate the eventual species that form. However, in the environment, especially in aerobic conditions, other ligands are more abundant, such as Cl⁻, organic thiols, SO₄²⁻, Br⁻, and I⁻. To identify important transformations from 'weathering' and predict the speciation of silver nanoparticles weathered in environmental samples, engineered AgNPs were weathered in various environmental conditions including: wastewater treatment byproducts, aerobic and anaerobic soils, and in simulated wetland mesocosms. Synchrotron-based X-ray absorption spectroscopy was used to speciate AgNPs aged under simulated weathering conditions in the laboratory. Comparisons between the speciation of AgNPs that had been weathered for up to 18 months in a simulated wetland and laboratory weathering can be used to create particles that mimic the observed changes in environmental samples. Protocols to rapidly weather engineered nanomaterials will allow researchers to use NPs with properties representative of the materials that will be in the environment rather than those of the pristine materials. This will enable better predictions of the environmental fate, transport, and effects of engineered nanoparticles.

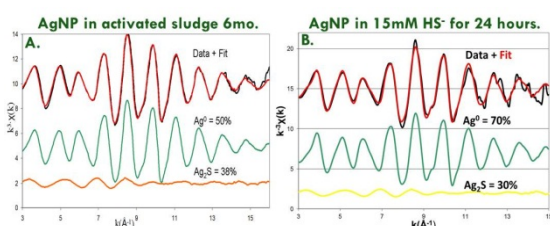


Figure 1: The original AgNPs containing ~90% Ag⁰ have been transformed to approximately 50% Ag⁰ and 30%Ag₂S after 6 months of ageing in activated sludge, shown in A. B shows the resulting particles from a laboratory ageing process that has produced a particle of somewhat similar composition after only 24 hours of ageing in Na₂S.

The Os isotopic record of organic rich sediments from the Benguela Upwelling System, Namibia

L. REISBERG^{1*}, D. BLAMART² AND C. ZIMMERMANN¹

¹CRPG (CNRS UPR2300), Université de Lorraine, BP 20, 54501 Vandoeuvre-les-Nancy, France

(*correspondence: reisberg@crpg.cnrs-nancy.fr)

²LSCE (CEA-CNRS-UVSQ), Avenue de la Terrasse, 91198 Gif-sur-Yvette Cedex, France

Several recent studies [1-5] have shown a correlation between osmium isotopic variations in marine sediments and glacial-interglacial cycling. These correlated variations have been used to argue for direct climatic control on weathering intensity and/or on the composition of erosional products. However these rapid fluctuations in the marine Os isotopic records suggest a residence time for Os in seawater (3 to 10 ka) that is much shorter than that inferred from mass balance (~ 25 to 40 ka, [6-8]). Furthermore, potential problems linked to sampling site or sediment type, such as basin isolation, detrital contributions, and low sedimentation rate, could bias many of the existing Os records.

To obtain a reliable, high resolution record of marine Os isotopic variations in Quaternary times, we are analyzing sediments from ODP Leg 175, Site 1084, drilled off the coast of Namibia beneath the Benguela Upwelling System. This is an open ocean site containing rapidly deposited (~ 18 cm/kyr) organic rich sediments, which should be unaffected by the possible problems that may have plagued earlier studies. We currently have results for 9 samples spanning the most recent 35 ka of this record. These samples have extremely high Re and Os concentrations (58-157 ppb and 0.19-0.34 ppb, respectively). Their ¹⁸⁷Os/¹⁸⁸Os ratios are quite constant (1.044 ± 0.013, 2σ), and show only a tiny hint of the nearly 7% decrease in ¹⁸⁷Os/¹⁸⁸Os during the last glacial maximum observed in several previous studies. Instead, the uniformity of the Benguela Os record is similar to that reported for an early Pleistocene record from the equatorial Pacific Ocean [9]. The discrepancies between the Os records from different sediment types and localities must be better understood before these records can be used to constrain relationships between climate and weathering.

[1] Oxburgh (1998) *EPSL* **159**, 181–191. [2] Dalai *et al.* (2005) *Chem. Geol.* **220**, 303–314. [3] Williams & Turekian (2004) *EPSL* **228**, 379–389. [4] Oxburgh *et al.* (2007) *EPSL* **263**, 246–258. [5] Burton *et al.* (2010) *EPSL* **295**, 58–68. [6] Oxburgh (2001) *G-cubed* 2000GC000104. [7] Levasseur *et al.* (1998) *EPSL* **174**, 7–23. [8] Paul *et al.* (2010) *GCA* **74**, 3432–3448. [9] Dalai & Ravizza (2010) *GCA* **74**, 4332–4345.

The geomicrobiology of gold: Fundamental processes to industrial applications

FRANK REITH¹, GREGOR GRASS², CARLA ZAMMIT¹,
GORDON SOUTHAM³ AND JOËL BRUGGER¹

¹The University of Adelaide, Geol. & Geophys., Adelaide
SA5005, Australia (Frank.Reith@csiro.au)

²University of Nebraska-Lincoln, Lincoln NE 68588-0666,
USA

³University of Western Ontario, London, ON, Canada N6A
5B7

The biosphere catalyzes a variety of biogeochemical reactions that transform gold (Au) [1, 2]. Microbial weathering contributes to the mobilization of Au by releasing Au trapped in minerals and by solubilizing it via complexation. Subsequent microbial destabilization of Au (I/III)-complexes coupled to bio-precipitation and biomineralization leads to secondary Au formation, completing the cycle. Secondary Au occurs as nano-particles as well as micro-crystalline and 'bacteriomorphic' Au, the latter being a controversial form of 'biogenic' Au. Recent research provides an understanding of genetic and biochemical mechanisms that microorganisms utilize to drive this biogeochemical cycle. These studies show that: (1) microorganisms mediate Au solubilization via excretion of metabolites, e.g. cyanide, amino acids and thiosulfate; (2) precipitate Au intra- and extracellularly, and in products of their metabolism leading to the formation of Au biominerals; and to achieve this (3) have developed biochemical responses to deal with toxic Au (I/III)-complexes.

Using genomic, proteomic and synchrotron spectroscopic techniques genes and proteins involved in Au detoxification have been characterized. For example, a transcriptional regulator (GolS) in the bacterium *Salmonella enterica* is activated specifically by Au-complexes. Activated GolS then activates the expression of a metallochaperone gene (*golB*) and of a transmembrane efflux ATPase (*golT*), which promote Au resistance [3]. Using these results a biosensor for Au is in development allowing the quantification of Au from environmental samples. This will provide a cost-efficient and environmentally sustainable technique for the improvement of Au exploration and ore processing.

[1] Reith *et al.* (2007) *ISME Journal* **1**, 567–584. [2] Southam *et al.* (2009) *Elements* **5**, 303–307. [3] Checa *et al.* (2007) *Mol. Microbiol.* **63**, 1307–1318.

Mobility of platinum and gold in the Australian regolith – Spectroscopic and electron microscopic analyses

FRANK REITH¹, CHRISTINE TA²,
BARBARA ETSCHMANN¹, CLAIRE LENEHAN²
AND JOËL BRUGGER¹

¹The University of Adelaide, Geol. & Geophys., Adelaide
SA5005, Australia (Frank.Reith@csiro.au)

²Flinders University, Adelaide SA5001, Australia

Biogeochemical cycling of gold (Au) and platinum (Pt) appears to play a fundamental role in the formation of secondary Pt and Au in placer deposits, and secondary 'biogenic' Pt and Au has been reported from Brazil and Australia [1, 2]. To compare Pt and Au mobility, Pt/Au nuggets, soils and groundwaters were collected from a platiniferous and auriferous site near Fifield, New South Wales, Australia. Collected materials were analyzed using (FIB)-SEM-(EDXA/EBSD), ICP-MS, EPMA, ICP-MS/OES, X-ray tomography, synchrotron- μ XRF, and thermodynamic modeling.

Secondary morphologies, presence of nano-particle and formation of micro-crystalline enrichment zones of Pt/Au on surfaces of Pt/Au grains suggest (bio)geochemical dissolution and re-precipitation that promote the mobility of Pt and Au in surface environment. This is supported by X-ray tomography of a rare specimen of deep lead material (Fe-oxides, silicates and clays) with embedded Pt- and Au grains. Grain surfaces display filigree and perforated structures, strong rounding of grains and the formation of nano- and micro-particles. Synchrotron μ XRF-mapping and FIB-SEM of polished sections uncovers differences in Au and Pt mobility. This is supported by groundwater data and geochemical modeling, suggesting lower Pt compared Au reactivity, and hence mobility, in surface environments.

[1] Cabral *et al.* (2011) *Chem. Geol.* **281**, 125–132. [2] Reith *et al.* (2010) *Geology* **38**, 843–846.

Distinguishing periods of crustal growth and recycling by U-Pb dating, Sr, Pb and Hf isotopes among the Eastern Cordilleran granitoids of South Peru

MARIËL REITSMA^{1*}, U. SCHALTEGGER¹, R. SPIKINGS¹,
M. CHIARADIA¹, A. ULIANOV² AND A. GERDES³

¹Université de Genève, Rue des Maraîchers 13, 1205 Geneva, Switzerland (*correspondence: martje.reitsma@unige.ch)

²Université de Lausanne, Switzerland

³Goethe University, Frankfurt am Main, Germany

The backbone of the Eastern Cordillera of south Peru is built of plutons that have previously been mapped as Permo-Triassic. They were related to an extensional event that generated continental basins at the surface, filled with the sediments of the Mitu Group.

The aim of this study is to decipher age trends among the granitoids and assess their contribution to crustal growth. U-Pb laser ablation ICPMS dating of zircons shows that the plutons of the north-west trending Cordillera de Carabaya are middle to upper Triassic in age, while the plutons in the Abancay deflection are older: Ordovician, Carboniferous and Permian. Triassic plutons continue in north-western direction to the south of the Abancay deflection.

Hf-isotope data show positive ϵ_{Hf} (~+2 to +4) for the Paleozoic plutons indicating a mantle dominated source while the Triassic plutons have ϵ_{Hf} around 0 to -4 indicating mixing of mantle and crustal sources.

The Triassic plutons match exactly the age of the sediments of the Mitu group. Therefore, we conclude that these granitoids formed via partial crustal anatexis associated with extension. The offset of the plutons around the Abancay deflection could be interpreted as a step over in the Mitu rift. The Ordovician, Carboniferous and Permian plutons coincide with times of known continental arc magmatism along the western Gondwana margin and were emplaced in a back-arc setting.

Hf-isotope results for both tectonic settings indicate variable amounts of juvenile input from the mantle and/or from a lower crustal source, reflecting an increasing importance of a crustal component in the Triassic. However, with the present data we cannot quantify crustal growth versus crustal recycling yet.

Historical perspective of passive aerosol remote sensing: Bridging the years

LORRAINE A. REMER AND OMAR TORRES

NASA Goddard Space Flight Center, Greenbelt MD 20771
USA (Lorraine.A.Remer@nasa.gov,
Omar.O.Torres@nasa.gov)

For nearly three decades space sensors designed for other purposes were used to observe, quantify and characterize atmospheric aerosols. During this 'heritage period', algorithm development focused on three primary methods. (1) Occultation methods that measure the extinction of solar radiation and provide vertical profiles of aerosol extinction through the stratosphere. (2) Dark target methods that use the brightening of the scene to infer aerosol loading. (3) UV methods that use the deviation of the observed signal from expected Rayleigh scattering values. Besides these three main methods applied to the SAM/SAGE, AVHRR and TOMS measurements, respectively, to produce long aerosol time series, other methods have been developed to make use of multiangle, polarization and geosynchronous capabilities. These satellite aerosol products applied to data collected in the 1980s and 1990s made way for the era of the modern sensors that began with the launch of Terra in late 1999. The modern sensors: MODIS, MISR, OMI etc., were designed with aerosol in mind, but specifically with the goal of providing information that would help reduce uncertainties in estimates of climate forcing. The quantitative information they provided was unexpectedly also used in other applications including air quality forecasting, public health studies, and long-range transport of dust and pollutants. Thus, the modern satellite data helps to bridge the scales, as well as the years.

An experimental study of brine-CO₂ metal fractionation: Applications to the geological storage of CO₂

KIRSTEN U. REMPEL*, AXEL LIEBSCHER,
WILHELM HEINRICH AND GEORG SCHEITLER

GFZ German Research Centre for Geosciences,
Telegrafenberg, 14473 Potsdam, Germany
(*correspondence: rempel@gfz-potsdam.de)

In this study, we have measured the fractionation of Fe, Cu, Zn and Na between brine and carbon dioxide at pressure-temperature conditions applicable to the saline aquifers used for the geological storage of CO₂, in order to evaluate the potential for trace element remobilization within the injected CO₂ plume. The experiments were carried out at 6.5-16 MPa and 60°C in a Ti autoclave loaded with a 20 wt% NaCl solution containing a known concentration of Fe, Cu or Zn, in addition to pressurized CO₂. Paired samples of brine and CO₂ were extracted from separate capillary lines and analyzed for metal concentrations.

The vapour-brine partition coefficients ($D_i^{v/l} = c_i^v/c_i^l$) ranged from 4×10^{-4} - 2×10^{-3} for Fe, 8×10^{-5} - 4×10^{-4} for Cu, 4×10^{-6} - 2×10^{-4} for Zn, and 1×10^{-6} - 1×10^{-3} for Na. The fractionation of these elements into the CO₂ did not cause a measurable decrease of their concentrations in the brine. The total element concentrations in the CO₂ samples ranged from 0.2 to 1.4 mg/kg (ppm) Fe, 0.1 to 0.6 mg/kg Cu, 0.004 to 0.4 mg/kg Zn and 0.6 to 92 mg/kg Na, and generally displayed a small positive correlation with CO₂ density. The values of $D_i^{v/l}$ in a CO₂ storage reservoir at 7-28.5 MPa and 35-98°C, in which the density of CO₂ is ~0.3-0.7 g/cm³ (as compared to 0.1-0.6 g/cm³ in this study), could be expected to be approximately equivalent to those determined from these experiments.

Considering the metal concentrations typical of brines in CO₂ storage aquifers that have reacted with CO₂ and sandstone (20-200 mg/kg Fe, 0.3-1 mg/kg of Cu, 3-5 mg/kg Zn), and neglecting the increased solvent capability of higher-density CO₂, these results suggest that a plume of injected CO₂ could contain up to 0.1 mg/kg Fe, 0.3 µg/kg Cu and 1 µg/kg (ppb) Zn, in addition to 16 mg/kg Na. At a Sleipner (North Sea)-sized reservoir used to store 14 Mt of CO₂, this would lead to the mobilization of about 1 t Fe, 5-10 kg Cu and Zn, and 200 t Na. In terms of long-term CO₂ storage, the potential consequences of these results include the precipitation of carbonate minerals in shallower, more distal regions of the aquifer and the transferral of metals to adjacent aquifer systems.

Combining NanoSIMS with STXM/TEM imaging to shed new light on organic matter contained in micron-sized particles

L. REMUSAT^{1*}, D. DERRIEN², P.J. HATTON², P. NICO³
AND J.-N. ROUZAUD⁴

¹CNRS/Muséum National d'Histoire Naturelle, Paris, France
(*correspondence : remusat@mnhn.fr)

²INRA Nancy, Champenoux, France

³Earth Science Division, LBNL, Berkeley, USA

⁴CNRS / ENS Paris, Paris, France

During the past 10 years, NanoSIMS has opened a new window on the study of the spatial distribution of light elements and their isotopic composition in natural samples. This instrument, with its high sensitivity, high precision and high spatial resolution, is suitable to study organic matter (OM) in meteorites and soil aggregates. Nevertheless, this technique suffers from the influence of the nature and the topography of the sample surface on the ion yield (the so called matrix effect) making the unambiguous characterization of the carbonaceous phases sometimes problematic. Moreover, the instrument cannot deliver molecular information, often required for the study of OM.

We illustrate here, through several examples, the benefits to combine NanoSIMS imaging with TEM and STXM, in order to improve the characterization of the carbonaceous materials and to strengthen the conclusions arisen from NanoSIMS images. This is a challenging task because these cutting edge techniques, while sharing high spatial resolution capabilities, have very different instrumental constraints.

The combination TEM+NanoSIMS was used to characterize the carbonaceous phases isolated from an Enstatite chondrite by HF/HCl dissolution. Graphite and poorly organised OM were identified by TEM (and Raman spectroscopy). With NanoSIMS, we measured the D/H and ¹³C/¹²C isotopic ratios along with the H/C and N/C elemental ratios of each phase, without ambiguity. Hence, we entirely characterized the carbonaceous phases separately to understand their relationship and origin.

We could also assess the fate of labelled OM after a 10 years *in situ* incubation experiment in a natural forest by combining NanoSIMS and STXM. While NanoSIMS was able to map ¹⁵N-labelled OM in soil microaggregates recovered from this forest, it has to be combined with STXM imaging (of the same aggregates) to reveal the molecular structure of the organic constituents. The combination of these instruments allows us to follow, at the submicron scale, the processes leading to the soil OM recycling.

Trace and rare earth elements characteristics of scheelite from the Sanjiazi tungsten deposit in Siping area, Northeastern China

Y.S. REN^{1*}, H. WANG¹, N. JU¹ AND C.Z. WU²

¹College of Earth Sciences, Jilin University, Changchun 130061, China (*correspondence: renys@jlu.edu.cn)

²State Key Laboratory for Mineral Deposits Research (Nanjing University), Nanjing 210093, China

The Sanjiazi skarn scheelite deposit is lately discovered in northeast China and there are many key questions on its genesis still unresolved. Scheelite is a widespread mineral in many hydrothermal deposits, its trace and rare earth elements can be used to constrain the derivation of the metal and mineralising fluids [1, 2]. Trace elements and rare earth elements (REE) compositions of the scheelite from Sanjiazi deposit were analyzed by ICP-AES.

Scheelite in Sanjiazi deposit is depleted in Sr, Be, Co, Ni, Ta and with enrichment of such metallogenic elements as Pb, Zn, Mo, Bi and Ag. Generally, these enriched trace elements, together with W, are prone to accumulate in magmatic hydrothermal fluids and precipitate in mesothermal condition. Moreover, scheelite shows accordant primitive mantle-normalized trace element spidergram with the Mesozoic granite and pre-mineralizing diorite porphyry dikes, indicating that they have the common material source.

The total content of REE in scheelite is 134.59ppm. The content of the LREE is nearly equal to that of the HREE. Chondrite-normalized REE patterns of the scheelite are overall flat curves with obvious Eu peak, which indicates a strong LREE/HREE fractionation. Scheelite has strong positive Eu anomalies ($\delta\text{Eu}=2.05$), weak negative Ce anomalies ($\delta\text{Ce}=0.77$), low LREE/HREE (1.09) and $(\text{La}/\text{Yb})_N$ (0.54). The REE characteristics of scheelite in Sanjiazi deposit is similar to those in some skarn tungsten deposits in south China associated with magmatic hydrothermal fluid [4].

A conclusion can be safely drawn that the Sanjiazi tungsten deposit belongs to skarn ones, its ore source was derived from the granitic magmatic fluid instead of ore-hosting skarn. The Mesozoic granitic magmatism played an important role in scheelite mineralization in this area.

This research was supported by basic research grants from Jilin University (Grants 200903025 and 201004001).

[1] Brugger *et al.* (2000) *Contrib Mineral Petrol.* **139**, 251–264. [2] Xiong *et al.* (2006) *Acta Petrologica Sinica.* **22**(3), 733–741. [3] Zeng *et al.* (1998) *Geology-Geochemistry.* **26**(2), 34–38.

REE fractionation during crustal anatexis: Constraints from the South Bohemian batholith (Bohemian Massif)

M. RENÉ

Institute of Rock Structure and Mechanics, Academy of Sciences, Prague 8, Czech Republic (rene@irms.cas.cz)

The processes controlling rare earth element (REE) behaviour during origin of S-type granite melts have profound implications for REE abundances in these granites. For typical protoliths of S-type two-mica granites, such as are metapelites of the Moldanubian Zone from the Bohemian Massif (Central European Variscides), a high amount of bulk rock LREE are sited in monazite and of HREE in garnet, apatite and zircon. The LREE and Th concentrations of a metapelite-derived melt are buffered by monazite stability. During anatexis, dissolution of monazite, apatite and zircon in the melt results in increasing bulk REE abundances and LREE/HREE ratios with increasing temperature of melting and a negative Eu anomaly in the melt. Both these features are displayed in the REE geochemistry of two-mica granites from the South Bohemian batholith (SBB) in the Bohemian Massif.

Three main geochemical two-mica granite types can be distinguished in the SBB: the low-Th Deštná granite, the intermediate-Th Eisgarn granite and the high-Th Lipnice and Steinberg granites. Th concentrations and REE element patterns are quite distinct class marks for the above mentioned three geochemical types of two-mica granites. The highest bulk content of REE is significant for the Lipnice and Steinberg granites (207–242 ppm), whereas the lowest bulk of REE was observed in the Deštná granites (33–69 ppm). The content of REE is controlled by variable amount of apatite, monazite and zircon enclosed usually in biotite and/or in apatite. The accessory minerals assemblage in the Deštná granite consists of monazite, zircon, apatite and xenotime usually enclosed in K-feldspar. The Eisgarn granitic melt was generated from dehydration melting of biotite at temperatures in the range 830–850 °C, whereas the Deštná granitic melt was generated by dehydration melting of muscovite at temperatures in range 670–750 °C, in agreement with REE concentrations. The highest Th contents in monazite and high Th/U ratios are significant for monazites from the Lipnice and Steinberg granites. On the other hand, monazites from the Deštná granites show higher values of U and Y.

This study was supported by the Ministry of Education, Youth and Sports of the Czech Republic (project No. ME10083).

Quantification of waste silicates for mineral carbonation

P. RENFORTH^{1*},
C-L. WASHBOURNE² AND D.A.C MANNING²

¹Department of Earth Sciences, University of Oxford, Oxford, OX1 3AN, United Kingdom

(*correspondence: Phil.Renforth@earth.ox.ac.uk)

²School of Civil Engineering and Geosciences, Newcastle University, NE1 7RU, United Kingdom

Historic Production

Silicate minerals are an ubiquitous component of some anthropogenic material streams (cement, construction waste, slag, fuel ash etc.). Generally, they are produced by calcining carbonate minerals in the presence of silica (mine/aggregate waste is composed of naturally occurring silicates). We estimate that humans have produced approximately 89-103 billion tonnes (Gt) of silicate material since the early 1800's (Table 1; [1]). The fate of this material is likely one of several namely, disposal in the ocean or in landfill, spread onto land, or material in engineering. While some of this material has carbonated in the environment [e.g. 2], it is possible that a substantial quantity remains available for carbon capture (with a total potential in the order of 10^3 MtC).

Material	Current (Mt a ⁻¹)	Historic (Mt)
Aggregate fines	3, 300	unknown
Mine waste	2, 000-6, 500	unknown
Cement kiln dust	420-568	9, 000-12, 000
C & D waste	1, 400-5, 900	*
Slag	380-500	12, 100-15, 900
Fuel Ash	198-383	76, 000-14, 600

Table 1: Global production estimates for anthropogenic silicates since the early 19th century. *historic production of C&D waste is unknown, but the upper limit is based on the historic production of cement (60 Gt). See [1] for more details.

Current production

Current annual production of silicate material is estimated to be approximately 7.6-17.2 Gt. With an estimated carbon capture potential of around 190-332 Mt of carbon. Production of silicates is increasing by approximately 2 % a⁻¹, largely in China, carbonation of which is likely to an increasingly important role for mitigating some of the associated carbon emissions.

[1] Renforth, *et al.* (2011) *Environ Sci Technol* **45**(6), 2035-41. [2] Manning (2001) *Min Mag* **65**(5), 603-10.

Further progress towards synchronizing geochronometers

PAUL R. RENNE^{1,2}

¹Berkeley Geochronology Center, 2455 Ridge Rd., Berkeley, CA, USA 94709 (prenne@bgc.org)

²Dept. of Earth and Planetary Science, Univ. California, Berkeley, CA, USA 94709

A recent calibration of the ⁴⁰Ar/³⁹Ar system [1] has largely reconciled the ⁴⁰Ar/³⁹Ar and ²³⁸U/²⁰⁶Pb geochronometers, but reveals several apparent inconsistencies with previous results. For example, recalculating a previous result [2] for the Cretaceous/Paleogene boundary (KPB) produces an age of 66.236 ±0.060 Ma (1σ here and throughout), slightly older beyond stated errors than an astronomically tuned age of 65.957 ±0.040 Ma [3] for the KPB at Zumaia (Spain). To investigate this disparity, renewed analysis of circum-KPB events has been initiated. Arguably the most definitive age for the KPB would be that for the Beloc (Haiti) tektites. Previous results for these tektites are consistent with a KPB age though not with sufficient precision to advance the present discussion. With rigorous attention to neutron fluence monitoring via the Fish Canyon sanidine (FCs) standard, a suite of Beloc tektites was irradiated along with sanidine from a Z-coal tonstein (stratigraphically ~60 cm above the KPB) from the Hell Creek area of Montana (USA). Three positions of the standard closely bracketing the samples yielded an average *J*-value with 0.02% precision. Seven tektites with Ca/K between 2.8 and 4.8 heated incrementally in 14-18 steps with a CO₂ laser and analyzed with a single collector MAP 215 mass spectrometer all yielded 100% concordant age spectra. The weighted mean of the seven plateau ages, calibrated per [1], is 65.946 ±0.067 Ma, indistinguishable from the astronomical age [3]. Combined with previous results [4, 5] a weighted mean age of 66.043 ±0.049 Ma is obtained for the Beloc tektites. Additional work in progress will further refine the age of the tektites and enhance their importance to a precise age for the KPB. Calibrated per [1], 71 single crystals of sanidine from the Z-coal yielded an age of 65.926 ±0.066 Ma. No xenocrysts are evident in the data, justifying step-heating analysis of multigrained aliquots currently in progress. These results disfavor the possibility raised by [1] that the astronomical age [3] of the KPB is miscalibrated by a 405 ka eccentricity cycle and serve to validate intercalibration between the Ar/Ar, U/Pb and robust astronomical chronometers.

[1] Renne *et al.* (2010) *GCA* **74**, 5349–5367. [2] Swisher *et al.* (1993) *CJES* **30**, 1981–1996. [3] Kuiper *et al.* (2008) *Science* **320**, 500–504. [4] Izett *et al.* (1991) *Science* **252**, 1539–1542. [5] Swisher *et al.* (1992) *Science* **257**, 954–958.

Continental flood basalts and biotic crises: Does the Paraná-Etendeka exception prove the rule?

PAUL R. RENNE^{1,2}

¹Berkeley Geochronology Center, 2455 Ridge Rd., Berkeley, CA, 94709, USA (prenne@bgc.org)

²Dept. Earth & Planetary Science, Univ. California, Berkeley, CA, 94720

The temporal correlation between continental flood volcanism and severe paleoenvironmental effects including mass extinctions are well known although the causal mechanism (s) remain unclear. Various metrics of the magnitude of either phenomenon (e.g. % taxa extinct or volume of magma erupted) define positive correlations but the extent of scatter in such relationships implies that other variables are important. Some of the larger CFB's that fail to coincide with profound extinction events (e.g. Ferrar-Karoo) turn out to be temporally distributed over several million years and their anomalously feeble impact may be due to lower effusion rates reducing atmospheric loading rates for volcanogenic volatiles. Among the largest CFB's clearly erupted mainly over a short time interval (< 3 Ma; e.g. Siberian, CAMP and Deccan), the Paraná-Etendeka province (PEP) stands out distinctly as an outlier in the correlation with biotic crises. Extensive incremental-heating Ar/Ar data demonstrate unequivocally that the PEP was brief (>90% erupted 135-132 Ma; calibration per [1]), and previous studies suggesting a protracted event spanning ~10 Ma were flawed. The resolution of this apparent conundrum may lie in the importance of thermogenic volatiles (mainly CO₂, methane and sulfates) released from country rocks during CFB events, as has been proposed in many recent studies. Virtually throughout the PEP, volcanic effusions were emplaced atop up to 450 m of eolian sands of the Botucatu and Etjo Fms., and the nearest-surface carbonaceous strata (< 80 m thick Irati Fm.) at the time of the PEP event were >2 km beneath the surface. We suggest that thermogenic CO₂ was minimal in the PEP event due to a combination of (1) relatively sparse carbonaceous sediments in the thermal aureole; (2) depth (lithstatic pressure) of these sediments being sufficiently high to retain CO₂ in metamorphic assemblages and inhibit brittle fracturing, limiting transmissivity for thermogenic volatiles. Moreover, PEP magmas are exceptional among the largest brief CFB's in the dominance of lithospheric melt sources, suggesting minimal magmatic contributions to volatile loading of sulfates and CO₂.

[1] Renne *et al.* (2010) *GCA* **74**, 5349–5367.

Iron species in soils on a mofette site studied by Fe K-edge XANES

T. RENNERT^{1*}, K. EUSTERHUES¹, V. DE ANDRADE², J. PRIETZEL³ AND K.U. TOTSCHKE¹

¹Institut für Geowissenschaften, FSU Jena, Germany
(*correspondence: thilo.rennert@uni-jena.de)

²NLSL-II, Brookhaven, USA

³Lehrstuhl für Bodenkunde, TU München, Germany

Ascending geogenic CO₂ is a soil-forming factor on mofette sites: With increasing soil CO₂, the amounts of pedogenic Fe decrease, and Fe oxides are poorly crystalline according to extraction with oxalate and dithionite [1]. To further study the Fe speciation (especially that of Fe (II)), we applied spatially resolved X-ray absorption near-edge spectroscopy (XANES) to soil samples from a mofette site in the NW Czech Republic. The samples originated from spots with 4 and 100% CO₂ in the soil atmosphere. Point XANES spectra (1 μm²) at the Fe K-edge (7112 eV) were collected at beamline ID 21 of the ESRF, Grenoble, in fluorescence mode. Altogether, we recorded 73 spectra on regions of interest identified from 5 fluorescence maps of 3 thin sections prepared from undisturbed soil samples. Linear combination fitting of reference spectra from a whole of 51 references including various Fe (II)- and Fe (III)-bearing minerals and organic species was used for Fe-species identification. In almost all cases, two references were sufficient as checked by the sum of squared differences.

The Fe-fluorescence maps explicitly showed a heterogeneous spatial distribution of Fe with accumulation in larger pores (e.g. former root channels) and depletion in the soil matrix. We conclude small particles (< 1 μm), because point spectra could not be explained by a single reference spectrum. We identified smectites, illite and ferrihydrite in the Fe-accumulation zones. Iron in the Fe-depletion zones was mostly present in clay minerals such as different smectites, illites and chlorites in 68 spectra. Especially at 100% CO₂, we identified Fe (II)-containing minerals such as green rust, vivianite, siderite and magnetite in the soil matrix. According to XANES, Fe sulphates and Fe sulphides were not present. We detected only slightly more Fe (II) complexed by organic species at 4% CO₂ than at 100% CO₂ indicating that CO₂ impedes the association of organic matter with Fe-containing minerals. This is in line with the observation of mainly non-decomposed, probably particulate organic matter in soils on mofette sites and only a small fraction of organo-mineral associations [1].

[1] Rennert *et al.* (2011) *Eur. J. Soil Sci.* in press

Constraining the fidelity of sulfate-oxygen in the geological record

VICTORIA RENNIE* AND ALEXANDRA V. TURCHYN

Dept. Earth Sciences, University of Cambridge

(*correspondence: vcr22@cam.ac.uk)

The oxygen isotope composition of aqueous sulfate ($\delta^{18}\text{O}_{\text{SO}_4}$) in natural environments reflects microbially-mediated oxygen isotope exchange with water during bacterial sulfate reduction, as well as oxygen isotope fractionation during sulfide oxidation. When the $\delta^{18}\text{O}_{\text{SO}_4}$ is preserved in the geological record, it is a potentially powerful tool for reconstructing these key microbial metabolisms (sulfate reduction and sulfide reoxidation) over time. This may be of critical importance in the NeoProterozoic, when the existence and evolution of these metabolisms is intimately related to the redox evolution of the Earth's surface environment.

The viability of using the $\delta^{18}\text{O}_{\text{SO}_4}$ to elucidate these processes in both modern and ancient environments rests on the assumption that there is minimal abiotic exchange between sulfate-oxygen and water-oxygen during the variety of conditions imposed by sample storage, mineral extraction, and laboratory processing. Previous work has shown that oxygen isotope exchange between sulfate and water occurs readily at very low pH (<1) and/or at high temperatures (>100°C). Aqueous samples are routinely acidified prior to analysis, but current estimates for timescales of exchange under these conditions rely on extrapolation from highly dissimilar solutions.

We present results from exchange experiments mimicking pore fluids under a variety of conditions. These rule out short and medium-term exchange of sulfate-oxygen with water during sample treatment over a range of acidic conditions. Additionally, the presence of aqueous sulfide in sedimentary pore fluids may facilitate sulfate-oxygen exchange with water-oxygen via the transient formation of thiosulfite complexes. Our experiments constrain the range of pore fluid (and natural) conditions over which $\delta^{18}\text{O}_{\text{SO}_4}$ will remain stable. Finally, in contrast with aqueous sulfate, results from extracted carbonate-associated-sulfate (CAS) show that mineral bound $\delta^{18}\text{O}_{\text{SO}_4}$ is not solely a function of the oxygen isotope composition of the aqueous sulfate during carbonate crystallization. This points towards further controls on $\delta^{18}\text{O}_{\text{SO}_4}$ in CAS possibly imposed by the presence of the carbonate lattice.

Investigating the transport of strontium through biogenic hydroxyapatite Barriers

J.C. RENSHAW*, S. HANDLEY-SIDHU,
F. SINCLAIR SMITH, Q. GRAIL, M. CUTHBERT, M RILEY
AND L.E. MACASKIE

University of Birmingham, Edgbaston, Birmingham B15 2TT,
UK (*correspondence: j.c.renshaw@bham.ac.uk)

Hydroxyapatite (HAp) has potential as a material for the remediation of metal contaminated waters [1] and in reactive barriers [2]. *Serratia* sp. cells bio-manufacture nanophase hydroxyapatite (Bio-HAp) from the substrates glycerol 2-phosphate and Ca^{2+} [3]. This Bio-HAp has properties that increase metal uptake (e.g. decreasing crystallite size, increasing specific surface area and organic content).

Column experiments were conducted to investigate the transport of Sr^{2+} (0.5 mg) through Drigg sand (sampled near low level waste repository) and Drigg sand containing either 0.25% commercial (Com-HAp) or Bio-HAp. Figure 1 shows the elution of Sr^{2+} through columns containing groundwaters (GW) with high levels of competing ions (100 and 50 mg L^{-1} of Ca^{2+} and Mg^{2+} , respectively). The Com-HAp and Bio-HAp retained 2.5 and 3.7 mg of Sr^{2+} per 1 g of HAp, respectively. Work is now being undertaken with GW containing lower cation concentrations. Numerical modelling is also being carried out to test various hypotheses regarding Sr^{2+} transport processes.

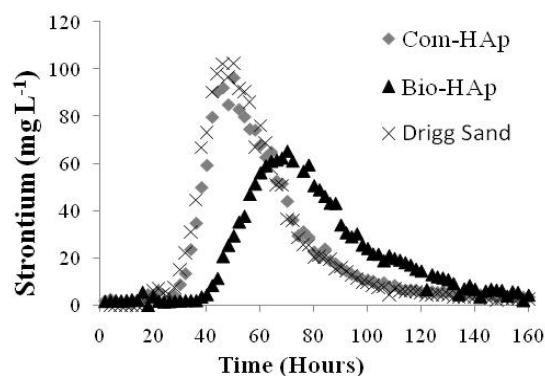


Figure 1: The Transport of Sr^{2+} through Drigg Sand (x), with Com-HAP (♦) and Bio-HAp (▲)

- [1] Handley-Sidhu (2011) *Biotechnol. Lett.* **33**, 79–87.
[2] Simon (2004) *Sci. Total Environ.* **326**, 249–256.
[3] Thackray (2004) *J. Mater. Sci. Mater. Med.* **15**, 403–406.

Time scales of metasomatism, differentiation and degassing at Volcán de Colima

O. REUBI¹, K.W.W. SIMS², J. EIKENBERG³,
M.K. REAGAN⁴, N.R. VARLEY⁵ AND B. BOURDON^{1,6}

¹ETH Zurich, Switzerland (olivier.reubi@erdw.ethz.ch)

²University of Wyoming, USA

³Paul Scherrer Institute, Switzerland

⁴University of Iowa, USA

⁵Universidad de Colima, Mexico,

⁶Ecole Normale Supérieure de Lyon and CNRS, France

Volcán de Colima, Mexico (VDC) nearly continuous activity since 1998 provides a unique opportunity to assess the time scales characteristic of intermediate arc volcanoes. VDC andesites have $(^{238}\text{U}/^{230}\text{Th}) = 1$, but have significant excesses of ^{231}Pa and ^{226}Ra . These excesses, and relatively low Th contents, indicate that addition of Th-rich sediments in secular equilibrium to the mantle source cannot account for ^{238}U - ^{230}Th equilibrium, as generally advocated. In the VDC case, the U-series suggest that slab fluids carrying U were not added to the mantle wedge in the last 350 kyr and ^{226}Ra excesses are most likely mantle melting signals. ^{226}Ra and ^{231}Pa excesses indicate that the time scales of differentiation from primary mafic to dacitic melt (composition of the crystallizing melt) are short and < 1.6 kyr.

Most 1998-2010 magmas have $(^{210}\text{Pb}/^{226}\text{Ra}) = 1$, however small ^{210}Pb deficits are measured in few samples. This indicates that the magmas erupted at the onset of the eruptive phase (1998) degassed either more than 100 yr ago or within few months of eruption. Observed changes in petrology and the SO_2 flux measured prior to 1998 concur to suggest that significant degassing occurred within few months of eruption. Increasing maximum ^{210}Pb deficits with time are consistent with progressive degassing of a magma batch since 1998, but require several influxes of undegassed magmas and incomplete mixing between the magma batches. Influxes of undegassed magmas may cause the observed shifts in activity from Vulcanian to effusive.

Long residence (> 6 Ma) time of Paleoproterozoic seawater sulfate revealed by *in situ* and *ex situ* sulfur isotope measurements

MARLENE REUSCHEL^{1*}, M. WHITEHOUSE²,
V.A. MELEZHNIK³, A. LEPLAND³, A.E. FALLICK⁴ AND
H. STRAUSS¹

¹Corrensstrasse 24, D-48149 Münster, Germany

(*correspondence: marlene.reuschel@uni-muenster.de)

²Swedish Museum of National History, Box 50007, SE-10405 Stockholm, Sweden

³Geological Survey of Norway, Leiv Erikssons vei 39, N-7491 Trondheim, Norway

⁴Scottish Universities Environmental Research Centre, Rankine Avenue, East Kilbride, G75 0QF, Scotland, UK

The 2.0 Ga Tulomozero Formation, Fennoscandian Shield, NW Russia, consists of shallow marine carbonates and silicilastics, dissolution breccias and widespread syndepositional marine evaporites, now mostly present as pseudomorphs after Ca-sulfates.

Ex situ measured carbonate-associated sulfate (CAS) and breccia-associated sulfate (BAS) throughout the entire formation ($\delta^{34}\text{S}_{\text{CAS}} = 10.9 \pm 2.7$ ‰, $\delta^{34}\text{S}_{\text{BAS}} = 9.0 \pm 1.1$ ‰) resemble the *in situ* SIMS sulfur isotope data from relics of sulfate evaporites in ubiquitous pseudomorphs after Ca-sulfates ($\delta^{34}\text{S}_{\text{anhydrite}} = 9.6 \pm 1.0$ ‰; $\delta^{34}\text{S}_{\text{barite}} = 11.0 \pm 3.1$ ‰).

The $\delta^{34}\text{S}$ record of the Tulomozero sulfates matches the sulfur isotopic composition of other broadly time equivalent evaporite successions [1, 2]. Furthermore, the homogeneity of the sulfate sulfur isotope record within the Tulomozero Formation together with an estimated minimum depositional time of the formation (based on average carbonate precipitation rates) suggests a residence time of seawater sulfate in the Mid-Proterozoic of at least 6.5 Ma.

Consequently, the apparent presence of Ca-sulfate evaporites and the homogeneity of sulfate sulfur isotope data from various lithologies support the existence of a sizeable seawater sulfate reservoir already in the Mid-Paleoproterozoic ocean.

[1] Schröder *et al.* (2008) *Terra Nova* **20**, 108–117. [2] Guo *et al.* (2009) *Geology* **37**, 399–402.

Electrical conductivity of the serpentinised mantle and fluid flow in subduction zones

BRUNO REYNARD^{1,2}, KENJI MIBE²
AND BERTRAND VAN DE MOORTELE¹

¹Université de Lyon, CNRS, ENS de Lyon, Parvis Descartes, 69007, Lyon, France (bruno.reynard@ens-lyon.fr)

²Earthquake Research Institute, University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-0032 Japan (mibe@eri.u-tokyo.ac.jp)

In the mantle wedge of subduction zones, electromagnetic profiles reveal high electrical-conductivity bodies. In hot areas ($> 700^{\circ}\text{C}$), water released by dehydration of the slab induces melting of the mantle under volcanic arcs that can explain the observed high conductivities. In the cold ($< 700^{\circ}\text{C}$) melt-free fore-arc mantle wedge, fluid water migrates and causes serpentinisation detected as low seismic wave velocities in the mantle wedge. High conductivities in the serpentinized wedge may picture serpentinisation or instantaneous fluid flow depending on serpentine electrical conductivity. We measured the electrical conductivities of three natural serpentine samples from subduction zone context using complex impedance measurements, and find they have low electrical conductivities ($< 10^{-4} \text{ S. m}^{-1}$) similar to those of dry mantle minerals below 700°C . Because of the negligible conductivity of serpentine, electrical conductivity in the hydrated mantle wedge is only sensitive to the fluid content and salinity, not to serpentinisation. A small fraction (*ca.* 1% in volume) of connective high-salinity fluids accounts for the highest observed conductivities. The low-salinity fluids ($\leq 0.1 \text{ m}$) released by slab dehydration evolve towards high-salinity ($\geq 1 \text{ m}$) fluids during progressive serpentinisation of the mantle wedge. These fluids can mix with arc magmas at depths and account for high chlorine/water ratios in arc lavas.

Modelling vertical stable isotope and elemental distributions in the upper ocean

BEN C. REYNOLDS AND GREGORY F. DE SOUZA

ETH Zurich, Institute of Geochemistry and Petrology, Zurich, Switzerland (*correspondence: reynolds@erdw.ethz.ch)

The stable isotope compositions of elements dissolved in seawater are a valuable source of information on ocean biogeochemistry. Depth profiles of elemental ratios and isotope compositions often show large vertical gradients near the surface due to the uptake and fractionation by biota in the surface ocean. However, interpretations of observed distributions are often based on overly simplistic models of the fractionation behaviour, such as the Rayleigh equation [1], which ignore dynamic mixing in the oceans. The processes governing the spatial and chemical gradients do not fit the fundamental assumptions underlying Rayleigh-type behaviour. In order to more effectively describe the processes governing the depth profiles we argue that simple one-dimensional advection-diffusion-reaction (1-D ADR) models should be applied. These models incorporate the interaction between biogeochemical cycling and physical redistribution, and thus help to realise the true potential of stable isotopic tracers to quantify biogeochemical cycling.

Applications of our models to stable isotope variations in the upper ocean demonstrate that, within the thermocline, elemental concentration gradients and isotope distributions are strongly affected by physical mixing processes. The biological cycling, however, controls the composition of the surface mixed layer. Our models provide a combined physical-biological framework for the interpretation of novel metal stable isotope variations currently being determined. It is apparent from the models that estimations of the fractionation factors derived using the Rayleigh equation will systematically underestimate the true values; the degree of underestimation depending upon the relative importance of mixing. We show how our models can be applied to published datasets.

[1] Rayleigh (1902) On the distillation of binary mixtures. *Phil. Mag.* **4**, 521.

Assessment of water/rock interaction to safeguarding drinking water quality

M. REZVANIKHALILABAD

Mahabghodss, Integrated studies on water, soil and environment Division, Affiliated to Ministry of Power, Tehran, IRAN, P.O. Box: 19395-6875 (mahnazrezvany@yahoo.com)

Water storage, transfer and deliver to end users for drinking and sanitary purposes have been a challenge over the years in IRAN. IWRM strategies were focused to ease the Scio-economical aspects of the water shortage that vulnerability of the resources and the Environmental flow simply was ignored. Geological characteristics of artificial lakes and their natural or manmade transfer routs, exclusively studied from geotechnical prospects. Water/Rock interaction of bed rocks or reservoir body was neglected.

Chamgardalan dam located in IYLAM province, which water/rock interaction made an odor and taste problem in reservoir water is the best example [1]. Reservoir rocks consist of interbedded coal layers highly rich in sulfur and iron changed the quality of the dam lake water over years. The costly remediation study is ongoing (2009 till now). Contamination changes the quality of the water as effective as intensive interaction of water with bed rocks. In small projects in local or regional scale considering such studies will be costly and developers may not include it in their action plans. National or international fundamental research should provide such information.

In the new approach a methodology established to consider the effect of geological formation on the quality of surface water in the basin scale. Faults, intrusives, salt domes & massive evaporation sediments, closed & operating mines, progressive alteration, and etc. were assessed. Defined guideline played a major role in IWRM study of Caspian and Uromieh lake basins in north of Iran which has been carried out in 2010 [2]. The result concluded in generating a 1:250000 scale geological map on potential effect of geological formations on surface water quality regarding the heavy metals & trace elements, salinity and sediment production. The integrated map will give a glimpse of possible potential which has to be assessed meticulously.

- [1] Khajehzadeh (2011) '*Clean Water*' Work shop, Iran
 [2] Chehrehnegar (2010) Iran water Resource management Conf. Proc.

The variation of magnetic susceptibility with grain size: Its implication on forensic studies

C. RIBEIRO, A. GUEDES*, B. VALENTIM, H. SANT'OVAIA, H. RIBEIRO AND F. NORONHA

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

Detectable quantities of magnetic and paramagnetic minerals are almost always found in soils, being the magnetic susceptibility the sum of all contributions from the forming minerals, and varying due to concentration and composition those minerals. The magnetic susceptibility (MS) measurements of soils at room temperature are non-destructive. Additionally, does not require sample preparation, and can be used as a simple and fast method which may be operable in small samples. So, MS is an excellent tool for studies of soils being used as trace evidence in forensic investigations.

During this study, twenty four soil samples were collected on two different coastal sites from North Portugal, Mindelo and Cabedelo. At each site twelve samples were collected with a plastic spade from the surface soil. The samples were subjected to dry sieving using a column of sieves, resulting in different size classes: >2mm; [2mm-1mm]; [1mm-0.5mm]; [0.5mm-0.25mm]; [0.25mm-0.125mm]; [0.125mm-0.063mm] and <0.063mm. The MS analyses were performed directly on 1g of each size fraction after homogenisation, applying an external magnetic field of 300 A/m to the sample, and a Kappabridge, model KLY-4S of Agico balance equipped with the Sumean software used. The MS was calculated in m³/kg. It was observed that in all samples the MS increases from coarse to fine grain size. The coarser fractions >2mm and [2mm-1mm] generally show negative values of MS and this is generally followed by low positive values of MS that increase ten times on the next fine fraction. These data show that fine fractions are the mostly enhanced in terms of MS. Finally, higher reproducibility was observed on the lower size fractions.

We conclude that although the magnetic susceptibility analysis is suitable to be used in a forensic soil investigation, it is important to adopt the same protocol during the analysis.

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

Phosphorus mobility in lake sediments

D.C. RIBEIRO, G. MARTINS, A.G. BRITO,
AND R. NOGUEIRA

University of Minho, Campus de Gualtar, 4710-057 Braga,
Portugal (dcribeiro@deb.uminho.pt)

For several decades, the paradigm that phosphorus release in sediments is the consequence of the absence of oxygen in the hypolimnium is recurrent among limnologists. At that time, the relation between the reduction of Fe (III) complexes and phosphorus (P) release in anoxic sediments was stated as hypothesis and later demonstrated. Although the theoretical statements matched the practical findings, these could not be generalized since several field observations and laboratory experiments lead to other conclusions. This has led to a need of deeper understanding of factors that influence the phosphorus mobility besides oxygen concentration.

P mobility in lake sediments was assessed through a microcosm experiment. Sediments from Lake Furnas (Portugal) were examined through a P sequential extraction procedure before and after a shift in redox potential achieved by means of O₂ concentration variation. Microsensors were used to measure pH and O₂ concentration in the sediments, during oxic and anoxic periods. The sediments that were under anoxic conditions released P from Fe minerals (BD fraction) compared with the initial conditions. The P bounded to Al minerals remained approximately the same comparing with the initial conditions (NaOH fraction), indicating that this fraction remains stable with redox potential changes. When the reactor was exposed to O₂, Fe minerals re-adsorbed P which is consistent with the classical paradigm. However, we found that Al minerals released P in the oxic phase of the experiment leading to a P concentration raise in water column. The reason was not due directly to O₂ concentration but to a raise in pH. A possible explanation is related with the recent findings that oxygen in the oxic layers could oxidize H₂S in deeper sediment layers through a microbial network connected with nano-wires from H₂S in the deep anoxic sediment layer to oxygen in the upper layers, with concomitant pH raise.

Calcium minerals bounded to P remained stable between anoxic and oxic conditions (HCl fraction), as well as the refractory pool (NaOH 85 °C). P bounded to Al and Fe represent the most mobile fraction and is an indicator of exhaustion of sediments' retention capacity.

Zoned calc-silicated boudins in quartz-pelitic metatextitic rocks, NW Portugal

M.A. RIBEIRO*, M. AREIAS, A. DÓRIA AND P. FERREIRA

Centro Geologia, Faculdade de Ciências, Univ. Porto R.
Campo Alegre, 4169-007 Porto, Portugal
(*correspondence: maribeir@fc.up.pt)

In the coastal zone of NW Portugal, at north of Porto, a banded and sheared migmatitic structure outcrops, with a general NNW-SSE to NW-SE trend. This structure shows strong asymmetric interlayer folds with generally subvertical axes, plunging to SE. Metatextites are widely prevalent, over diatexite lithologies. These are leucocratic to mesocratic with no foliation or locally with an incipient one, with a very irregular orientation. The metatextite lithologies present a well defined foliation in the metapelitic or quartz-pelitic melanosome, trending N160°-N175°, 75°-90° NE, or N15°, 90°, but with considerable dispersion. The neosome occurs as irregular lenticles, elongated parallel to this foliation.

Calc-silicated rocks occur in small ovoid or ellipsoid bodies, always with internal zoning, more or less concentric: in the core, a zone of granoblastic texture with quartz +clinopyroxene+wollastonite+garnet+sphene+ plagioclase +/- biotite, surrounded by a zone of granoblastic texture of lower granularity with quartz+biotite+plagioclase+sphene+ garnet+/- clinopyroxene+amphibole. The outer zone (metatextites) is more irregular and presents heterogranular texture with variation in the % of biotite associated with quartz, muscovite and feldspar +/- sillimanite. The core zone of the ellipsoid bodies is relatively richer in CaO and Al₂O₃ while the intermediate zone is enriched in SiO₂ and Na₂O. The surrounding metatextites present higher content of K₂O and similar content of Na₂O, regarding the buffer zone.

The foliation of the metatextites is deflected around the calc-silicated ellipsoidal bodies of variable size (5 cm to 1 m), and its major axis elongation has general direction NNW-SSE, parallel to the foliation of the surrounding migmatites. These bodies represent 'resister' of palaeosome in the migmatites that have undergone metasomatism during the migmatitisation and boudinage during the coeval shear deformation of the surrounding metatextites, trending NNW-SSE. The protolith of these calc-silicated rocks may be a Ca-rich quartz-pelitic metasedimentary rock. It is thought to correspond to a Ca-plagioclase-rich greywacke.

This work has been financially supported by POCI 2010 (FCT-Portugal, COMPETE/FEDER).

Conditions for uranium transport in unconformity-related U deposits

A. RICHARD^{1*}, C. ROZSYPAL¹, J. MERCADIER¹,
D.A. BANKS², M. CUNY¹, M.C. BOIRON¹
AND M. CATHELIN¹

¹G2R, Nancy-Université, CNRS, BP 239, 54506 Vandoeuvre-lès-Nancy Cedex, France

(*correspondence: antonin.richard@g2r.uhp-nancy.fr)

²School of Earth and Environment, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, UK

Our knowledge of massive metal transfer within the Earth's crust is limited by the lack of direct analysis of deep fluids and experimental work. During the Mesoproterozoic Era (1.6-1.0 Gyr ago), giant uranium deposits were formed from large-scale circulation of uranium-bearing brines at the interface between sedimentary basins and their crystalline basements (unconformity-related uranium deposits) [1, 2].

However, the key processes leading the exceptionally high ore grades and tonnages of these deposits, especially the transport of uranium in the brines, remained poorly understood.

Here, we show that the uranium was transported under unexpectedly low pH conditions and at the highest concentrations recorded for crustal fluids so far.

By using laser ablation inductively coupled plasma mass spectrometry analysis of natural fluid inclusions we found that the uranium concentration varies over four orders of magnitudes in the ore-forming brines (from 10^{-6} up to 2.8×10^{-3} mol.l⁻¹ U).

We combined these results with the first experimental determination of the solubility of U (VI) in H₂O-NaCl mixtures analogous to the ore-forming brines (up to 6 mol.l⁻¹ NaCl) and we found that the pH (between 3 and 4 at 155°C) is the major control on U (VI) solubility in these conditions.

More generally, models for the formation of 'world-class' hydrothermal ore deposits imply either protracted fluid flow with relatively low metal concentration, or more discrete events characterised by exceptionally metal-rich fluids. Our results strongly suggest that the second hypothesis can be applied to the world's richest uranium deposits.

[1] Richard *et al.* (2010) *Terra Nova* **22**, 303–308. [2] Boiron *et al.* (2010) *Geofluids* **10**, 270–292.

Taking advantage of both U-Th and U-Pb disequilibrium methods for speleothem geochronology

D.A. RICHARDS^{1*}, C.J.M. SMITH¹, P.L. SMART¹,
A.R. FARRANT², R.R. PARRISH³ AND D.C. FORD³

¹Geographical Sciences & Bristol Isotope Group, Univ. Bristol, UK

(*correspondence: david.richards@bristol.ac.uk)

²British Geological Survey, UK

³NERC Isotope Geosciences Laboratory, UK

⁴Geography and Earth Sciences, McMaster Univ. Canada

The success of speleothems as accurate chronological markers of landscape evolution and climate change is well acknowledged, but accuracy and precision become particularly limiting beyond 350 ka for a number of reasons beyond the theoretical, including interlaboratory comparison and common standard/half-life usage. We illustrate here plans to take advantage of high-precision U-Th methods in concert with U-Pb techniques [1-3], which have the added advantage of community-supported accuracy (via EARTHTIME), to date important material in the range 0.35 to 1 Ma.

We are currently optimising a combination of U-Th-Pb techniques that utilise solution and *in situ* methods with MC-ICP-MS at the BIG and NIGL to analyse a variety of secondary calcite deposits previously demonstrated to be beyond the age range of traditional methods. We focus on an unusually U-rich flowstone sample ($>60 \mu\text{g g}^{-1} \text{ }^{238}\text{U}$) from the Grotte Valerie system in the Mackenzie Mountains, NWT, Canada [4]. Ten high-resolution sub-samples were cut as wafers from the growth layers identified in original publication. Several sub-samples have an extremely high $^{230}\text{Th}/^{232}\text{Th}$ atomic ratio (> 3), which demonstrates that the Th isotope signal is dominated by the radiogenic component. We obtained an age and 2σ uncertainty of 120 ± 1.2 ka from the youngest phase of growth. U-Th ages for older sub-samples, between 8.5 and 30 mm above base are not finite, and are therefore > 500 ka. We present preliminary U-Pb ages and *in situ* LA U-Th-Pb and gamma mapping for this older material. The latter are also used to screen future sub-samples useful for a host of applications.

[1] Cliff *et al.* (2010) *Quat. Geochron* **5**, 452–258. [2] Polyak *et al.* (2008) *Science*, **319**, 1377–1380. [3] Woodhead *et al.* (2006) *Quat. Geochron*, **1**, 208–221. [4] Harmon *et al.* (1977) *Canadian J. Earth Sci* **14**, 2543–2552.

From the Lower Amazon to the Mekong: How floodplains modulate fluxes of carbon from land to the sea

JEFFREY E. RICHEY*, JOHN M. MELACK
AND KIMBERLEY N. IRVINE

(*correspondence: jrichey@uw.edu)

The large rivers of the tropics account for a significant fraction of the flux of carbon to the oceans and of fluvial and lacustrine CO₂ and CH₄ to the atmosphere. Through dynamic hydrologic, geomorphological, and biogeochemical processes, their floodplains and deltas provide a significant modulation to the materials transported by the river. In the process, the template set by these surface processes produces strong chemical disequilibria at the interface between water and sediments, impacting reactions down through the sediment column. But the magnitude, and even the specific dynamics, of these processes is poorly known. The last sampling stations on major rivers are typically above the delta and channel regions of tidally-impacted lower rivers, precisely to avoid dealing with the complexities. Which means that not only are time-series of the fluxes and controls from upriver not well-known, what happens in the lower river is even more poorly characterized. Here we examine recent results from the lower Amazon River and its floodplain, in comparison to the lower Mekong and the Tonle Sap Great Lake. About 20% of the Amazon basin is seasonally inundated, with extensive floodplains along several thousand kilometers of the main channel. These aquatic environments are sites of high evasion rates of methane and carbon dioxide, up to ten times the riverine flux to the ocean, and equivalent to sequestration by the forest. Considerable spatial and seasonal differences in carbon dioxide concentrations and evasion occur in the large shallow lakes common in the lower floodplains, with floodplain and geomorphological processes attenuating the chemical signal at the 'traditional' measuring station of Obidos. In contrast, floodplains of the Mekong are constrained to the lower reaches, with fluxes impacted by the Tonle Sap great lake. Higher pH than the Amazon results in greater export of respired carbon as bicarbonate relative to pCO₂. Implications for boundary conditions for deltaic sediment chemistry will be discussed.

High-temperature kinetic isotope fractionation in silicate systems: Laboratory and natural examples

F.M. RICHTER

Geophysical Sciences, The University of Chicago, Chicago, IL 60637, USA (richter@geosci.uchicago.edu)

The talk will focus on kinetic processes (see Table below) in silicate systems that result in easily measured stable isotope fractionations. The table below provides selected references that will provide the interested reader with a good introduction to the present state of affairs.

Process	Isotopic systems	laboratory examples	natural examples
Evaporation	Mg,Fe,Si, O	[1], [2], [3], [4]	CAIs [5] spherules [6]
Chemical diffusion	Li,Ca,Mg, K	[7],[8], [9]	Vinal Cove, Maine [10]
Grain-boundary diffusion	Li		Tin Mtn.[11] Pegmatite
Thermal diffusion	Mg,Ca, Fe, Si, O	[12],[13]	

In those cases where there is both laboratory and natural examples, I will focus on the commonality of what has been found. Recent developments in better understanding kinetic isotope fractionations by molecular dynamics simulations [8] and transition state theory [14] will also be discussed.

[1] Davis *et al.* (1990) *Nature* **347**, 655–658. [4] Dauphas *et al.* (2004) *Anal. Chem.* **76**, 5855–5863. [3] Richter *et al.* (2007) *GCA* **71**, 5544–5564. [4] Knight *et al.* (2009) *GCA* **73**, 6390–6401. [5] Clayton *et al.* (1988) *Phil. Trans. Roy. Soc. London A* **325**, 483–501. [6] Taylor *et al.* (2005) *GCA* **69**, 2647–2662. [7] Richter *et al.* (2003) *GCA* **67**, 3905–3923. [8] Bourg *et al.* (2010) *GCA* **74** 2249–2256. [9] Watkins *et al.* (2011) *GCA in press*. [10] Chopra (2010) *PhD dissertation*, Univ. Chicago. [11] Teng *et al.* (2006) *EPSL* **243**, 701–710. [12] Richter *et al.* (2009) *GCA* **73**, 4250–4263. [13] Huang *et al.* (2010) *Nature* **464**, 396–400. [14] Dominguez *et al.* (2011) *Nature in press*.

Cytochromes and iron reduction

K. RICHTER AND J. GESCHER*

Department for Microbiology, University of Freiburg,
Germany (*correspondence:
johannes.gescher@biologie.uni-freiburg.de)

The key innovation that enables cells to respire on metals like ferric iron or manganese is the development of a respiratory chain to the cell surface. Most of the known bacterial ferric iron reducers are proteobacteria. These cells all have in common the canonical blueprint of a Gram-negative cell with cytoplasm, cytoplasmic membrane, periplasm and outer membrane as separated reaction compartments. We study the electron transport chain to the cell surface using *Shewanella oneidensis* MR-1 as a model organism. C-type cytochromes are the dominant electron transferring proteins in *Shewanella*. They establish a conductive connection to the cell surface and catalyze the final reduction step onto a metallic electron acceptor. Interestingly, *S. oneidensis* as well as other dissimilatory iron reducers produces a multitude of different cytochromes while growing under dissimilatory ferric iron reducing conditions. Our work aims at elucidating as to why expression of this high number of cytochromes might result in a selective advantage. We can show that periplasmic cytochromes build a dynamic electron-transferring network. We can furthermore show that these cytochromes can catalyze ferric iron reduction. Hence, so called outer membrane cytochromes that are localized to the cell surface simply allow for contact between respiratory electrons and the electron acceptor. Although these surface localized cytochromes are crucial for wild type cells to respire on ferric iron or manganese, we could surprisingly establish that they are not necessary. Two simple point mutations can enable a *Shewanella* mutant to find a way around this necessity for outer membrane cytochromes. We currently complete our studies concerning these point mutations but will already provide evidence for the possible functions of the genetic exchanges.

The release of Hf isotopes during weathering

J. RICKLI, A.R. KEECH, C. ARCHER AND D. VANCE

Bristol Isotope Group, School of Earth Sciences, University of Bristol, Wills Memorial Building, Queen's Road, Bristol, BS8 1RJ, UK (*correspondence: J.Rickli@bristol.ac.uk)

Studies of river and ocean waters suggest that Hf isotopes are released incongruently during weathering of the continental crust. The governing processes in soils are poorly understood because the release of Hf isotopes from soils during weathering has thus far hardly been explored. Such an understanding is crucial to the eventual use of Hf isotopes for the reconstruction of past weathering conditions. Here we explore Hf isotope behaviour in a soil chronosequence from Scotland, spanning an age-range of 0.1-13ka.

Bulk soil Hf isotopes digested in a pressure bomb span a relatively small range between $\epsilon_{\text{Hf}} = -22.1$ and -19.7 . Hot plate digests, which exclude most Hf from zircons, are more radiogenic and also show a larger isotopic range ($\epsilon_{\text{Hf}} = -20.1$ to -16.0). The isotopic compositions of both digestion procedures are well correlated, which indicates that zircons attenuate the variability that is imparted by weathering of the zircon-free portion and seem largely inert on the time scales of the chronosequence. Although all soil profiles consistently show a depletion of radiogenic Hf in their upper horizons, documenting the removal of radiogenic Hf, the evolution of the soils with time is not very systematic. In particular the 10 ka profile is less radiogenic throughout, which is likely to indicate heterogeneity in the parent material of the chronosequence.

Currently, it is difficult to assess the proportion of removed Hf from the soils and derive an estimate of the corresponding Hf isotopic composition released to the hydrosphere. Hf/Zr ratios in the bulk soils (bomb digestions) are relatively homogenous and a calculation of the depletion of Hf from these geochemical twins seems inappropriate. A correlation of Hf/Zr with Hf isotopes which would support such an approach is not observed.

In summary the data shows that Hf isotopes removed from soils is more radiogenic than the bulk. This preferential removal of radiogenic Hf mainly relates to the zircon free portion of the soil, in which weathering imparts a variability of 4 ϵ_{Hf} . These findings will be consolidated by establishing the Hf budget of the rocks (zircon free crustal Hf vs bulk Hf) and the measurement of Hf isotopes in the draining rivers.

Oxygen and silicon partitioning between molten iron and silicate melts up to 70 GPa and 4000 K

A. RICOLLEAU^{1*}, J. BADRO¹, J. SIEBERT^{1,2},
D. ANTONANGELI^{1,2}, M. CANTONI³, C. HEBERT³,
D.T.L. ALEXANDER³ AND P. GILLET³

¹Institut de Physique du Globe de Paris, France
(*correspondence: ricolleau@ipgp.fr)

²Institut de Minéralogie et de Physique des Milieux
Condensés, Paris, France

³École Polytechnique Fédérale de Lausanne, Switzerland

The Earth's core is mainly composed of a Fe-Ni alloy. The core density compared to that of pure iron highlights a deficit that calls for the presence of light elements in addition to Fe and Ni to be explained. Si and O are among the likely candidates. Core formation is speculated to occur in a deep magma ocean in which the molten metal equilibrates with the silicate melt. The depth of this magma ocean, constrained by siderophile element partitioning, appears larger than previously thought. Thus, the experimental studies carried so far that have focused on Si and O partitioning between molten metal and silicates only up to 25 GPa, or at higher pressure, between metal and (Mg, Fe)O to interpret the behavior of oxygen in iron melts, have to be extrapolated to be relevant for the conditions of Earth's core formation.

In this study, we investigated directly the partitioning of oxygen and silicon between molten iron and silicate melts from 40 to 70 GPa using the laser-heated diamond anvil cell. We loaded the DAC with samples of olivine surrounding pure iron metal. Three olivine compositions, from 0 to 8 wt% FeO, were loaded with iron at 50 GPa to study the effect of oxygen fugacity on partitioning. Recovered samples were milled with the Focused Ion Beam technique and analyzed with electron microprobe and Transmission Electron Microscopes to obtain compositions of quench metal and silicate. The partition coefficients of oxygen and silicon between metal and silicate were determined as a function of pressure and oxygen fugacity. Quenched analyzed samples clearly show an oxidation of the silicate during the experiments. We report large amounts of oxygen (6-12 wt%) and silicon (2-10 wt%) in the metal at fO_2 around IW-1. The obtained results are used with literature lower-pressure data to thermodynamically parameterize the partitioning of oxygen and silicon. Oxygen and silicon solubility trends at high pressure are different than what expected on the basis of the extrapolation of lower pressure data.

A comparison of the reactivity at the solid-solution interface of nano- and micro-crystalline TiO₂ phases

MOIRA K. RIDLEY^{1*}, MICHAEL L. MACHESKY²
AND JAMES D. KUBICKI³

¹Texas Tech University, Lubbock, TX 79409, USA
(*correspondence: moira.ridley@ttu.edu)

²Illinois State Water Survey, Champaign, IL 61821, USA
(machesky@illinois.edu)

³The Pennsylvania State University, University Park, PA
16802, USA (jdk7@psu.edu)

The acid-base surface reactivity of rutile (α -TiO₂), with the (110) crystal face predominant, has been studied extensively. Specifically, theoretical simulations, X-ray techniques and potentiometric titration studies have provided molecular-scale and macroscopic details on the ion adsorption behaviour of rutile. Results of the collective studies have been integrated into the multisite complexation (MUSIC) model. Similar detailed studies examining the surface charging properties of nano-crystalline anatase samples are now being conducted.

Primary surface charging curves of rutile in LiCl, NaCl, KCl, and RbCl electrolyte media are compared with similar titration data for nanoparticle anatase samples. The effect of electrolyte media and ionic strength on the primary charging behaviour of anatase was studied as a function of nanoparticle size (3–40 nm diameter). The primary charging curves of rutile and all nano-anatase samples are generally analogous, when normalized to their respective pH_{zpc} values. At low ionic strength (0.03 M) the development of negative surface charge was similar for all electrolyte cations. However, with increasing ionic strength negative surface charge development was enhanced as the bare crystallographic radii of the cations decreased. Subtle differences in the macroscopic charging behaviour of the 3 nm diameter anatase sample were noted, particularly below the pH_{zpc} value were Cl⁻ counterions screen the surface from bulk solution.

For rutile, X-ray data and MD simulations show that electrolyte cations are adsorbed as inner-sphere complexes, principally in tetradentate geometry. Similarly, DFT-MD simulations show inner-sphere sorption of monovalent cations onto anatase; however, bidentate sorption predominates. For both anatase and rutile, a CD-MUSIC model, coupled with a Basic Stern layer description of the electric double (EDL), successfully integrates all microscopic information with the macroscopic experimental results. Though for the smallest anatase particles, it is necessary to account for some curvature of the EDL.

Supply-limited and kinetic-limited chemical erosion

CLIFFORD S. RIEBE^{1*}, KEN L. FERRIER²,
W. JESSE HAHM¹ AND JAMES W. KIRCHNER^{3,4}

¹Dept. Geology & Geophysics, U. Wyoming, WY, USA
(*correspondence: criebe@uwoyo.edu)

²Dept. Earth Atmospheric & Planetary Sciences, MIT, USA

³Dept. Earth & Planetary Science, U. Calif., Berkeley, USA

⁴Swiss Federal Institute for Forest, Snow, & Landscape
Research (WSL), CH

Downslope transport of hillslope sediment is often usefully cast in terms of two end-members of a spectrum of erosional regimes. At one end of the spectrum, 'transport-limited' physical erosion develops when downward propagation of weathering outpaces erosional losses from a slope, such that the removal of material is limited only by the sediment transport rate [1]. At the other end of the spectrum, 'weathering-limited' erosion develops when sediment transport matches the rate at which physically competent material loses its structural integrity, such that erosional removal of material is limited by how fast it breaks down by weathering [1]. As originally defined, the concepts of transport-limited and weathering-limited erosion only strictly apply to physical fluxes, yet they are commonly misappropriated in discussions of chemical fluxes. We suggest the interpretive framework for hillslope processes needs to be clarified and expanded for studies of chemical fluxes. Here we define and discuss two end-members in a spectrum of possible chemical erosion regimes. On one end, 'supply-limited' chemical erosion develops when physical erosion rates are slow enough (or regolith residence times are long enough) that further chemical erosion of regolith is not possible due to exhaustive depletion of reactive phases [2, 3]. On the other end, 'kinetic-limited' chemical erosion develops when physical erosion is so fast that chemical erosion can only partially deplete regolith of its weatherable phases before they are removed from slopes [3]. Using published data from field and modeling studies, we show how supply-limited and kinetic-limited chemical erosion can be distinguished from one another based on differences in relationships between chemical erosion rates and mineral supply rates—two variables that can be measured in mountainous landscapes using cosmogenic nuclides.

[1] Carson & Kirkby (1972) *Hillslope Form & Process*.

[2] Riebe *et al.* (2004) *Earth Planet. Sci. Lett.* **224**, 547–562.

[3] West *et al.* (2005) *Earth Planet. Sci. Lett.* **235**, 211–228.

Inferring process from provenance using apatite (U-Th)/He ages of coarse sediment in mountain streams

CLIFFORD S. RIEBE^{1*}, CLAIRE E. LUKENS¹,
LEONARD S. SKLAR², JONATHAN D. BEYELER²
AND DAVID L. SHUSTER³

¹Dept. Geology & Geophysics, U. Wyoming, WY, USA
(*correspondence: criebe@uwoyo.edu)

²Dept. Geosciences, San Francisco State Univ., CA, USA

³Berkeley Geochronology Center, CA, USA

The lithology and size distribution of sediment in a streambed reflects a jumble of integrated processes, from the breakdown of bedrock on slopes to selective transport and comminution as particles bash together in transit downstream. If this jumble could somehow be disentangled, it would reveal much about how physical and chemical processes shape landscapes. Here we show how processes of sediment production, transport, and breakdown can be resolved in new quantitative light using a novel methodological adaptation of existing sediment tracing techniques. If apatite-helium (AHe) cooling ages in bedrock increase with elevation, the distribution of AHe ages in stream sediment reveals the distribution of elevations of sediment source areas [e.g. 1]. To the extent that differences in source elevations reflect differences in geomorphic processes [1, 2], AHe ages in sediment can provide a powerful indicator of the dominant modes of landscape change in a watershed [1, 3]. However, previous AHe tracer studies have focused solely on sand, which represents a small fraction of bed sediment in steep mountain streams where the technique has been applied. Hence, insight on the production and delivery of sediment from hillslopes remains incomplete. Moreover, source elevations of sand reveal little about the movement and downstream fining of coarse sediment in channel networks. Here we show how a much fuller understanding of weathering, erosion, and sediment transport can be obtained by quantifying AHe ages in all grain size classes, including sand, gravel, cobbles, and boulders. What controls the grain size distribution of sediment supplied to channels? Where do boulders come from? How long do they persist in mountain streams? How important is particle comminution in the downstream evolution of grain size distributions? We show that answers to such fundamental questions about surface processes are within closer reach through AHe tracing of coarse sediment.

[1] Stock *et al.* (2006) *Geology* **34**, 725–728. [2] Tranel *et al.* (2011) *Bas. Res.* **23**. [3] McPhillips & Brandon (2010) *Earth Planet. Sci. Lett.* **296**, 373–383.

A HPSEC-ICP-MS study on the affinity of trace elements (Fe, Cu, I) to dissolved organic matter in natural water samples

T. RIEDEL AND H. BIESTER

Institut für Umweltgeologie, Technische Universität Braunschweig, Germany (thomas.riedel@tu-bs.de)

The speciation of trace elements in natural waters strongly influences their mobility and geochemical behavior in the environment. Especially, the presence of dissolved organic matter (DOM) in soil and peat runoff may favor complexation of certain metals, thereby increasing the solubility. Earlier studies were focused on the concept of metal binding to organic molecules which were thought to be of considerable size (some ten to hundred thousand Da in molecular weight). The existence of large organic substances, however, has recently been challenged. It was proposed, on the basis of several different studies, that DOM may consist of much smaller molecules, probably in the size fraction of only a few hundred to thousand Da. This raises the question if these smaller fractions can be separated by analytical techniques thereby enabling a study of the metal-binding capacity of 'small' DOM.

To resolve this question we used inductively coupled plasma mass spectrometry hyphenated with gel filtration liquid chromatography. The size exclusion column used was selected to efficiently separate substances with relatively low ionic radii thus resolving predominantly smaller fractions of DOM. Samples were river waters taken from remote sites in Patagonia, Chile as well as from the Harz mountain region, Northern Germany. All samples were filtered with 0.45 μm . Samples were initially measured in their original composition. The influence of pH was studied via the addition of nitric acid.

We found remarkable differences between the investigated metals with up to four different peaks in the chromatograms suggesting that a number of colloids/complexes of different size exist which can be separated. While some elements occurred exclusively in one or two fractions (Fe) others occur in all fractions (I, Cu) suggesting a rather non-specific binding. The addition of protons yielded the expected shift from larger to smaller fractions, possibly because metals desorb from the binding sites on the DOM or colloids/particles dissolve.

Further investigations aim to exploit the characteristic size distributions observed to create fingerprints of natural waters that help to understand the environmental distribution and cycling of these trace metals.

Microbially mediated iron reduction in the methanic zone of sediments from the Western Argentine Basin

N. RIEDINGER^{1*}, M.J. FORMOLO², S. HENKEL³, B.K. REESE⁴, H.J. MILLS⁴, A. VOSSMEYER⁵, G.L. ARNOLD⁶, J. SAWICKA⁶, J. TOMASINI⁷, G.D. LOVE¹, T.W. LYONS¹ AND S. KASTEN³

¹Dept. of Earth Sciences, Univ. of California, Riverside, CA 92521 USA

(*correspondence: natascha.riedinger@ucr.edu)

²Dept. of Geosciences, The Univ. of Tulsa, OK 74104 USA

³Alfred Wegener Institut. for Polar and Marine Research, 27570 Bremerhaven, Germany

⁴Dept. of Oceanography, Texas A&M Univ., College Station TX 77843 USA

⁵Dept. of Marine Sciences, Univ. of Georgia GA 30602 USA

⁶Max Planck Institut. for Marine Microbiology, 28359 Bremen, Germany

⁷ANCAP, Montevideo, 11100, Uruguay

Variable depositional conditions in marine sediments can have a strong impact on the associated biogeochemical cycles. In areas with high sedimentation rates, including mass transport-related deposition, (highly-) reactive mineral phases can be buried rapidly. This situation leads to the availability of reactive compounds for microorganisms in deep-subsurface anoxic environments. To unravel the influence of dynamic depositional conditions on biogeochemical processes in rapidly deposited sediments we applied inorganic and organic geochemical analyses and microbiological methods on marine sediments from the western Argentine Basin collected during the RV Meteor Expedition M78/3 (May-July) 2009. Our results show that the sediments are characterized by high concentrations of highly reactive iron phases accompanied by low amounts of organic carbon throughout the sediment column. Pore water accumulations of hydrogen sulfide are restricted to a small interval at the sulfate-methane transition zone. Below this zone, methane concentrations increase strongly with depth in association with appreciable availability of highly reactive Fe (III) phases. Elevated iron concentrations in the pore water in the same depth interval indicate ongoing iron reduction. Based on preliminary results we suggest that contributions from organo-clastic Fe reduction in these sulfide-depleted sediments can be neglected. Instead, because of the abundance of methane and reactive ferric Fe in the absence of sulfide, we propose that reduction of biologically available Fe phases in the methanic zone is coupled to methanogens via hydrogen or to anaerobic oxidation of methane.

Short-lived nuclides of the U and Th-series probing recent pedogenic processes in soils

S. RIHS^{1*}, J. PRUNIER^{1,2}, B. THIEN^{1,3}, D. LEMARCHAND¹,
M.C. PIERRET¹ AND F. CHABAUX¹

¹LHyGeS/UdS, 1 rue Blessig, 67084 Strasbourg cedex, France
(*correspondence: rihs@unistra.fr)

²Present address: LMTG/ Université Paul Sabatier, 14 avenue
Edouard Belin 31400 Toulouse, France

³Present address: Paul Scherrer Institut, CH-5232 Villigen
PSI, Switzerland

The recent chemical dynamic occurring in a podzolic forest soil section (from the Strengbach watershed, France) was investigated using U and Th-series nuclides, including short-lived nuclides. Analyses of (²³⁰Th), (²²⁶Ra), (²³²Th), (²²⁸Ra) and (²²⁸Th) activities in the soil particles, the seepage waters, the roots and the mature leaves of the beeches growing on this soil were performed by mass spectrometry (TIMS) or gamma spectrometry. Moreover, the exchangeable fraction was extracted from the soil particle and analysed. The simultaneous analysis of the different soil (*sl*) compartments allows to demonstrate that the overall Ra and Th transfer scheme is fully consistent with the acido-complexolysis weathering mechanism prevailing in podzols. Using a continuous open-system leaching model, the coupled (²²⁶Ra/²³⁰Th) and (²²⁸Ra/²³²Th) disequilibria measured in the different soil layers permit to date the contemporary processes such as recent (< 18 years) change in organic-colloids migration occurring in the shallow soil horizons. The Monte Carlo simulation approach used to resolve this system shows that a semi-infinite range of Th-isotopes leaching rates can explain the observed data, but minimum values can be inferred, leading to an upper limit age for the beginning of the perturbation. The model predicts distinct leaching rates of Th isotopes, in excellent agreement with the apparent preferential ²³⁰Th over ²³²Th leaching recorded in seepage water. The lower soil horizons are also affected by such Th mobilization, though lasting over several centuries at least, with a much smaller leaching rate.

Ra and Th isotopic ratios also appear to be valuable tracers of some mineral-water-plant interactions occurring in a soil. The (²²⁸Ra/²²⁶Ra) ratio discriminate the Ra flux originating from leaves degradation and from mineral weathering in the shallow -10cm seepage soil waters. This ratio, combined to the ²³²Th-²²⁸Ra-²²⁸Th radioactive disequilibria measured in the different soil compartments allows to constraint the shallow bio-geochemical cycle of Ra, including residence time in vegetation cycling and scavenging in the soil exchangeable fraction.

Intrabasaltic paleosols from the North Atlantic Igneous Province record late Paleocene global climate trends and hyperthermals

M.S. RIISHUUS^{1*} AND D.K. BIRD²

¹Nordic Volcanological Center, Institute of Earth Sciences,
University of Iceland, IS-101 Reykjavik, Iceland
(*correspondence: riishuus@hi.is)

²Department of Geological and Environmental Sciences,
Stanford University, Stanford, California 94305, USA
(dbird@stanford.edu)

Weathering of basaltic tephra and lava produces clays preserved in intrabasaltic paleosols. We propose that hydrogen isotopes of smectite clays formed by weathering of intraflow tephra (redbeds) of the North Atlantic Igneous Province preserve isotopic records of past global climate. In support we present smectite δD compositions of 70 tephra from West (~61.5-60.0 Ma) and East (~56.5-55.0 Ma) Greenland (64-66°N paleolatitude) for comparative analysis with global paleoclimate trends and aberrations recorded in higher-resolution marine records.

The observed smectite δD compositions range from -145 to -104 ‰. In the East Greenland section smectite δD varies around -130 to -120 ‰ at ~56 Ma prior to an abrupt increase to a maximum of -104 ‰ before returning gradually to -117 ‰ at ~55 Ma. This trend corresponds inversely to the $\delta^{18}O$ deep-sea foraminifera record depicting a warming trend from mid-Paleocene (~59 Ma) towards the Early Eocene Climatic Optimum (~52 Ma) superimposed with the Paleocene-Eocene Thermal Maximum (~55.5 Ma). The ~5 m. y. older West Greenland tephra display an initial abrupt increase in smectite δD from around -135 to -130 ‰ up to ~-120 ‰, followed by a more gradual decrease to ~-140 ‰. The more depleted δD compositions reported from West Greenland relative to East Greenland are in agreement with the cooler global conditions that prevailed in the earliest Paleocene (65-58 Ma). While the general decrease to ~-140 ‰ correlates with global cooling towards 59 Ma, we suggest that the initial increase in smectite δD from West Greenland could be recording a similar, but weaker, hyperthermal as the PETM.

We speculate that both the East and West Greenland continental flood basalt volcanism had an indirect short-lived warming effect through release of methane from organic-rich sediments by contact metamorphism from overflowing lavas and sill intrusions, as well as a direct longer-lasting cooling effect through degassing of SO₂.

Dissolved Fe in the Western Atlantic Ocean: Distribution, sources, sinks and cycling

M.J.A. RIJKENBERG^{1*}, L.J.A. GERRINGA,¹ P. LAAN¹,
V. SCHOEMANN¹, R. MIDDAG¹,
S.M.A.C. VAN HEUVEN², L. SALT¹, H.M. VAN AKEN¹,
J.T.M. DE JONG¹ AND H.J.W. DE BAAR^{1,2}

¹Royal Netherlands Institute for Sea Research, PO Box 59,
1790 AB Den Burg, The Netherlands

(*correspondence: Micha.Rijkenberg@nioz.nl)

²University of Groningen, PO Box 11103, 9700 CC
Groningen, The Netherlands

Iron (Fe) plays a key role in the regulation of primary production and dinitrogen fixation in large parts of the world oceans. Because there is an increasing urgency to understand the role of the oceans in global climate, it is paramount that we understand the biogeochemical cycle of bio-essential elements such as Fe. Despite this recognized importance there is still limited knowledge of the sources, sinks, chemistry and internal cycling of Fe. To fill this gap in our knowledge, the distribution and organic speciation of dissolved Fe (DFe) have been measured during three Dutch GEOTRACES cruises. Together, these cruises form a comprehensive, high resolution, full-depth section through the western Atlantic Ocean from Iceland to 58°S. In this presentation we will evaluate the distribution of DFe and its speciation using many other parameters such as dissolved inorganic carbon, total alkalinity, pH, dissolved oxygen, fluorescence, the macronutrients phosphate, nitrate and silicate and trace elements like dissolved aluminum (DAL) and dissolved manganese (DMn), to understand the processes that determine the distribution of DFe.

The influence of CO₂ on phase relations at Mount St. Helens

J.M. RIKER¹, J. BLUNDY¹, C.J.G. VAN HOEK²
AND S.R. VAN DER LAAN²

¹School of Earth Sciences, University of Bristol, Bristol, BS8
1RJ, UK (*correspondence: jenny.riker@bristol.ac.uk)

²Ceramics Research Centre, TATA Steel RD&T, P.O. Box
10000, 1970 CA, Ijmuiden, The Netherlands

Volatile components play a fundamental role in the ascent and eruption of silicic arc magmas. Although the effect of water on phase relations in these systems is well-studied, CO₂ is also present and may at times be abundant, for example, during instances of gas fluxing. Recent work on melt inclusions from Mount St. Helens suggests CO₂ may exert a strong influence on both depths of vapor saturation and shallow crystallization [1].

To this end, we have performed a series of experiments at shallow crustal pressures in rapid-quench cold seal pressure vessels. Experiments were designed to simulate equilibrium crystallization at depths between the magma chamber and the surface. Run temperatures (880 °C), pressures (<3 kbars), and fugacities (NNO+1) are constrained by natural erupted products, while fluid compositions vary from pure H₂O to XCO₂ = 0.5. This work builds on previous experimental studies of phase equilibria at Mount St. Helens [e.g. 2, 3].

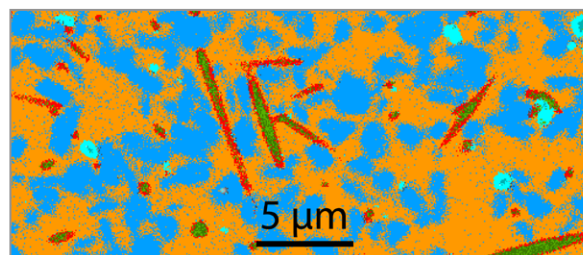


Figure 1: Phase map produced by PARC (880 °C, 500 bars).

High-resolution spectral maps allowed for detailed characterization of run products. Maps were acquired on a Field Emission Gun SEM and processed using a novel software program for automated **PhAse Recognition and Characterization (PARC)** [Fig. 1]. PARC enabled rapid identification of sub-micron crystals and compositional analysis of all phases by quantitative EDS. Our results shed light on the conditions of crystallization and melt inclusion formation at Mount St. Helens, with implications for the volatile budgets of arc magmas.

[1] Blundy *et al.* (2010) *EPSL* **290**, 289–301. [2] Rutherford *et al.* (1985) *JGR* **90**, 2929–2947. [3] Gardner *et al.* (1995) *BV* **57**, 1–17.

Contribution of the reactive mineral surface area on CO₂ mineralization under natural conditions

JEAN RILLARD^{1,2} AND PIERPAOLO ZUDDAS¹

¹Earth Sciences Department, University of Lyon1
(jean.rillard@etu.univ-lyon1.fr)

²INERIS, French National Institute for industrial Environment and RISK- FRANCE

A natural hydrothermal field is considered to be a useful analogue of carbon dioxide mineralization because it integrates the long-term interaction signal. The hydrothermal field of Galicia is characterized fluids resulting from a granit reservoir with pCO₂ from 103 to 105 Pa and pH from 10 to 6. Fluids are characterized by an increase of major elements correlated to pCO₂. We evaluated the effect of deep CO₂ perturbation. We evaluated the effects of deep CO₂ perturbation on the fluid-rock interaction system. Mineral reactivity which produces changes in the fluid mineral composition is mainly dependent on the 'real' reactive surface area.

The mineral surface area participating in reactions resulting from this pCO₂ gradient was estimated by an inverse model approach. Input data was based on the chemical composition of the fluids we sampled. The rate of mineral dissolution was estimated by the observed pH and equilibrium conditions.

Moreover, the major elemental concentrations allowed us to quantify the variation of the reactive surface area of minerals involved with the overall water-rock interaction.

The irreversible mass transfer process, ruled by the continuum equilibrium condition, was defined by the overall degree of reaction advancement, using a set of polynomial equations solved independently of time scale. We found that reactive surface area of calcite, albite and K-feldspar increases by 2 orders of magnitude over the entire CO₂ fluid-rock interaction process, while the reactive surface area of biotite increases by 4 orders of magnitude. This shows that fluid neutralisation and consequent CO₂ mineralization under the form of carbonate species is greatly dependent on the behaviour of the reactive surface area of the mineral association in this geological context. We propose that biotite plays a basic role on the pH stabilisation and redox control of environmental perturbation and CO₂ mineralization.

Origin and evolution of ferromanganese crusts from South Atlantic

M. RIMSKAYA-KORSAKOVA, I. VVEDENSKAYA AND A. DUBININ

P.P. Shirshov Institute of Oceanology RAS, Moscow, Russia
(korsakova@ocean.ru)

Ferromanganese crusts are important tools in palaeoceanography for seawater microelement composition reconstruction and palaeocurrents identification. In this study the trace element content of crusts collected in South Atlantic at Mid Atlantic Ridge (st.2176), Angola Basin (st.2179) and Cape Basin (st.2188 and seamount st.2193) was determined.

We perform the layer-specific chemical analysis to estimate hydrogenous and hydrothermal contribution into crust formation. All crusts surfaces are dominantly hydrogenous that is proved with their chemical composition, namely trace elements enrichment and high positive Ce anomaly. Sample 2176 enriched with iron (up to 27%) and Mn/Fe ratio across the whole crust is about 0.4. We found high Co (up to 0.24%), Cu (0.1%) and As (0.04%) concentrations. Content of typical hydrogenous elements decreases from surface into deep crust layers reflecting changes in origin of matter.

The surface of sample 2179 (Angola Basin) abnormally enriched with Co (0.92%), Th (89 ppm) and Ce (0.29%). The REE composition of the crust upper layers exhibit high Ce anomaly (3.8-5.4) manifesting their hydrogenous signature, in contrast to lower layers with Ce anomaly value about 1.3. The lower layers are also depleted with other trivalent REEs and Y, and enriched with chalcophile elements like Zn and Cu, that indicates the hydrothermal origin of Fe oxyhydroxides.

The crust sample 2193 comes up to 20 kg in weight and characterized with dense texture without visible layers. Preliminary results show the sample enrichment with trace elements (Co – 0.82%, Ni – 0.33%, Pb – 0.22%, Ce – 0.20%, W – up to 170 ppm, Bi – 52 ppm, Th – 47 ppm) and Mn in contrast to other samples. The surface of crust probably undergo the dissolution due to strong near bottom currents flow.

The obtained data reveal a complex history of crusts formation, which origin often associated with submarine weathering (halmyrolysis), hydrothermal transportation reflected in chalcophile elements Cu and Zn concentrations. Subsequent crusts growth supplied with hydrogenous accumulation of matter from seawater.

Marine aerosol oxalic acid from in-cloud oxidation of glyoxal

MATTEO RINALDI^{1*}, STEFANO DECESARI¹,
SANDRO FUZZI¹, DARIUS CEBURNIS²,
COLIN D. O'DOWD², JEAN SCIARE³, JOHN P. BURROWS⁴,
BARBARA ERVENS^{5,6} AND MARIA CRISTINA FACCHINI¹

¹Institute of Atmospheric Sciences and Climate, National Research Council, Bologna, Italy
(*correspondence: m.rinaldi@isac.cnr.it)

²School of Experimental Physics & Environmental Change Institute, National University of Ireland Galway, Ireland

³Laboratoire des Sciences du Climat et de l'Environnement, CNRS-CEA-IPSL, Gif-sur-Yvette, France

⁴Institute of Environmental Physics and Remote Sensing, University of Bremen, Germany

⁵Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, USA

⁶Chemical Sciences Division, Earth System Research Laboratory, NOAA, Boulder, CO, USA

Oxalate was detected in 'clean sector' marine aerosol samples at Mace Head (53°20'N, 9°54'W) and Amsterdam Island (37°48'S, 77°34'E) in concentrations ranging from few ng m⁻³ to tens of ng m⁻³. Measurements went on in 2006 at Mace Head and from 2003 to 2007 at Amsterdam Island. The oxalate concentration in marine aerosol showed a clear seasonal trend at both sites, with maxima in spring-summer and minima in fall-winter, as other marine biogenic aerosol components (e.g. methanesulfonic acid, non-sea-salt-sulfate and aliphatic amines). These results suggest the existence of a natural source of oxalic acid over the oceans.

Observed oxalate was distributed along the whole aerosol size spectrum, with both a sub and a supermicrometer mode, suggesting the co-existence of different formation routes over remote oceanic regions.

Several formation processes can explain the presence of oxalate in marine aerosol. Here, it is proposed that the cloud mediated oxidation of gaseous glyoxal, recently detected over remote oceanic regions in concentrations of the order of 100 ppt, may be an important source of submicrometer oxalate in the marine boundary layer. Supporting this hypothesis, satellite retrieved glyoxal column concentrations over the two sampling sites exhibited the same seasonal concentration trend of marine aerosol oxalate. Furthermore, chemical box model simulations showed that the observed submicrometer oxalate concentrations were consistent with the in-cloud oxidation of typical marine air glyoxal mixing ratios, as retrieved by satellite measurements, at both sites.

Monoterpene emission dynamics from Arctic to Tropics

JANNE RINNE¹, ALMUT ARNETH²,
JÖRG-PETER SCHNITZLER³ AND ALEX GUENTHER⁴

¹University of Helsinki, POB 48, 00014 U. Helsinki, Finland
(*correspondence: janne.rinne@helsinki.fi)

²Lund University, Soelvegatan 12, 22362 Lund, Sweden
(almut.arneth@nateko.lu.se)

³Helmholtz Zentrum München, Ingolstädter Landstr. 1, 85764 Neuherberg, Germany
(jp.schnitzler@helmholtz-muenchen.de)

⁴National Center for Atmospheric Research, POB 3000, Boulder CO 80307, USA (guenther@ucar.edu)

Monoterpene emissions, while globally much smaller than isoprene emissions, can dominate emissions from certain regions and ecosystems [1]. As larger molecules, they are also much more likely to take part in secondary aerosol formation than isoprene.

The traditional monoterpene emission algorithm by Guenther *et al.* [2] was based on an assumption that the monoterpene emission can be described as evaporation from large storage pools. This leads to temperature dependent emission algorithm. However, quite soon it became obvious that monoterpene emission from certain plants and ecosystems showed more or less light dependent behavior [3, 4]. This was taken as indication that a part of the emission originates directly from synthesis. The ¹³C labeling experiments, in which rapid labeling of a part of monoterpenes is observed, further confirm the linkages between photosynthesis and part of the monoterpene emission [4, 5]. The importance of large storage reservoirs as important source of emission from many coniferous species is indicated by large unlabeled fraction of monoterpene emission from these plants [5]. Thus one can describe the emission using a scheme of parallel emission pathways.

By combining data on monoterpene emissions, content in plant tissue, and labeling patterns reported in literature we can generalize the emission dynamics within plant functional types. This will yield a more comprehensive picture on monoterpene emission dynamics from ecosystems ranging from Arctic to Tropics.

[1] Guenther *et al.* (1995) *J. Geophys. Res.* **100**, 8873–8892.

[2] Guenther *et al.* (1991) *J. Geophys. Res.* **96**, 10799–10808.

[3] Staudt & Seufert (1995) *Naturwissenschaften* **82**, 89–92.

[4] Shao *et al.* (2001) *J. Geophys. Res.* **106**, 20483–20491.

[5] Ghirardo *et al.* (2010) *Plant Cell Environ.* **33**, 781–792.

Characterization and identification of minerals in rocks by ToF-SIMS and principal component analysis

S. RINNEN^{1*}, C. STROTH¹, A. RISSE²,
C. OSTERTAG-HENNING² AND H.F. ARLINGHAUS¹

¹Physikalisches Institut, University of Muenster, 48149
Muenster, Germany

(*correspondence: stefan.rinnen@wwu.de)

²Bundesanstalt fuer Geowissenschaften und Rohstoffe, 30655
Hannover, German (Christian.Ostertag-Henning@bgr.de)

For a variety of geoscientific topics a technique which unambiguously identifies minerals in rock samples would be very advantageous. In addition to optical methods, chemical mapping on the element level with different techniques has gained importance during recent years. For investigating gas-fluid-rock reactions it is important to be able to detect small secondary minerals and mineral alterations formed during the reactions – in combination with a high spatial resolution this could be achieved by mapping the incorporation of isotope labels. Therefore, a method using time-of-flight-secondary mass spectrometry (ToF-SIMS) is being developed that aims at identifying minerals and mineral alterations.

ToF-SIMS has the advantage that the entire mass spectrum is recorded quasi-simultaneously, so that a great number of elemental and molecular ion signals can be used to characterize the minerals. Here, the statistical method of principal component analysis (PCA) is a powerful tool for identifying the ion signals with great differentiation potential between individual minerals. We have used ToF-SIMS and PCA to analyze various rock-forming minerals. A spectral library was produced for all minerals investigated. For this, positive and negative ToF-SIMS spectra were taken from polished grains of rock-forming minerals (silicates, carbonates, sulfates, oxides, etc.). Signals from elemental and molecular ions that allocate to at least one of the minerals were used for the PCA analysis.

Afterwards, we used ToF-SIMS to image areas of rock samples containing unknown minerals. Spectra from individual zones were extracted and used to identify these minerals either by comparing them with the spectral library or by PCA analysis. The data clearly show that the high lateral resolution achievable with ToF-SIMS is very advantageous for the detection and identification of e.g. small newly formed phases of minerals at the edges of other components. Additionally, PCA was successfully used to classify silicates according to their crystal structures by comparing SixOy signal ratios and chemical compositions.

Assessing the factors controlling the temporal variations of weathering fluxes in a tropical watershed: Mule-Hole (South India)

J. RIOTTE¹, J.J. BRAUN^{1,2}, J.C. MARECHAL,
A. VIOLETTE¹, P. DESCHAMPS^{1,3}, L. RUIZ⁴, C. LAGANE¹,
M. SEKHAR², S. SUBRAMANIAN², C. KUMAR²
AND S. AUDRY¹

¹GET, UMR 5563, UPS-IRD-CNRS 14 av. E. Belin 31400
Toulouse, France

²IFCWS, Indian Institute of Science, Bangalore 560012 India

³CEREGE, CNRS-Aix-Marseille University, BP80 13545
Aix-en-Provence, France

⁴INRA, UMR1069, SAS, 35000 Rennes, France

We investigated the present-day and long term weathering and erosion fluxes in tropical forested watershed (Mule Hole, South India). The watershed, monitored since 2003, is located in the sub-humid zone (MAR = 1100mm/yr) of a sharp climatic gradient induced by the Western Ghats and mostly fed by the South West monsoon.

The present-day evapotranspiration from the forest accounts for 85% of the annual rainfall, with two major consequences: (1) limitation of groundwater recharge and disconnection with the stream, and (2) limitation of the stream flow, which is highly ephemeral [1]. However, the stream deconvolution indicates that almost 80% of dissolved species but Na transited through the vegetation as a result of leaf recreation and litter decay. These results emphasize the ambiguous role of the vegetation that limits the runoff but enhances dissolved fluxes in the stream.

The present-day denudation rate is 28mm/kyr. It is dominated by erosion, ~25mm/kyr, and by groundwater flux, 3mm/kyr, whereas the dissolved flux in the stream is very low, 0.3mm/kyr. The long term -100kyr- denudation rate was measured by ¹⁰Be on the stream bedload. It accounts for only one third of the present-day value which means that the watershed experienced much lower erosion fluxes during the last climatic cycle, likely under drier climate. This is confirmed by the occurrences of pedogenic carbonates in the basin soils. Their U-Th datings reveal the coexistence of several generations, essentially during the Last Glacial Maximum and to a lesser extent during the Holocene [2]. Rainfall conditions during the carbonate formation were semi-arid (MAR= 400 to 700mm/yr), i.e. enough for deepening the weathering front, but not for maintaining erosion fluxes.

[1] Maréchal *et al.* (2009) *J. Hydrol.* **364**, 272–284.

[2] Violette *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 7059–7085.

Mechanisms for the attainment of sulfide saturation in magmas derived from subcontinental lithospheric mantle

EDWARD M. RIPLEY

Department of Geological Sciences, Indiana University,
Bloomington, Indiana, USA 47405 (ripley@indiana.edu)

Magmatic, sulfide-rich, Ni-Cu-(PGE) deposits occur in settings where potential interaction between mantle-derived magma and country is enhanced (and hence a particular significance to subcontinental lithospheric mantle). Although the presence of S-bearing country rocks should not be dismissed when exploring for Ni-Cu-(PGE) deposits, it is clear that immediate country rocks often may have very little to do with the process of ore genesis. For this reason local country rocks may be poor choices for end-members in various types of geochemical mixing calculations, and data collected from the igneous rocks and associated sulfide mineralization must be carefully evaluated to assess the extent of magma interaction with country rocks. In the case of komatiites the introduction of sulfur from relatively local country rocks has been well-documented. For deeper-seated systems the involvement of immediate country rocks as magma contaminants has been more difficult to prove.

Troctolitic intrusions of the Duluth Complex (Midcontinent Rift System) are hosted by sulfide-bearing pelitic rocks which provide a viable source of sulfur in a contamination process. Sulfur isotope values of the mineralized rocks show a strong crustal signature, but their variability also signifies the involvement of multiple sulfide-saturated pulses. In a system of multiple intrusions various pulses may interact with different country rocks in the conduit system, and as a result be characterized by distinct chemical and isotopic signatures. Situations such as these lead to a conclusion that assimilation of crustal S occurred in deeper chambers within the magmatic system.

When the incorporation of S from country rocks is not indicated, the size of the magma system becomes particularly important. Contamination of mafic magmas by silicic country rocks may lead to sulfide saturation and if orthopyroxene crystallization results rather than olivine, an added benefit is the availability of Ni ($D\text{-Ni (pyr)} < D\text{-Ni (ol)}$). However, in cases where S addition has not occurred extremely efficient collection of sulfide, from large masses of magma, is required for the formation of economically viable mineralization.

Long distance electron transmission couples sulphur, iron, calcium and oxygen cycling in marine sediment

N. RISGAARD-PETERSEN^{1*} AND L.P. NIELSEN²

¹Center for Geomicrobiology, Department of Biological Sciences, Aarhus University, 8000 Aarhus C, Denmark

(*correspondence: nils.risgaard-petersen@biology.au.dk)

²Section for Microbiology, Department of Biological Sciences, Aarhus University, 8000 Aarhus C, Denmark
(biolpn@biology.au.dk)

Geochemical observations in marine sediment have recently documented that electric currents may intimately couple spatially separated biogeochemical processes (1). When marine sediment rich in iron sulphide was exposed to oxygen we observed how the electric currents resulted in significant geochemical alterations in the upper centimetres of the anoxic sediment:

Sulphides were oxidized to sulphate in anoxic sediment layers. Electrons from this half-reaction were passed to the oxic layers cm above. In this way the domain of oxygen was extended far beyond its physical presence. Bioelectrical sulfide oxidation leads to electric field formation, sulfide depletion and acidification of the upper centimeters of the sediment. This promoted ion migration and dissolution of carbonates and iron sulfides. Sulfide released from iron sulfides was the major e-donor in the system. Ferrous iron released from iron sulfides was to a large extent deposited in the oxic zone as iron oxides and Ca^{2+} eventually precipitates at the surface as due to high pH caused by cathodic oxygen reduction.

The result show how long distance electron transmission allows oxygen to drive the allocation of important minerals and possibly many trace elements deep in marine sediment.

[1] Nielsen *et al.* (2010) *Nature* **463**, 1071-1074.

Alteration of carbonates in saline aquifers due to CO₂ and accessory gases at geological storage conditions

A. RISSE*, K. HEESCHEN, S. STADLER
AND C. OSTERTAG-HENNING

Federal Institute for Geosciences and Natural Resources
(BGR), Stilleweg 2, D-30655 Hannover, Germany
(*correspondence: Andreas.Risse@bgr.de)

The estimation of an environmentally and economically feasible purity of carbon dioxide for geological storage presumes a comprehensive understanding of the geochemical interactions of CO₂, accessory gas components in the separated gas stream, e.g. H₂O, O₂, N₂, SO_x, NO_x, CO, H₂, H₂S, aqueous highly saline fluids and natural minerals.

The main focus of this geochemical subtask within the project COORAL (= CO₂ - Purity for Capture and Storage) is on experimental work with mineral-H₂O-CO₂-electrolyte- (accessory gas, e.g. SO₂, O₂, NO_x)-systems at *in situ* pressure (p) and temperature (T) conditions and the combination with geochemical modeling applying the numerical code PHREEQC.

A literature survey and systematic parameter evaluation demonstrated that some mineral-fluid-gas systems (shown for calcite-H₂O-CO₂-electrolyte) cannot be adequately described as to a partially simplified incorporation into the model, a lack of data at relevant pT conditions, and/or extrapolation-induced errors of the underlying thermodynamic data sets, confirming the need for additional experimental work at elevated pT conditions.

We show natural mineral and fluid alteration data of dissolution experiments of up to 700 h duration in the system calcite-H₂O-CO₂-(SO₂)-NaCl. Results were obtained with a static batch reactor system equipped with chemically inert and flexible gold-titanium-cells at operating conditions of 200 bars and 120 °C. Dissolution data indicate a stronger release of Ca from calcite in the presence of NaCl or/and CO₂ (and acid generating SO₂) in agreement with published findings. Net dissolution rates of calcite at various calcite-H₂O-CO₂-(SO₂)-NaCl systems will be presented and discussed.

While experimental data without CO₂ are well represented by thermodynamic calculations, rather strong discrepancies from measured data are e.g. observed for simulations of experiments in the presence of CO₂. We discuss reasons for deviations and limitations induced by the databases used.

STXM and XAS study of kaolinite conversion into berthierine-like mineral

C. RIVARD^{1*}, E. MONTARGES-PELLETIER¹,
M. PELLETIER¹, L.J. MICHOT¹, D. VANTELON²,
C. KARUNAKARAN³, F. VILLIERAS¹ AND N. MICHAU⁴

¹LEM, Université de Lorraine-CNRS, BP40, 54501
Vandoeuvre-lès-Nancy, France
(*camille.rivard@ensg.inpl-nancy.fr)

²Synchrotron Soleil, Gif-sur-Yvette, 91192, France

³Canadian Light Source, University of Saskatchewan,
Saskatoon, SK S7N 5C9, Canada

⁴ANDRA, 1/7 rue Jean Monnet, Parc de la Croix Blanche,
92298 Châtenay-Malabry Cedex, France

Experiments

In the context of radioactive waste repository in geological formation, kaolinite-Fe⁰ interactions were investigated at the crystallochemical level. Batch experiments were carried out in anoxic conditions at 90°C, for durations of one, three and nine months, by mixing Georgia Kaolinite (KGa2), powder Fe⁰ and aqueous solution (NaCl, CaCl₂). Such parameters were chosen to mimic repository conditions.

Results

First results indicated very fast iron metal consumption, morphological changes and iron-enrichment of clay particles.

X-ray diffraction, Fe K- and L-edges microspectroscopy (μ -XAS, STXM) evidence the rapid formation of an iron-rich 7 Å clay phase, with a structure close to that of berthierine or chamosite. At micrometric and nanometric scales, most iron is ferrous and octahedrally coordinated. However, some of the newly formed iron-rich clay particles display significant amounts of Fe³⁺ with variable Fe²⁺/Fe³⁺ ratio (Figure 1). In order to get further crystallochemical information, iron data were complemented by experiments at both the Si and Al-K edges. Si K-edge spectra display variations mainly due to particles orientation. Al K-edge spectra reveal no change in aluminium status of pristine clay. Although berthierine and chamosite bear both Al^{IV} and Al^{VI}, only Al^{VI} seems to be present in the neoformed iron rich-clays.

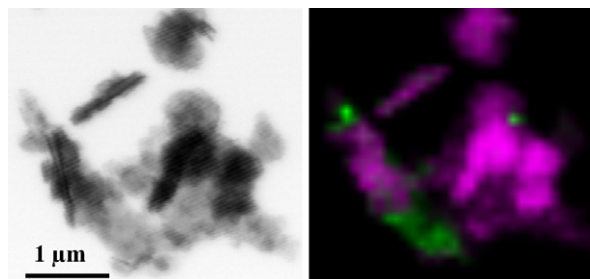


Figure 1: STXM image at 715 eV (Fe L3-edge) and corresponding two components fit (pink Fe²⁺, green Fe³⁺).

Li isotopes a powerful tool to trace hydrothermal impact during chemical weathering processes

KARINE RIVÉ¹, SÉTAREH RAD², MANUEL GARCIN²
AND ROMAIN MILLOT²

¹CEGEO, 159 allée chardin, Villeneuve d'ascq, France

²BRGM, 3, avenue Claude-Guillemain, Orléans, France

Li isotopes has been recently used to study water-rock interactions at Earth surface. Li is a fluid-mobile element that tends to preferentially partition into the fluid phase during water-rock interaction. The relative mass difference between the two isotopes is considerable, generating large mass dependent fractionation during chemical weathering processes, even at high temperature.

In the present work, the ${}^7\text{Li}/{}^6\text{Li}$ (expressed as $\delta^7\text{Li}$) was analyzed in Allier River, one of the major river basins of France. We have undertaken a systematic study of weathering products of the river. The lithology is dominant by granite rocks with current upstream, while it is mainly basaltic and Oligocene sediments in the downstream with hydrothermal manifestation.

Water samples were collected during several field trips. Our results show a large variation in Li isotopes within the catchment from 4.44 ‰ to 23.52 ‰. Li signature show a geographical distribution as it decreases from upstream to downstream over 400km. It appears that the upstream portion of the river present Li signature with higher fractionation with a mean value of 18 ‰ whereas it is only 6 ‰ in the downstream. This last portion of the river is impacted by hydrothermal activity, indeed these values reflect low temperature water-rock interaction in upstream and high water-rock interactions in the downstream, which the lowest values correspond to thermal mineral water plant. Li isotopes can be used here as a tracer of hydrothermalism. Moreover it seems that Li isotopes present a negative correlation with metal elements concentrations, which means that in a natural system hydrothermal activity induce liberation of those elements in the dissolved phase of the river during chemical alteration.

Those promising applications from Li isotopes to better understand chemical weathering processes will be discussed.

Identification of transboundary geothermal aquifers by hydrogeochemistry

N. RMAN^{1*}, T. SZŐCS² AND A. LAPANJE¹

¹Geological Survey of Slovenia, Dimičeva ul. 14, 1000 Ljubljana, Slovenia

(*correspondence: nina.rman@geo-zs.si

²Geological Institute of Hungary, Stefánia út 14., 1143 Budapest, Hungary

Problem identification and applied methodology

The transboundary character of the Mesozoic, Miocene and Pliocene geothermal aquifers in the Mura-Zala basin in the SW Hungary and NE Slovenia was investigated by various hydrogeochemical techniques. Chemical analyses of 24 cold- and thermal groundwater samples were performed in 2010 for the T-JAM project, followed by additional sampling in 2011 for the TRANSENERGY project.

Results and discussion

Main components and trace elements analyses confirm the vertical stratification of geothermal aquifers as already suggested by many [1, 2, 3], but also indicate transboundary flow systems. Hydrogeological connections and groundwater age are interpreted from the stable ($\delta^{18}\text{O}$, δD , $\delta^{13}\text{C}$) and radioactive groundwater isotope (tritium, ${}^{14}\text{C}$) analyses.

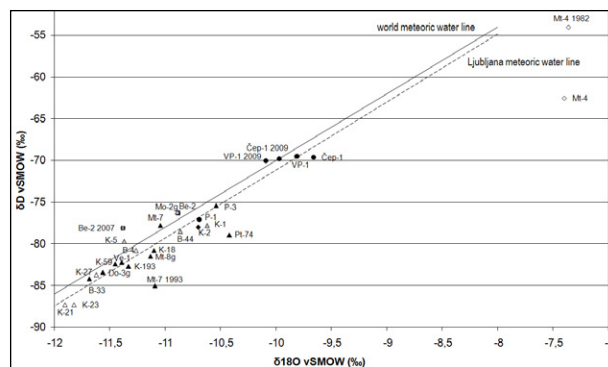


Figure 1: Distribution of $\delta^{18}\text{O}$ and δD in the samples.

Organic compounds, dissolved and separated gas, and noble gas analyses indicate differences in evolution and prevalent geochemical processes in the aquifers. Distinction between active and stagnant flow systems is also evident from our results.

[1] Kralj & Kralj (2000) *Env. Geol* **39/5**, 488–500. [2] Lapanje (2006) *Geol* **49/2**, 347–370. [3] Tóth *et al.* (2006) MÁFI Report

Proteogenomics of a marine sediment community dominated by ANME-1

I. ROALKVAM¹, R. STOKKE¹, H. HAFLIDASON²
AND I.H. STEEN^{1*}

¹Department of Biology, Centre for Geobiology, University of Bergen, 5020 Bergen, Norway
(*correspondence: ida.steen@bio.uib.no)

²Department of Earth Science, University of Bergen, 5020 Bergen, Norway

Sulfate-reducing methanotrophy by anaerobic methanotrophic archaea (ANME) and sulfate-reducing bacteria (SRB) is a major biological sink of the green house gas methane in anoxic methane-enriched marine sediments. The physiology of a microbial community in the G11 pockmark at Nyegga dominated by free-living ANME-1 was investigated by a proteogenomic approach. Total DNA was subjected to 454-pyrosequencing (829, 527 reads) and 16.6 Mbp sequence information was assembled into contigs. Taxonomic analysis supported a high abundance of Euryarchaea (70%) with 66% of the assembled metagenome belonging to ANME-1. Extracted proteins were separated on 1D-SDS-PAGE, and gel slices were in-gel tryptic digested and subjected to liquid chromatography and mass spectrometry (LTQ-Orbitrap XL). Of 356 identified proteins, 245 were expressed by ANME-1. Expression of cold-adaptations and gas vesicle proteins reflects adaptation of the ANME-1 community to a permanently cold environment and possibly to positioning in specific sediment depths, respectively. Furthermore, except N₅N₁₀-methylene-tetrahydro-methanopterin reductase all enzymes in the reverse methanogenesis pathway as well as red-ox protein components homologous to SRB, were expressed by ANME-1. Sulfite reductase and adenosine-5'-phosphosulfate (APS) reductase in the dissimilatory sulfate reduction pathway were expressed by sulfate reducing δ -proteobacteria. In addition, an APS-reductase affiliated with cluster IV comprising Gram-positive SRB and related sequences [1], was present in the proteome.

[1] Meyer and Kuever (2007), *Microbiology* **153**, 2026-2044

Deep-sea coral records of surface water properties in Gulf of Mexico and the South Eastern United States over the last millennium

E.B. ROARK^{1*}, N.G. PROUTY², A.E. KOENING³
AND S.W. ROSS⁴

¹Department of Geography, Texas A&M University, College Station, TX 77843

(*correspondence: broark@geos.tamu.edu)

²US Geological Survey, 400 Natural Bridges Drive Santa Cruz, CA 95060

³US Geological Survey, MS 973 Denver Federal Center Denver, CO 80225

⁴Center for Marine Science, University of North Carolina at Wilmington, Wilmington, NC 28409

In this study we report on the use of radiocarbon measurements to investigate growth rates and age distributions of deep-water black corals (*Leiopathes* sp.) in the Gulf of Mexico and the southeastern United States. Results from five specimens show that these animals have been growing continuously for at least the last two millennia, with growth rates ranging from 8 to 22 $\mu\text{m yr}^{-1}$. These results are compared to SEM work to image growth rings and measure relative trace elements concentrations. The counting growth rings counts by two different methods on the SEM images and peaks in iodine concentration are in good agreement (typically within the ¹⁴C uncertainty and a 10% counting uncertainty) with the radiocarbon results allowing for the development of independent age models.

In this study we also use a multi-proxy approach in order to better understand the combination of biological and physical factors controlling the isotopic and trace element content of deep-sea corals. Both $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ signatures along with trace element paleoindicators of eutrophication and oxygen levels (V, Mo, U, Re, Cu and I) can be used to infer changes in surface water conditions related to nutrient loading, eutrophication, and hypoxia in the Gulf of Mexico over the last millennium. Important changes are noted over the last 900 years and over the last century.

The evolution of the marine Zn reservoir: Comparing the proteomic and sedimentary records

L.J. ROBBINS^{1*}, S.V. LALONDE² AND K.O. KONHAUSER¹

¹1-26 Earth Science Bldg., University of Alberta, Edmonton, Ab. T6G 2E3, Canada

(*correspondence: lrobbins@ualberta.ca)

²European Institute for Marine Studies, Technopôle Brest-Iroise, Place Nicholas Copernic

²9280 Plouzané, France (stefan.lalonde@univ-brest.fr)

Banded iron formations as proxies for Zn

In the transition-metal complement of living cells, zinc plays a central role. It is the most common inorganic co-factor employed by eukaryotic metalloenzymes, and second or equal to iron in prokaryotic metalloenzymes [1]. In Eukarya, many Zn-binding proteins appear to have evolved relatively recently, leading to the proposal that limited marine Zn availability prior to the Neoproterozoic may have impacted the course of eukaryotic evolution [1]. We seek to evaluate this hypothesis by examining sedimentary proxies for the evolution of the marine Zn reservoir over geological time, specifically Precambrian banded iron formations (BIF), younger ironstones and exhalites. By combining the BIF record with experimental results for Fe-Zn-Si co-precipitation we are able account for the competitive effects of silica during absorption. We present estimates of seawater Zn concentrations from the Archean through to the modern; while there appears to be mild enrichment in the Phanerozoic, we extrapolate Archean Zn concentrations that are roughly comparable to modern. These findings have strong bearing on potential consistency between genetic and geological records for the evolution of Earth's surface environment.

[1] Dupont *et al.* (2010) *PNAS* **107**, 10567–10572.

Rheological constraints on the deformation of Snake River-type ignimbrites: An experimental study

GENEVIEVE ROBERT^{1*}, GRAHAM D. ANDREWS², JIYANG YE¹ AND ALAN G. WHITTINGTON¹

¹Department of Geological Sciences, University of Missouri – Columbia, Columbia, MO, USA

(*correspondence: genevieve.robert@mail.mizzou.edu)

²Department of Earth and Environment, Franklin and Marshall College, Lancaster, PA, USA

We have studied the rheology of two ashfall units associated with the eruption of the pervasively rheomorphic Grey's Landing (GL) ignimbrite (a Snake River-type ignimbrite) from the Miocene Rogerson formation, Snake River Plain volcanic province, USA. Lava-like lithofacies of the GL ignimbrite are either crystallized, devitrified, or perlitized, and do not necessarily represent the original material that came out of the vent to be subsequently deposited, welded and deformed by flow (rheomorphism). We therefore chose to use the fused basal co-ignimbrite ashfall tuff (GLB) and the upper co-ignimbrite tuff (GLU) as potential 'starting material' for the GL ignimbrite. The basal ash is laminated, moderately porous (~15%), and contains 10–20% crystals; in contrast the upper ash is massive, nearly aphyric, glassy and contains ~5% porosity.

We measured the apparent viscosity of each unit over ~835–1005°C, a range of temperatures relevant to eruption and deposition of these ignimbrites. The viscosities of the upper and lower units converge in the low-temperature range (~835°C) and diverge at higher temperatures (at 900°C, the viscosity of GLU is $10^{10.3}$ Pa s whereas that of GLB is $10^{10.8}$ Pa s).

Strains ranging from 10 up to 1000 are recorded in the Grey's Landing ignimbrite. However, our viscometry results suggest that dry melts making up the deposit either require unreasonably high stresses (>1MPa) or long deformation timescales (days to weeks) inconsistent with field observations to produce the observed strain in the deposit. It follows that dissolved water reducing the viscosity of the pyroclasts at the deposition temperature and/or strain heating keeping temperatures high or even increasing temperatures during deposition and deformation are necessary to explain the field observations. Models investigating the relative contributions of dissolved water and strain heating in facilitating rheomorphism will be presented.

Potential REE deposits along the Red Sea coast of Egypt

JAMES ROBERTS^{1*} AND TAREK IBRAHIM²

¹University of Pretoria, Pretoria, South Africa

(*correspondence: james.roberts@up.ac.za)

²El Mansoura University, Cairo, Egypt,

(elsahabi@yahoo.com)

In Egypt, exploration for heavy mineral deposits with their associated REE minerals has traditionally concentrated on the Mediterranean coast, and large garnetiferous heavy mineral sands have been identified at localities near Alexandria. However, the Red Sea coast is also an ideal environment for the formation of such deposits [1]. The Red Sea Coast in the southernmost portion of Egypt has a long geological history of erosion and sediment transportation, and several alluvial deposits rich in economic heavy minerals have been identified in the coastal strip between Ras Banas and the border with Sudan. Accumulations of heavy minerals have been observed along Red Sea beaches at Ras Manazel, Khudaa, Shalateen, Wadi Diit, and along the coastal stretches between these locations. These deposits have formed not only by transport processes related to offshore currents in the Red Sea, but also by drainage networks operating in the Eastern Desert of Egypt. Satellite imagery of the drainage networks indicates that the granites of the Sudanese highlands are the source of the heavy minerals, with minor input from granites in the southern Egyptian highlands. Deposits inland from the current Red Sea coastline may have been formed before the opening of the Red Sea, and subsequent erosion and reworking through flash flooding and other catastrophic transport mechanisms has created more recent deposits along the current coastline. The deposits contain not only ilmenite, rutile, magnetite, and garnet, but also large concentrations of radioactive minerals such as thorite, zircon and monazite. Preliminary studies have shown that some of the deposits are extremely rich in REE minerals (1–2% zircon by weight, 0.5% monazite by weight). The mineralogical composition of the deposits matches those of the granites in Sudan and southern Egypt, which have been explored extensively for uranium for the last 10 years. These deposits are thus a viable target for further exploration, with the intent to extract the REE minerals as well as the titaniferous ilmenite.

[1] Dawood, El-Naby (2007) *Mineralogical Magazine* **71**, 389–406. [2] Balestrieri, Abbate, Bigazzi, Ali (2009) *Earth Surf. Process. Landforms* **34**, 1279–1290.

Rare earth element association with foraminifera

N.L. ROBERTS^{1*}, A.M. PIOTROWSKI¹, T.I. EGLINTON²
AND M.L. LOMAS³

¹Department of Earth Sciences, Downing Street, Cambridge, UK (*correspondence: nr297@cam.ac.uk)

²Geological Institute, Sonneggstrasse 5, Zürich, Switzerland

³Bermuda Institute of Ocean Sciences, St George's, Bermuda

Nd isotopes are becoming widely used as a paleoceanographic tool for reconstructing past changes in water mass source [1]. Recent analysis of Nd isotopes on sedimentary planktonic foraminifera at the Bermuda Rise has proven to be a robust alternative to bulk sediment leachates, for reconstructing bottom water circulation [2]. However, in order to use foraminiferal Nd isotopes as a proxy for bottom water composition, we need to establish how, where and when rare earth elements (REEs) become associated with foraminifera.

We have measured REE concentrations and Nd isotopes on plankton tow and sediment trap foraminifera from the NW Atlantic, and compared with sedimentary foraminifera from marine cores in the same region. This allowed an evaluation of REE association with planktonic foraminifera at various stages of settling through the water column, and diagenesis near the sediment-water interface.

We find approximately 80% of plankton tow and sediment trap Nd is scavenged by particulate organic carbon and metal oxides. These phases are remineralised as particles fall through the water column allowing partial equilibration of foraminiferal Nd isotopes with ambient dissolved sea water. Once at the sediment-water interface, respiration of organic matter between foraminiferal primary calcite layers provides a reducing micro-environment within which diagenetic phases precipitate. These phases increase foraminiferal REE concentrations by ~10 fold through inorganic partitioning from bottom and pore waters.

Calculated partition coefficients suggest manganese carbonate is the predominant diagenetic host for REEs in planktonic foraminifera at the Bermuda Rise. This carbonate phase is difficult to remove during reductive cleaning, and is also resistant to down core REDOX changes, allowing reconstruction of robust bottom water Nd isotope records by measuring mixed planktonic foraminifera. Our findings have important implications for the use of planktonic foraminifera, both for surface and bottom water Nd isotope reconstruction.

[1] Piotrowski *et al.* (2005) *Science* **307**, 1933–1938.

[2] Roberts *et al.* (2009) *Science* **327**, 75–78.

Continental growth spurts during supercontinent break-up

NICK M.W. ROBERTS

NERC Isotope Geosciences Laboratory, Kingsley Dunham
Centre, Keyworth, Nottingham, NG12 5GG, UK
(nickmwroberts@gmail.com)

Accretionary orogens are the primary host of both growth and loss of continental crust, at least since the Archaean. At present-day, growth and loss are balanced globally, leading to a constant continental volume [1]. Retreating accretionary orogens will feature greater continental growth than those in advancing mode (e.g. [2, 3]). Continental growth largely occurs via subduction-driven magmatism, whereas continental loss largely occurs via subduction erosion and sediment subduction. Since the latter typically involves partial recycling into magmas, both growth and loss of continental crust are represented in the magmatic record.

Using a global zircon-Hf dataset [4], the magmatic record preserved in zircons is examined to determine the relative amount of global continental growth versus recycling. Excursions into positive and negative ϵ_{Hf} -time space relative to a global mean, represent increased continental growth and recycling respectively. The data show strong negative excursions at ~ 2.0 - 1.7 Ga, ~ 1.0 Ga, and ~ 550 Ma, reflecting increased continental recycling during periods of supercontinent amalgamation. Well-defined positive excursions are seen at ~ 1.7 - 1.3 Ga and ~ 0.8 - 0.6 Ga, interpreted as increased continental growth-rate during periods of supercontinent break-up, and likely reflecting an increased degree of retreating accretionary orogens. The Archaean lacks strong positive or negative excursions, reflecting either a lack of supercontinent formation, or a differing role of accretionary orogenesis during this period.

Preservational bias during the supercontinent cycle may lead to an increased zircon record during supercontinent formation [5]; however, the degree of mantle input recorded by Hf-in-zircon indicates that continental growth-rate is actually increased during supercontinent break-up. Elucidating the exact degree of continental loss through Earth history remains a challenge, but is vital for determining the true nature of continental growth.

[1] Hawkesworth *et al.* (2010) *Jour. Geol. Soc. London* **167**, 229–248. [2] Kay *et al.* (2005) *Geol. Soc. Am. Bull.* **117**, 67–88. [3] Kemp *et al.* (2009) *EPSL* **284**, 455–466. [4] Belousova *et al.* (2010) *Lithos* **119**, 457–466. [5] Hawkesworth *et al.* (2005) *Science* **323**, 49–50.

Marine controls on atmospheric radiocarbon: The glacial and deglaciation

LAURA F. ROBINSON¹, ANDREA BURKE²
AND JESS F. ADKINS³

¹Dept. Marine Chemistry & Geochemistry, Woods Hole
Oceanographic Institution, 266 Woods Hole Rd. 02543
Woods Hole, MA. USA (lrobinson@whoi.edu)

²Dept. Geology & Geophysics, Woods Hole Oceanographic
Institution, 266 Woods Hole Rd. 02543 Woods Hole, MA.
USA (aburke@whoi.edu)

³MC 100-23, 1200 E. California Blvd. Pasadena, CA 91125
(jess@gps.caltech.edu)

Radiocarbon is an important isotope because its radioactive decay provides constraints on the rates and timing of processes today and in the past. It is well mixed in the atmosphere, where its history is reasonably well constrained back through the last 50,000 years. By contrast the radiocarbon content of the ocean varies by about 150 per mil depending on equilibration with the atmosphere and subsequent isolation that allows decay to proceed.

There is evidence for an even greater dynamic range in the marine realm during the last glacial and deglaciation. For example, published records from intermediate waters in the northern hemisphere are up to 500 per mil depleted relative to the contemporaneous atmosphere, and have been used as evidence for a isolated, carbon-rich reservoir in the deep ocean. There is little doubt that interaction with the ocean is a major driver of atmospheric CO₂ and radiocarbon on these timescales, but the mechanisms continue to be debated in the literature. In this abstract we focus on building a coherent compilation of the state-of-the-art of marine radiocarbon records, and then use these records to discuss potential mechanisms for abrupt changes in atmospheric carbon and radiocarbon.

Transfer of nutrients and carbon from the Southern Ocean to the Atlantic during the last deglaciation

LAURA F. ROBINSON, ANDREA BURKE
AND KATHARINE R. HENDRY

Woods Hole Oceanographic Institution, 360 Woods Hole Rd.
02543 Woods Hole, MA, USA

The interconnection of ocean circulation and nutrient cycling appears to be closely linked to atmospheric carbon dioxide and global temperature. In this abstract we make use of a novel proxy for silicic acid concentration, $d^{30}\text{Si}$ in deep-sea sponge spicules, together with new and published ^{14}C records to examine carbon and nutrient cycling in the deep Southern Ocean. We then link this cycling to intermediate and deep locations in the western basin of the Atlantic during the abrupt climate events of the last deglaciation to investigate how circulation, nutrients and CO_2 are coupled.

We have documented little difference between the silicic acid concentration of the deep Southern Ocean at the last glacial maximum compared to the modern. By contrast, it appears that circumpolar deep waters were significantly depleted in radiocarbon during the glacial period, indicative of a build up of carbon. Within the Southern Ocean itself we observe a break down of deep-water stratification during the deglaciation, at around the time of the Bolling Allerod.

Ocean circulation and nutrient cycling in the Atlantic during the three most recent Heinrich events, H2, H1 and the Younger Dryas appear to share certain characteristics, but the CO_2 response is not the same in each case. For example meridional circulation from sedimentary Pa/Th ratios appears to have been somewhat similar during H2 and H1. At the same time there is evidence for northward export of Si and low $^{14}\text{C}/^{12}\text{C}$ waters into the Atlantic. However in one case atmospheric CO_2 increased markedly, and in the other it did not. During the Younger Dryas when CO_2 was increasing, Pa/Th indicates only a partial reduction in advection but silicic acid and Cd/Ca indicate export of virtually unadulterated circumpolar deep waters throughout the intermediate depths of the Atlantic. Concurrently $^{14}\text{C}/^{12}\text{C}$ ratios at deep and intermediate depths in the North Atlantic were somewhat depleted, consistent with carbon-rich southern-source waters escaping from the Southern Ocean. We will use these similarities and differences to link our knowledge of the circulation of the ocean to atmospheric carbon records.

Deep subduction of crustal minerals in the mantle: Evidence from ophiolites

P. ROBINSON¹, R. TRUMBULL², J.-S. YANG³
AND A. SCHMITT⁴

¹Department of Earth Sciences, Dalhousie University, Halifax,
Nova Scotia, Canada

²Helmholtz Centre Potsdam, GFZ German Research Centre
for Geosciences, D14473, Potsdam, Germany

³Key Laboratory for Continental Dynamics, Institute of
Geology, Chinese Academy of Sciences, Beijing, 100037
China

⁴Department of Earth and Space Sciences, University of
California, Los Angeles, Los Angeles, California
90095-1567, USA

Crustal minerals, including zircon, corundum, feldspar, almandine garnet, kyanite, sillimanite and rutile, associated with ultrahigh pressure minerals, such as coesite, diamond, kyanite, and moissanite have been recovered in varying proportions from podiform chromitites of the Luobusa and Donqiao ophiolites of Tibet and the Semail ophiolite of Oman. The UHP minerals, and some of the crustal minerals, have been found in situ; the other grains have been recovered from mineral separates. Zircon is common in all three ophiolites and occurs as rounded to subangular grains, about 50-300 microns across, typically with very complex internal textures. A few euhedral prisms have regular oscillatory zoning indicative of a magmatic origin. $^{206}\text{Pb}/^{208}\text{U}$ SIMS dates for the Luobusa zircons range from 549 ± 19 to 1657 ± 48 Ma, whereas those from Donqiao have ages of 484 ± 49 to $2515\pm$ Ma, all much older than the ophiolites. Sixteen dates on zircons from the Semail ophiolite range in age from 84 ± 4 to 1386 ± 48 Ma. Most zircons from Oman are older than the ophiolite but 3 grains are essentially the same age as the ophiolite (92 ± 4 to 99 ± 5 Ma). These are euhedral prisms with oscillatory zoning. The zircons typically contain a variety of low-pressure inclusions, including quartz, rutile, orthoclase, mica, ilmenite and apatite. In addition, all of the zircons from the three ophiolites have REE and trace element compositions compatible with a crustal origin. The assemblage of crustal minerals, combined with the morphology and age of the zircon, strongly suggest derivation from crustal sediments subducted into the mantle, where they were mixed with UHP and highly reduced phases. The preservation of these minerals can be explained by their occurrence as inclusions in chromite grains.

Southern Ocean nitrogen and silicon dynamics during the last deglaciation

REBECCA S. ROBINSON¹, MATTHEW G. HORN¹,
CHARLOTTE P. BEUCHER² AND MARK A. BRZEZINSKI²

¹Graduate School of Oceanography, University of Rhode
Island, Narragansett, Rhode Island, USA

²The Marine Science Institute, University of California Santa
Barbara, Santa Barbara, California, USA

The reinvigoration of overturning in the Southern Ocean is hypothesized to have returned CO₂ from the deep ocean to the atmosphere at the end of the last ice age. Large peaks in opal accumulation have been put forward as evidence for an increase in wind driven upwelling between 10 and 15 kyr BP [1]. Here, we use coupled nitrogen and silicon isotope records alongside opal accumulation rates to provide quasi-quantitative estimates of Southern Ocean nutrient supply, by upwelling, and nutrient utilization across this interval. Significant changes in the consumption of N and Si across the two opal accumulation peaks indicate major changes in both upwelling and nutrient demand. We find N and Si consumption to be relatively incomplete during peak opal accumulation. Nutrient supply must have been significantly enhanced. Differences between the Si and N responses during opal peaks may stem from decreasing iron availability across the glacial termination. The reinvigoration of overturning circulation during the deglaciation is hypothesized to cause a transient peak in nutrient supply to the low latitudes [2]. This is supported by our data, which indicate that relatively high macronutrient concentrations were maintained in the Southern Ocean surface waters despite high demand.

[1] Anderson *et al.* (2009) *Science* **323**, 1443–1448. [2] Spero & Lea (2002) *Science* **296**, 522–525.

A re-compiling of Cretaceous SST proxy data

STUART A. ROBINSON, KATE LITTLER, PAUL BOWN
AND JACKIE LEES

Department of Earth Sciences, University College London,
Gower Street, London, WC1E 6BT, UK
(stuart.robinson@ucl.ac.uk)

The Cretaceous was generally a period of extreme global warmth, most likely caused by elevated atmospheric pCO₂ levels, during which geologically brief (<1 Myr duration) carbon-cycle perturbations were common. Thus, the geological record of this time period may hold clues as to the mechanics of the Earth system under different conditions to those experienced at the present-day and, also, to the long-term response of the planet to severe environmental perturbation. However, extraction of meaningful inferences about the Earth system from the Cretaceous geological record requires confidence in the proxies used to reconstruct environmental variables, such as temperature and pCO₂.

The last decade has seen significant shifts in the understanding and number of geochemical proxies used to reconstruct sea-surface temperatures (SSTs) in the Cretaceous. The recognition of early bottom-water recrystallization of planktic foraminifera has resulted in the re-appraisal of what is considered 'excellent' calcite preservation suitable for oxygen-isotope and Mg/Ca analysis. Organic geochemistry has provided a new proxy, TEX₈₆, that has permitted the generation of SST records in time periods and environments that were previously unobtainable by calcite δ¹⁸O. Additional insights have been provided by δ¹⁸O of phosphate from biogenic apatites and new water-phosphate fractionation equations have been defined. These new insights and developments provide the justification for a re-appraisal of the temporal and spatial variability in Cretaceous SSTs. We attempt here to provide an up-to-date synthesis of Cretaceous proxy SST data that is mindful of the lessons and developments of the last decade. Using this new compilation allows us to build a more comprehensive view of Cretaceous palaeoclimates and to explore a number of questions that are pertinent both to Cretaceous palaeoclimatology and wider inferences about the mechanics of the Earth system.

Rapid weathering of arsenopyrite in agricultural soils

T.C. ROBSON*, C.B. BRAUNGARDT
AND M.J. KEITH-ROACH

University of Plymouth, Plymouth, PL4 8AA, UK
(*correspondence: thomas.robson@plymouth.ac.uk)

Aerially distributed fine mineral waste particles (< 250 μm), the product of mining processes, are an important source of potentially toxic elements (PTEs) in the surface environment. However, there is a paucity of data on the short-term stability of PTE-rich particles in agricultural soils and the associated risk of producing contaminated crops when PTEs are released from mineral matrices.

This study aimed to determine whether sulphide ore minerals undergo geochemical alterations (i.e. oxidation-dissolution) at a rate that is relevant to crop growth (in the order of months – years). Arsenopyrite (FeAsS) was selected for this proof-of-concept experiment due to the toxicity of arsenic at low concentrations [1].

Two soils, contrasting in organic matter content and pH, were spiked with ground FeAsS (1, 600 $\mu\text{mol/kg As}$), sown with spring wheat (*Triticum aestivum*) and incubated under controlled conditions until the wheat ripened (90 days).

Following the incubation period, soluble (soil water extract) and exchangeable (0.1 mol/L phosphate buffer extract, pH 7.2) arsenic concentrations were significantly ($p < 0.05$) higher in spiked soils, compared with controls. Low soluble arsenic concentrations suggested that less than 0.1% m/m of the mineral-bound arsenic had been released and remained present as soluble species. On the other hand, exchangeable As concentrations indicated that up to 9 % m/m (in acid soil, pH 4.5) of the mineral-bound arsenic had been released and loosely bound within the spiked acid soil matrix. The lower exchangeable concentrations extracted from the organic, neutral pH soil (0.5% m/m) were consistent with the reported FeAsS dissolution rate minima at pH 7-8 [2].

Short-term weathering of FeAsS did not yield dangerous arsenic concentrations (4.2-5.3 nmol/g) in edible plant tissues under the test conditions, based on cereal consumption rates [3]. However, this study provides evidence for significant arsenic release from arsenopyrite within an agriculturally relevant, short exposure period. Further experiments are underway, with the aim of determining the alteration rate of FeAsS and other related minerals in agricultural systems.

[1] World Health Organisation (1983) WHO Food Additive Report Series, Geneva. [2] Yu *et al.* (2007) *ES&T* **41**, 6460-6464. [3] European Food Standards Agency (2010) Concise European Food Consumption Database.

Ecosystem-level impact signals of groundwater borne continental nitrate transfer to the Ria Formosa lagoon by Submarine Groundwater Discharge (SGD) traced along the mixing gradient by a multi-indicator approach

C. ROCHA^{1*}, C. VEIGA-PIRES², J. WILSON¹, J. ANIBAL²,
J-P. MONTEIRO³ AND J. SCHOLTEN⁴

¹Biogeochemistry Research Group, School of Natural Sciences, Trinity College Dublin, Dublin 2, Ireland
(*correspondence: rochac@tcd.ie, jewilson@tcd.ie)

²Universidade do Algarve, Campus de Gambelas, 8000 Faro, Portugal (cvpires@ualg.pt, janibal@ualg.pt)

³Faculdade de Ciências e Tecnologia, Universidade do Algarve, Campus de Gambelas, 8005-139 Faro, Portugal (jpmonte@ualg.pt)

⁴IAEA, Marine Environment Laboratories, 4 Quai Antoine 1^{er}, MC-98000 Monaco (J.Scholten@iaea.org)

Recognition of the role played by SGD in the transfer of contaminants to near shore marine environments underscores the need for tools and approaches that will facilitate regional assessments of its environmental impact, including localization, spatial extent and magnitude as well as the provision of uninterrupted chains of evidence that effectively demonstrate links between polluted groundwater sources on land and ecosystem level effects in the coastal zone.

We present an uninterrupted chain of evidence linking groundwater pollution to coastal ecosystem function for a leaky coastal lagoon system. Here, for the first time, this causal link is demonstrated in its entirety for a single ecosystem. The approach used combines Earth observation techniques, hydrological mass balance approaches, conservative, radiogenic and stable isotope tracers, nutrient dynamics along the mixing line and finally, direct physiological indicators of primary producer assimilation of groundwater borne nutrients at the marine end member.

Petroleomics: Past, present and future

RYAN P RODGERS¹, AMY M. MCKENNA¹,
CHRISOPHER L. HENDRICKSON¹
AND ALAN G. MARSHALL²

¹National High Magnetic Field Laboratory, 1800 E. Paul Dirac Drive, Tallahassee, FL 32310 USA
(rogers@magnet.fsu.edu, mckenna@magnet.fsu.edu, hendrick@magnet.fsu.edu)

²Department of Chemistry and Biochemistry, Florida State Univ., 95 Chieftan Way, Tallahassee, FL 32306 USA
(marshall@magnet.fsu.edu)

Advances in mass spectrometry enable identification of tens of thousands of species in petroleum and environmental samples at the molecular level (elemental composition assignment). Current ionization methods amplify the utility of such detailed compositional information through the selective ionization of basic, acidic and aromatic species (\pm ESI and APPI). The ability to fingerprint, identify and track compositional changes in complex natural mixtures spawned the field of 'Petroleomics'. Although the past and current applications are largely limited to high resolution Fourier transform ion cyclotron resonance mass spectrometry, the future of 'Petroleomics' lies in the expansion and method development on the latest instruments in all areas of analytical chemistry.

Here we present an overview of the birth and development of Petroleomics and highlight the latest developments in our 'petroleomic' research efforts with an emphasis on the diversification of analytical workflows to maximize attainable compositional information. Specifically, microdistillation, 2-D HPLC, GC x GC, LC-TOF, preparative scale LC and FT-ICR MS will be discussed. Geochemical, oil production and refinery applications that include down-hole, deposits, offshore platform, terrestrial production and distillate samples reveal the need for a diversified analytical approach combined with high field FT-ICR mass spectrometry for problem solving and advances in the fundamental knowledge of the composition and behavior of petroleum derived materials.

Work supported by Shell Global Solutions (Houston, TX), NSF CHE-10-49753, DMR-06-54118, and the State of Florida.

High-frequency climate cycles in the Westernmost Mediterranean during the last 20,000 yrs

M. RODRIGO-GÁMIZ^{1*}, F. MARTÍNEZ-RUIZ¹,
F.J. RODRÍGUEZ-TOVAR², F.J. JIMÉNEZ-ESPEJO¹
AND E. PARDO-IGÚZQUIZA³

¹Instituto Andaluz de Ciencias de la Tierra (IACT-CSIC-UGR), Granada, Spain

(*correspondence: martarodrigo@ugr.es, fmruiz@ugr.es, fjjspejo@ugr.es)

²Departamento de Estratigrafía y Paleontología, Universidad de Granada, Granada, Spain (fjrtovar@ugr.es)

³Instituto Geológico y Minero de España, Madrid, Spain (e.pardo@igme.es)

High-sedimentation rates in the westernmost Mediterranean (Alboran Sea basin) allow excellent resolution for paleoclimate reconstructions at millennial- to centennial-scales. Here, a novel cyclostratigraphic analysis has been conducted on a marine record, revealing major and secondary peaks related to climate cycles during the last 20,000 yrs. Spectral analysis on time-series corresponds to several multi-proxy groups, including detrital, redox, paleoproductivity, and paleotemperature-paleosalinity, which reveals cycles of different confidence level at particular periodicities. Main periodicities at 1,300, 1,515, 2,000, and 5,000 yrs plus secondary harmonics at 650, 1,087, and 3,000 yrs derive from diverse climate forcing mechanisms. Thus, the 1,300 yr cycle appear to be principally influenced by North Atlantic freshwater inflow. The 1,515 yr cycle, equivalence to the Bond cycle in the North Atlantic, is linked to the North Atlantic thermohaline circulation and changes in the intensity and position of the North Atlantic Oscillation (NAO) and the Inter-Tropical Convergence Zone migrations (ITCZ). Although the 2,000 yr cycle is only punctually registered, it supports a global connection with records distributed at high-, mid-, and low-latitudes, pointing to variations in solar activity as main climate forcing mechanism. In contrast, the cycle at 5,000 yrs is well-registered and presents a direct relationship with orbital forcing responses, also accompanied by monsoonal variations and NAO oscillations. Thus, the obtained spectral periodicities reinforce the evidence on the strong connection between Mediterranean and North Atlantic climates, being climate oscillations mainly forced by solar variations, the NAO and the ITCZ migrations.

Acknowledgements: Projects CGL2009-07603, CGL2008-03007, CTM2009-07715, CSD2006-00041, MARM 200800050084447, RNM-5212, RNM-3715, RNM-179, RNM-178.

Discrimination of sediment samples for forensic application using REE

A. RODRIGUES, A. GUEDES*, H. RIBEIRO, B. VALENTIM AND F. NORONHA

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

The geochemical signature of sediments is currently used as trace evidence in forensic investigations. In this research, geochemical studies have been carried out on Portuguese coastal sands aiming to ascertain its use for forensic purposes.

Rare Earth Elements (REE) concentrations were determined on samples collected on three coastal areas surrounded by different geological contexts, namely limestone, granite and metasediment. Eight sand samples were collected along transects perpendicular to the coastline, in beach and dune from each site. Each sample was manually collected with a plastic spade from the surface sediment, at a depth of approximately 0-5cm. From the sediment samples a standardized particle size fraction of <math><150\ \mu\text{m}</math> was obtained by dry sieving method and subsequently grinded to minimise the variation in the geochemical properties due to particle size.

The REE composition fraction was determined using four acid digestions ultratrace ICP-MS analysis at ACME labs (Canada), and concentrations calculated. Although the measured REEs concentrations can be compared directly for forensic purposes a normalisation reported to chondrite meteorites was performed [1].

A REEs normalised concentration and a hierarchical cluster analyses were performed to obtain discrimination between samples. They reveal differences between samples associated with different geological context, and permitted the discrimination between samples surrounded by granite from samples surrounded by limestone and metasediments. It was also possible to discriminate some of the samples based on their REE concentration and profile.

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

[1] Taylor & McLennan (1985) Blackwell Scientific Publications, 312p.

Geochemical signatures in detrital tourmalines as indicators for sediment provenance: The Baixo Alentejo Flysch Group, South Portuguese Zone

B. RODRIGUES^{1*}, P. DIAS², R.C.G.S. JORGE³ AND P. FERNANDES¹

¹CIMA, University of the Algarve, Campus de Gambelas, 8005-139 Faro, Portugal
(*correspondence: bmgrodrigues@sapo.pt, pfernandes@ualg.pt)

²CIG-R, University of Minho (patriciasdias@gmail.com)

³CREMINER LA/ISR, Dep. Geologia, Fac. Ciências da Universidade de Lisboa (rjorge@fc.ul.pt)

Microprobe analyses were made to infer the source of detrital tourmalines from the Mid to Late Carboniferous turbiditic deposits of the Baixo Alentejo Flysch Group (BAFG) of the South Portuguese Zone. A representative group of greywacke samples covering the whole range of the BAFG ages was collected for this study. Tourmalines have brown to brownish gray colors and do not show any optical zonation. In the Fe-Mg-Al diagram, the tourmalines fall into the fields of Ca-poor metapelites, metapsammites and quartz-tourmaline rocks. Microprobe analyses revealed a range of values between schorl and dravite end members, being closer to the latter, with variable contents of X-site vacancies (0.05-0.255 apfu), Ca (0.078-0.2 apfu), Na (0.627-0.924 and Al (5.746-6.622 apfu). The Fe/(Fe+Mg) and Na/(Na+Ca) ratios range from 0.32-0.45 and 0.79-0.91, respectively.

The presence of well-rounded tourmaline grains suggests that they could have derived from a source located at a great distance from the sedimentary basin, or from reworked sedimentary rocks. The occurrence of few euhedral grains indicates minor contribution from first cycle sediments. Together, these data suggest that the detrital BAFG tourmalines derived from multiple sources with the predominance of rocks with a felsic composition.

Bruno Rodrigues holds a PhD grant from the Portuguese Foundation for Science and Technology (n.º SFRH/BD/62213/2009).

The role of Mg in the formation of monohydrocalcite

J.D. RODRIGUEZ-BLANCO, P. BOTS,
T. RONCAL-HERRERO, S. SHAW AND L.G. BENNING

School of Earth and Environment, University of Leeds, Leeds,
LS29JT, UK (earjdrb@see.leeds.ac.uk)

Monohydrocalcite (MHC, $\text{CaCO}_3 \cdot \text{H}_2\text{O}$) is a calcium carbonate mineral which forms by biological and abiotic processes in a number of environments including caves or lake-bed sediments. MHC often forms in Mg-rich aqueous environments, but is metastable with respect to aragonite and calcite [1]. However, the mechanisms of its formation and the role or effect of Mg on its nucleation and growth are not understood. Hence, using a combination of *in situ* and real-time synchrotron-based scattering and off-line micro-spectroscopic characterization, we followed and quantitatively assessed the formation mechanism of MHC.

Experiments were carried out by mixing equimolar Ca, Mg and CO_3 solutions (0.7:0.3:1) and reacting them at 21°C for 12 hours. The MHC crystallisation reaction was followed *in situ* (1 min/frame) using Small and Wide Angle Scattering (SAXS/WAXS, Diamond Light Source, UK), and equivalent off-line experiments were quenched at various times for solids and solution analysis.

The WAXS profile (Fig. 1 main plot) revealed after ~ 50 minutes MHC crystals grew via a two-step reaction. Step 1 is the transformation of a poorly-ordered amorphous calcium carbonate precursor (inset 1) into MHC nanocrystals (inset 2). This stage is followed by a second growth step after ~8.5 hr of reaction (inset 3) which occurs concomitantly with the formation of minor hydromagnesite (HMg). The combined on- and off-line data have allowed us to elucidate the key role of Mg^{2+} in both the precursor stabilization as well as in the structure, crystallinity and growth mechanisms of MHC.

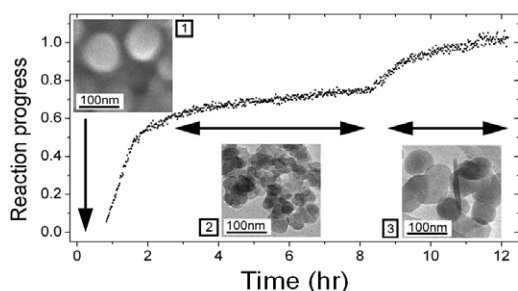


Figure 1: Reaction progress profile (1) precursor (2) MHC spheres at 3 h (3) MHC and HMg (plates) at 11 hr.

[1] Munemoto and Fukushi (2008) *Journal of Mineralogical and Petrological Sciences* **103**, 345-349.

High-pressure phases and dynamical properties of ZnAl_2O_4 and ZnGa_2O_4

P. RODRÍGUEZ-HERNANDEZ¹, A. MUÑOZ¹,
S. LÓPEZ-MORENO^{1,2} AND A. ROMERO²

¹MALTA Consolider Team, Departamento de Física Fundamental II and Instituto Univ. de Materiales y Nanotecnología, Universidad de La Laguna, 38205 La Laguna, Tenerife Spain (placida@marengo.dfis.ull.es)

²CINVESTAV-Querétaro, Libramiento Norponiente No 2000, Real de Juriquilla, Querétaro, Qro. Mexico

The structural dependence of oxide spinel AB_2O_4 compounds (A: divalent cation and B: trivalent cation) under pressure has received a lot of attention, mainly due to their occurrence in many geological settings of the Earth's crust and mantle, as well as in lunar rocks and meteorites. Many AB_2O_4 compounds crystallize in the cubic spinel structure (*Fd3m*), exemplified by MgAl_2O_4 . In this work, we report first-principles calculations of the structural, electronic, and vibrational properties of the cubic spinels ZnAl_2O_4 and ZnGa_2O_4 compounds under hydrostatic pressure. Besides, we report the variation in the structural parameters under pressure and compare directly with recent experimental

results. Finally, we study the possible pressure induced structural phase transitions for both compounds that have been confirmed from X-Ray diffraction experiments [1] and from *ab initio* studies [2]. Total energy calculations were done within the framework of the density functional theory (DFT) and the projector-augmented wave (PAW) method. The exchange and correlation energy was described within the local density approximation (LDA). We use a plane-wave energy cutoff of 500 eV to ensure a high precision in the calculations. Monkhorst-Pack scheme was employed for the Brillouin-zone (BZ) integrations with dense meshes to ensure convergence. We will report the Raman and IR phonon modes as well as the pressure coefficients and Grüneisen parameters of the spinel structure and the pressure dependence of the Raman and IR active modes in other high-pressure structures.

[1] Errandonea, D. Kumar, R.S. Manjon, F.J. Ursaki, V.V. & Rusu, E.V. (2009) *Phys. Rev. B* **79**, 024103. [2] López, S. Romero, A.H. Rodríguez-Hernández, P. & Muñoz, A. (2009) *Phys. Rev. B* **79**, 214103.

Colonization of contaminated sediments: Implications in recovery of mass extinctions events

FRANCISCO J. RODRÍGUEZ-TOVAR^{1*}
AND FRANCISCO J. MARTÍN-PEINADO²

¹Department of Stratigraphy and Paleontology, University of Granada, Spain (*correspondence: fjrtovar@ugr.es)

²Department of Soil Science, University of Granada, Spain

Biotic recovery after past bio-events is one of the difficult questions to interpret from mass extinction events. One of the recently proved useful approaches is the comparison with similar unfavourable environmental conditions in recent examples. To interpret the biotic recovery after the K-Pg impact event, characterized by an ejecta layer with high values in Ir as well as by positive anomalies of platinum-group elements and other elements (Zn, As, Cu, Ni, Co, Cr, Fe, etc.), the study of a contaminated area at the Tinto river has been conducted.

The marsh area of the Tinto river, next to the estuary of Huelva (SW Spain), is characterized by high concentrations of heavy metals accumulated in soils and sediments. These elements come from the draining and lixiviation of the river in relation to the Iberian Pyrite Belt, one of the most important polymetallic sulphide formation in Europe that has been exploited by human mining since ancient times. High concentrations of Zn, As, Cu and Tl, were found in the sediments of the marsh areas of two close locations (Palos de la Frontera, and Moguer). Values up to 1688 ppm of Zn, and 125 ppm of As were registered in the surface layer of the sediments; these levels are 2.2 and 2.5-fold, respectively, above the ecotoxicological levels reported in the bibliography. These concentrations should convert the substrate as inhabitable by organisms, but evidences of trace makers were found in this adverse media. Presence of biota colonizing into this high-polluted substrate prevents on a direct interpretation of the dramatic effect of some past bio-events based exclusively in the presence of high levels of toxic components.

The results agree with the recent ichnological evidence of a rapid colonization of the K-Pg boundary ejecta layer, classically interpreted as an inhabitable substrate, by organisms with a high independence with respect to substrate composition.

Paleoarchean barites record microbial reduction of a well-mixed marine sulfate reservoir

DESIREE L. ROERDINK¹, PAUL R.D. MASON,
JAMES FARQUHAR² AND THOMAS REIMER³

¹Department of Earth Sciences, Utrecht University, The Netherlands (roerdink@geo.uu.nl, mason@geo.uu.nl)

²Department of Geology and ESSIC, University of Maryland, College Park, USA (jfarquha@glue.umd.edu)

³Bernard-May-Str. 43, Wiesbaden, Germany (tobareim@alice.de)

Bedded barites from the Barberton greenstone belt (South-Africa) preserve a unique record of atmospheric, oceanic and microbial processes involved in the formation and evolution of the Paleoproterozoic (3.6-3.2 Ga) marine sulfate reservoir [1, 2]. Here, we present multiple sulfur isotope data from the ca. 3.5 Ga Londozi barite deposit in Swaziland, and the ca. 3.4 Ga Vergelegen, 3.26 Ga Stentor and 3.26-3.23 Ga Barite Valley deposits in South Africa. Individual deposits show relatively homogeneous mass-independent signatures ($\Delta^{33}\text{S}$, $\Delta^{36}\text{S}$) that support a significant contribution of sulfate from photochemical reactions in a low-oxygen atmosphere. Barites are enriched in ^{34}S (average $\delta^{34}\text{S} = 4.9\text{‰}$) relative to the inferred composition of atmospheric sulfate ($\delta^{34}\text{S} \approx -0.5\text{‰}$), suggesting an important role for global-scale microbial sulfate reduction as a ^{34}S -depleted sink. Modeling shows that variations in $\delta^{34}\text{S}$ per deposit can also be linked to active basin-scale biological reduction processes. Observation of relatively constant $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ in individual deposits and in barites of similar age from other cratons suggests that sulfate accumulated in a well-mixed oceanic sulfate pool, with a residence time similar to or slightly longer than the millennial timescale of barite formation. This global sulfate reservoir fed basins where barite precipitated and sulfate was microbially reduced, with minimal contributions from re-oxidation of sulfide and other sources of juvenile sulfur. Our results demonstrate that sulfate reducing micro-organisms played an important role in the early sulfate cycle similar to modern times, but with considerably less sulfide oxidation than seen in for example the Neoproterozoic [3].

[1] Huston, D.L. & Logan, G.A. (2004) *EPSL* **220**, 41–55.

[2] Reimer, T.O. (1980) *Precambrian Research* **12**, 393–410.

[3] Ono, S. *et al.* (2003) *EPSL* **213**, 15–30.

ID-TIMS as a tool for terrane provenance studies in polyorogenic complexes: A case from the SW-Norwegian Caledonides

CORNELIA ROFFEIS, FERNANDO CORFU,
ROY H. GABRIELSEN

Department of Geosciences, University of Oslo, Norway
(cornelia.roffeis@geo.uio.no, fernando.corfu@geo.uio.no,
r.h.gabrielsen@geo.uio.no)

The Caledonian mountain range along the western coast of Norway formed by the collision between Baltica and Laurentia in Silurian times. Several nappe sheets were thrust onto the Baltic basement and built up a mountain range which collapsed during following extensional tectonics and suffered severe erosion. Today the SW-Norwegian Caledonian nappe pile is fragmented into different tectonic units, overlying Baltic basement, without lateral connections.

In this work we look at the provenance of the Hardangervidda-Ryfylke Nappe Complex and its relations to the other nappes in the Caledonides. This nappe complex has been subdivided into three distinct nappe sheets, from bottom to top: the Dyrskard, Kvitnut and the Revsegg nappes. Previous dating with the Rb-Sr method had shown that the rocks formed in the Meso- to Neoproterozoic, but there was considerable uncertainty on the timing of metamorphic overprints and deformation. One specific question is whether the nappes have been emplaced together as one block, or as separate units, during the Caledonian orogeny.

We use ID-TIMS analyses, mainly on single grains of zircon, titanite and rutile from orthogneisses, metavolcanics, neosomes and pegmatites. Some of the main differences emerging at this stage concern the oldest units in the different nappes, which in the Kvitnut nappe point towards 1600 Ma whereas both the Revsegg and the Dyrskard nappes are around 1500 Ma. All three nappes have been affected by the Sveconorwegian orogeny. A most prominent effect is the emplacement of a large granitic body in the Kvitnut nappe at around 990 Ma, coeval with formation of local neosomes and the metamorphism of amphibolite and orthogneiss. The Caledonian overprint was also quite strong in all three nappe segments, disturbing the U-Pb systematics of zircon, forming new rutile, some titanite and local pegmatites. The latter have been affected by regional deformation and hence their age can be used to constrain the dynamics of the Caledonian processes in the region.

Redox-freezing and -melting of carbonates in the deep mantle and the role of transient carbides

A. ROHRBACH^{1,2} AND M.W. SCHMIDT¹

¹Inst. f. Geochemistry and Petrology, ETH Zürich,
Switzerland

²Inst. f. Mineralogy, University of Münster, Germany
(arno.rohrbach@uni-muenster.de)

The onset of deep melting in the Earth's mantle is likely to be related to small amounts of CO₂/carbonate [1] buried to depths below the 660 km discontinuity as a component in subducted oceanic lithosphere. Thus, we investigate redox processes between oxidized carbonates and the reduced ambient mantle that potentially hosts an Fe, Ni metal phase [2–4]. We locate the carbon/carbonate redox equilibrium in terms of f_{O_2} and the solidus temperature of carbonated peridotite at P and T relevant for the transition zone and lower mantle. Experiments were performed on a fertile peridotite composition containing 5 wt.% CO₂ at ETH. At 10–23 GPa, solidi temperatures are in the range of a mantle geotherm implying that small degree carbonatite melting is generally possible through thermal relaxation of subducted lithosphere. f_{O_2} controlled experiments indicate that the carbon/carbonate equilibrium is situated ≥ 2 log units above IW at 10–23 GPa, i.e. ≥ 2 log units higher than likely f_{O_2} conditions of ambient mantle. Consequently, carbonatite melts infiltrating the mantle are unstable and will suffer redox freezing through reduction of CO₂ to diamond causing their immobilization. On a local scale, carbonatite melts will consume Fe, Ni metal to leave a mantle domain that contains all iron as Fe²⁺ and Fe³⁺ in silicates and ferropericlase and all carbon as diamond [5]. The inverse process, carbonatitic redox melting, consuming Fe³⁺ and diamond would occur when such heterogeneities are entrained by upwelling mantle. Such melts cannot travel far within the metal bearing mantle matrix (as they would again reduce at depths > 250 km) and will only escape at less than ~120 km because the ambient f_{O_2} remains too low also in metal free mantle to about this depth [6]. We expect a zone of Fe, Ni carbides to form at the boundaries of such domains where the mass of carbonatite is insufficient to oxidize all metal present. Preliminary data indicate that such carbides melt surprisingly at a few 100 degrees below the mantle geotherm.

[1] Dasgupta & Hirschmann (2006) *Nature* **440**, 659–662.
[2] Frost *et al.* (2004) *Nature* **428**, 409–412. [3] Rohrbach *et al.* (2007) *Nature* **449**, 456–458. [4] Rohrbach *et al.* (2011) *J. Petrol.* **52**, 717–731. [5] Rohrbach & Schmidt (2011) *Nature* **472**, 209–212. [6] Stagno & Frost (2010) *EPSL* **300**, 72–84.

Compound-specific transverse dispersion in porous media: Darcy-scale experiments and pore-scale modeling interpretation

M. ROLLE^{1*}, D. HOCHSTETLER², G. CHIOGNA¹, P.K. KITANIDIS² AND P. GRATHWOHL¹

¹Center for Applied Geosciences, University of Tübingen, 72076 Tübingen, Germany

(*correspondence: massimo.rolle@uni-tuebingen.de)

²Department of Civil and Environmental Engineering, Stanford University, CA 94305, Stanford, USA

Multitracer laboratory bench-scale experiments and pore-scale simulations in different homogeneous saturated porous media were performed to (i) gain an improved understanding of the role of basic transport processes (i.e. advection and molecular diffusion) at the sub-continuum scale and their effect on the macroscopic description of transverse mixing in porous media; (ii) quantify the importance of compound-specific properties such as aqueous diffusivities for transport of different solutes.

A non-linear compound-dependent parameterization of transverse hydrodynamic dispersion is required to capture the lateral displacement observed in the experiments over a wide range of seepage velocities (0.1-35 m/day). With pore-scale simulations we can prove the hypothesis that the interplay between advective and diffusive mass transfer results in vertical concentration gradients leading to incomplete mixing in the pore channels. We quantify mixing in the pore channels using the concept of flux-related dilution index and show that different solutes undergoing transport in a flow-through system with a given average velocity can show a different degree of incomplete mixing. We conclude that physical processes at the microscopic level significantly determine the observed macroscopic behavior and, therefore, should be properly reflected in up-scaled parameterizations of transport processes such as local hydrodynamic dispersion coefficients. These findings are relevant also for the interpretation of isotopic signatures in groundwater [1] and for mixing-controlled reactive transport. In the latter case, a correct quantification of transverse mixing is of utmost importance to assess the length of contaminant plumes [2].

[1] Rolle *et al.* (2010) *Environ. Sci. Technol.* **44**, 6167–6173.

[2] Chiogna *et al.* (2011) *Water Resour. Res.* **47**, W02505, doi: 10.1029/2010WR009608.

Boron isotopes as pH proxy: Combination of boron speciation and isotope composition data

C. ROLLION-BARD^{1*}, D. BLAMART², J. TREBOSC³, G. TRICOT³, A. MUSSI⁴ AND J.-P. CUIF⁵

¹CRPG-CNRS, BP20, 54501, Nancy, France

(*correspondence: rollion@crpg.cnrs-nancy.fr)

²LSCE, 91198 Gif-sur-Yvette, France

³UCCS, 59652 Villeneuve d'Ascq, France

⁴UMET, Univ. Lille 1, 59655 Villeneuve d'Ascq, France

⁵IDES, Univ. Paris XI, 91405 Orsay, France

Reconstructing past atmospheric CO₂ level and elucidating its link with climate evolution is one of the most fundamental questions in Earth sciences. Boron isotopic composition ($\delta^{11}\text{B}$) of marine biocarbonates is considered to be a proxy for ocean pH. This technique has mainly been used in foraminifera and in tropical corals during previous climatic cycles and on longer geological time scales.

Dissolved boron in modern seawater occurs in the form of two species, trigonal boric acid $\text{B}(\text{OH})_3$ and tetrahedral borate ion $\text{B}(\text{OH})_4^-$, the proportion of which is dependent on pH of the solution. One of the key assumption in the use of $\delta^{11}\text{B}$ of carbonates as pH proxy is that only borate ions are incorporated into the carbonate. Here, we investigate the speciation of boron in deep-sea coral microstructures (*Lophelia pertusa* specimen) by using high field magic angle spinning nuclear magnetic resonance (¹¹B MAS NMR) and electron energy-loss spectroscopy (EELS). We observe both boron coordination species, but in different proportions depending on the coral microstructure, i.e. centres of calcification versus fibres. These results suggest that careful sampling is necessary before performing boron isotopic measurements in deep-sea corals. By combining the proportions of $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ determined by NMR and our previous ion microprobe boron isotope measurements, we propose a new equation for the relation between seawater pH and boron isotopic composition in deep-sea corals.

The interaction of Pd- and Pt-bearing chloride solutions with sulfide minerals: XPS, SPM and electrochemical study

A.S. ROMANCHENKO¹, O.F. GAYNULLOVA²
AND YU.L. MIKHLIN¹

¹Institute of Chemistry and Chemical Technology SB RAS, K. Marx Str., 42, Krasnoyarsk 660049, Russia
(alexrom@icct.ru)

²Siberian Federal University, Svobodny Av., 79 Krasnoyarsk 660062, Russia

The majority of platinum group element (PGE) deposits are of magmatic origin, and it has generally been assumed that PGEs are unreactive in aqueous media. However, Pt, Pd, and other metals may be mobile in surface environments, so adsorption and precipitation of PGE at sulfide minerals are of particular interest for the mineral processing, PGE analysis, etc. There are only few studies on this matter in the literature, for example, [1].

In the present work, we examined precipitation of Pd and Pt from aqueous PdCl₄²⁻ and PtCl₆²⁻ solutions onto pyrite, pyrrhotite and galena, including those previously reacted under different conditions, applying XPS, AFM, STM/STS, SEM, and cyclic voltammetry. It was found, in particular, that the deposition of Pt is slower than Pd; the quantities of the metals precipitated on pyrrhotite and pyrite are close. Preliminary oxidation of pyrrhotite surface results in an increase in the deposition of Pt, whereas the opposite trend was observed for pyrite. The results were interpreted in terms of the formation of Cl-, O- or S-bearing nanoscale species of Pd and Pt, with their proportion being a function of the reaction time and mineral pre-treatment (Fig. 1). The behaviour of the precipitated Pt and Pd entities was also studied.

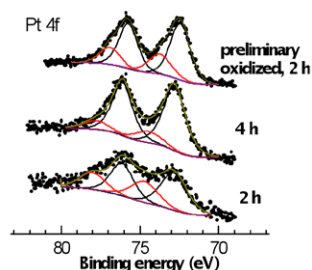


Figure 1: XP spectra from Pt deposited at pyrrhotite under various conditions (room temperature, 1 mM PtCl₆²⁻).

This work was supported by Grants from the Ministry of Education and Science of RF 02.740.11.0269, RFBR 09-05-98019, Grant of President of RF MK-5193.2011.5.

[1] Hyland *et al.* (1989) *Geochim. Cosmochim. Acta* **54**, 117-130.

PuO_{2+x}·nH₂O nanoparticles formation upon Pu(V,VI) sorption onto hematite

A.YU. ROMANCHUK^{1*}, A.V. EGOROV¹,
Y.V. ZUBAVICHUS², A.A. SHIRYAEV³
AND S.N. KALMYKOV¹

¹Lomonosov Moscow State University, Moscow, Russia
(*correspondence: romanchuk.anna@gmail.com)

²Kurchatov Institute, Moscow, Russia

³Frumkin Institute of Physical and Electrochemistry of RAS, Moscow, Russia

Plutonium (IV) as well as most of highly hydrolyzable cations forms intrinsic colloids that is demonstrated in many laboratory experiments mostly at relatively low pH values and high Pu concentrations. The gap of knowledge exists on the possibility and mechanisms of intrinsic colloids formation under conditions more relevant to the environment. The purpose of this study was to define the mechanisms of Pu (V, VI) interaction with hematite colloids including redox reactions and formation of intrinsic colloids.

It was previously shown [1] that Pu in high valence states is reduced to Pu (IV) upon sorption onto hematite. In case of Pu (IV) at very low total concentrations, e.g. ~10⁻¹⁴ M, the fast sorption of monomeric species on hematite occur, while in case of Pu (VI), the sorption is kinetically controlled by slow reduction on the surface. For total concentrations of Pu around 10⁻⁶ the reduction of Pu (V, VI) upon sorption onto hematite is confirmed by Pu L_{III} XANES. The reduction is accompanied by the formation of PuO_{2+x} crystalline nanoparticles with average size of 1-2 nm that was independently demonstrated by HR-TEM and Pu L_{III} EXAFS measurements.

The most challenging question is concerning Pu behavior at lower concentrations, i.e. around 10⁻⁹ M and less. Due to the increase of concentration near the surface, Pu (IV) could polymerize even at this relatively concentration that strongly effect both kinetics of sorption and leaching behavior. For the first time it was demonstrated by HRTEM that Pu (V, VI) reduction upon sorption result in the formation of low-crystallinity PuO_{2+x} nanoparticles.

[1] Romanchuk *et al.* (2011) *Radiochim. Acta* **99**, 137-144.

Nitrogen limitation in extremophilic hydrothermal ecosystems of Yellowstone National Park

S.J. ROMANIELLO^{1*}, H.E. HARTNETT^{1,2}, A.D. ANBAR^{1,2}, J.J. ELSER³ AND E.L. SHOCK^{1,2}

¹School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287-1404
(*correspondence: sromanie@asu.edu)

²Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1406

³School of Life Sciences, Arizona State University, Tempe, AZ

We present the results of ¹⁵N assimilation experiments conducted with hydrothermal chemotrophic and phototrophic microbial mats in Yellowstone National Park (YNP), USA. *In situ* ¹⁵N incubations were carried out with ¹⁵NO₃⁻, ¹⁵NH₄⁺, and ¹⁵N₂ during the summer 2009 and 2010 field seasons over a wide range of temperature and pH (50-92°C, pH = 2.1-9.3).

Measured rates of NO₃⁻, NH₄⁺, and N₂ assimilation vary widely between sites. The highest assimilation rates were generally found in photosynthetic mats. NO₃⁻-assimilation was detected at some high temperature sites but was conspicuously absent at others, even when these sites exhibited remarkable geochemical similarity. Measurable rates of N₂-fixation were measured in the phototrophic cyanobacterial mats. However attempts to detect N₂ assimilation in high temperature, alkaline, chemotrophic communities were unsuccessful.

NO₃⁻ assimilation rates determined in 2009 using 1-4 μM initial NO₃⁻ were generally <10% of 2010 rates using 100 μM initial NO₃⁻ at reoccupied sites (e.g. Figure 1). These results imply that nitrate assimilation may be strongly understaturated at *in situ* NO₃⁻ concentrations (<1.5 μM). This suggests that nitrogen limitation may be an underappreciated aspect of hydrothermal ecosystem biogeochemistry.

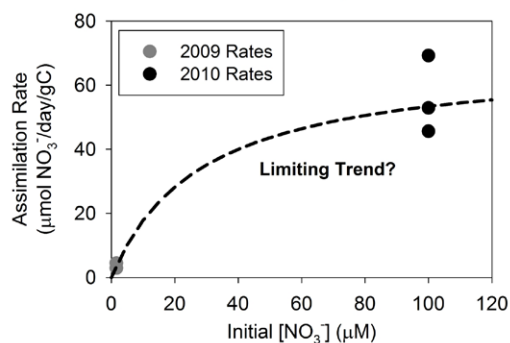


Figure 1: Nitrate assimilation rate as a function of initial NO₃⁻ concentration at a hot spring near Obsidian Pool, YNP.

Concerning organization of geochemical environment as a study object for geochemistry

S.L. ROMANOV^{1*} AND E.M. KOROBOVA²

¹Unitary Enterprise .Geoinformation systems., Belarus National Ac. of Sciences, 220004 Minsk, Surganov Str., 6, Belarus (*correspondence: romanov_s_1@mail.ru)

²Vernasky Institute of Geochemistry and Analytical Chemistry, Rus.Ac. of Sci., 119991 Moscow, Kosygin Str., 19, Russia, Korobova@geokhi.ru)

In the light of concepts of theoretical geochemistry the environment is presented by a set of hierarchically ordered and geochemically discontinuous objects such as biosphere or lithosphere which in their part consist of a quantity of the smaller structural units – rocks, gases, proteins. On the molecular level the latter present sets of typical components made of a relatively limited number of chemical elements. In general the environment is treated as the present result of the continuous chemical reactions. However the paradox is that the observed environment can not be interpreted as a result of all the possible chemical reactions. To produce such an object as the World Ocean, or an ore deposit the necessary chemical elements should occur in the corresponding volume, the corresponding form and sufficient quantity. In the other words the physically significant result of interaction of all the substances is characterized by significant masses presented in the particular volume. Therefore the quantity of all the chemical elements present on the Earth may be treated as material bodies of the particular elements such as iron, oxygen or actinium.

Such an approach is logically unrepugnant and permit to formulate an important corollary. All chemical elements and compounds that are in the environment regardless of form, quantity and aggregate state are organized as material bodies which have general and specific properties such as weight, dynamics and space configuration. Furthermore, their bodies exhibit characteristics of a three-dimensional fractal.

This assertion does not contradict any of the basic tenets of science and allows us make a more general conclusion. Parameters of the existing geochemical environment at all levels of organization are naturally predetermined by specific interaction of a small number of material bodies, that are stable in time and space and are the basic components of the universe.

If these statements are true (they are at least logically consistent) then the environment can be considered as constantly evolving, naturally organized and well-balanced superposition of special geochemical bodies, which in framework of notions of theoretical geochemistry may become the main object of this science. Such object is in full measure able to provide formal interpretation and comparison of all the existing geochemical data using the means of modern physics and mathematics.

Assessment of arsenic toxicity using bioassays. Application in contaminated soils

A. ROMERO-FREIRE¹, G.N. ANTÚNEZ,
F. MARTÍN-PEINADO^{1*}, M.O. ESCOTO² AND A. ROCA¹

¹Soil Science Department. Faculty of Sciences. University of Granada. 18002 Granada, Spain
(*correspondence: fjmartin@ugr.es)

²Natural Resource Management and Environment. National University of Agriculture. P.C. 9. Catacamas. Honduras

In last decades, arsenic has become a serious environmental problem due to the extensive use and to its potential high toxicity [1]. Arsenic trends to accumulate in soils because its low mobility in this media, although water-soluble fractions are highly bioavailable [2]. Soil toxicity bioassays are based on the evaluation of the toxic effect of the solid phase or the soil solution over a living organism [3].

Potential As toxicity from bioassays with *Vibrio fischeri* and *Lactuca sativa* germination test was estimated. These assays were done in artificially contaminated solutions (ranging from 0.1 to 100 ppm As), and in water extracts from soils spiked with 100 ppm As. Both bioassays had a different response in the artificially contaminated solutions. According to the EC50 values (Table 1), the *Lactuca sativa* test showed higher sensitivity to the toxicity than *Vibrio fischeri* bioassay.

	EC50 (mg/kg)	
	Value	95% CI
<i>Lactuca sativa</i>	2.46	1.36 - 4.48
<i>Vibrio fischeri</i>	12.33	7.83 - 19.42

Table 1: EC50 values in the contaminated solutions. CI: Confidence interval at 95%.

Four soils with different properties were contaminated with 100 mg As kg⁻¹ soil. Soil organic matter ranged from 1.2 to 6.8%, calcium carbonate from 0 to 39%, and clay content from 9 to 33%. In all cases the As concentration in soil solutions was below 0.03 mg kg⁻¹. The results of toxicity bioassay with the solutions coming from the contaminated soils indicated no toxic response in the case of lettuce germination test or *Vibrio fischeri* bioassay. Further studies are needed to check the main parameters controlling the reduction of toxicity in relation to soil properties.

Acknowledgement: Research project CGL2010-19902.

[1] Adriano (1986) Springer-Valag. 533 p. [2] Beesley *et al.* (2010) *Env. Poll.* **158**, 2282–2287. [3] Martín *et al.* (2010) *Int. J. Chem. Eng. Art* ID 101390.

Imaging the removal of radionuclides from solution by NZVI using HRTEM

M.E. ROMERO-GONZALEZ^{1*}, GABRIELLA KAKONYI¹
AND IAN M ROSS²

¹Cell-Mineral Research Centre, The University of Sheffield, Kroto Research Institute, Sheffield, UK

(*correspondence: m.e.romero-gonzalez@sheffield.ac.uk)

²Kroto Centre for High Resolution Imaging and Analysis, The University of Sheffield, Kroto Research Institute, Sheffield S3 7HQ, UK

Nano zero valent iron (NZVI) has been promoted as a remedial strategy for a range of contaminants present in the environment. Its applications range from the remediation of chlorinated compounds in sediments to arsenic in groundwater and aquifer material. Its properties such as size, mobility through porous media and reactivity offer advantages for remediation of contaminants under a variety of remedial strategies: used as complement material on iron barriers, direct injection to aquifers and targeted emplacement in subsurface zones.

We explore here the use of NZVI as an external barrier to radionuclide deep nuclear repository waste containment. Rates of removal of U (VI) removal in suspensions of NZVI (nanoFer 25 and 25S) were performed in batch systems in presence of ordinary portland cement (OPC) at pH 9 and 12. All experiments were conducted in an anoxic glovebox free of CO₂. Samples were taken for the quantification of U (VI), Ca and total Fe by ICP-MS. Samples were also analysed using a HRTEM JEOL 2200FSC. The HRTEM provides a maximum 0.05 nm spatial resolution, this allowed the imaging of the reaction products at atomic scale.

The results showed that NZVI can effectively remove uranium (VI) from solution under a range of conditions. The presence of high Ca concentrations reduce the efficiency of NZVI to remove U (VI) when compared to systems without Ca. However, the overall efficiency of the NZVI-cement system was little compromised since U (VI) was effectively removed from solution under all studied conditions.

The HRTEM results indicated mainly a coprecipitation mechanism for the removal of U (VI) from solution at highly alkaline pH. Therefore the potential to use NZVI technology to increase the efficiency of barriers around a deep nuclear waste repository is very promising. Additionally, HRTEM has proven to be a very valuable tool on the investigation of nanoparticle interactions with porous media.

Hydrogen isotopic signatures of algal biomarkers as a proxy of hydroclimatic variability in Lake Isabel, Mexico

L. ROMERO^{1*}, H.G. HAUG^{1,2}, U. KIENEL^{1,3} AND D. SACHSE¹.

¹Institut für Erd- und Umweltwissenschaften, Karl-Liebknecht-Strasse 24, 14476 Potsdam, Germany
(*correspondence: romero@geo.uni-potsdam.de)

²Geologisches Institut, Department Erdwissenschaften, ETH Zürich, Sonneggstrasse 5, 8092 Zürich, Switzerland

³German Research Centre for Geosciences-Helmholtz-Centre Potsdam, Telegrafenberg, 14473 Potsdam, Germany

Based on the observed linear relationships between the isotopic composition of the source water and the δD values of aquatic and terrestrial lipid biomarkers, the analysis of the isotopic signature in these organic molecules preserved in sediments has become a new tool for paleohydrological reconstruction. However the influence of additional factors (i.e. growth rate, salinity, and temperature) on the δD values of algal lipids remains poorly understood. Therefore, sediments from a short core corresponding to the time period 1943-2003 A.D from a hypersaline crater lake located on Isla Isabel, 30km off the Pacific Coast of Mexico, were analysed for lipid biomarker δD values and compared to instrumental climate data. δD values of the 1,15C₃₂ diol, a specific biomarker for algal populations, showed a significant relationship with the instrumental record of rainfall amount confirming its potential as a proxy of past hydroclimatic conditions. Unexpectedly, deuterium-enrichment in diols was observed during wetter conditions while these were significantly depleted during drier periods. We hypothesize that under this strongly seasonal climate regime algal growth conditions play an important role in determining algal lipid δD values. This calibration study between the isotopic signatures and the climatic record shows the complexity but also the potential of hydrogen isotope analyses of lipids as proxy to reconstruct the past climatic variability.

The role of inorganic additives in evaporitic carbonate precipitation

T. RONCAL-HERRERO^{1,2*}, P. BOTS²,
J.D. RODRIGUEZ-BLANCO², S. SHAW²
AND L.G. BENNING²

¹Department of Geosciences, University of Oslo, PB 1047, Blindern, Oslo, Norway

²School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, United Kingdom
(*correspondence: eartr@leeds.ac.uk)

Interactions between carbonate-bearing groundwaters and sulphate minerals in evaporitic settings lead to the formation of carbonate deposits [1]. However, our understanding of the reaction kinetics in these processes is still fragmented.

An experimental study following the formation of CaCO₃ phases from gypsum (GYP, CaSO₄·2H₂O) in the presence of 1 to 100 mM of Mg, Zn, Sr, or PO₄ was carried out at 25°C. GYP ($\varnothing < 420 \mu\text{m}$) was reacted with 50 mM Na₂CO₃ at a GYP/liquid ratio of ~ 0.007 in stirred closed reactors. The experiments were run at two different initial pH settings (*a*) pH ≈ 11.4 , due to the Na₂CO₃ or (*b*) pH ≈ 6.8 , where the solutions was also supersaturated with CO_{2(g)}. Solids were characterized over time by X-ray diffraction and high-resolution microscopy imaging while changes in aqueous concentrations were determined by ion chromatography.

The results of both sets showed that the dissolution of GYP (release of Ca²⁺) lead to a relatively fast nucleation and growth of CaCO₃ polymorphs. As long as the solution had excess carbonate, the continuous dissolution of gypsum was mirrored by a simultaneous precipitation of CaCO₃. In all cases, the first phase nucleating on the gypsum surface was amorphous CaCO₃ (ACC). Depending on experimental approach or the presence of additives, ACC transformed gradually to various CaCO₃ polymorphs. At condition (*a*) the GYP completely dissolved in ~ 24 h and the initial ACC transformed into calcite within 2 days, while in approach (*b*) GYP took only ~ 5 h to fully dissolve and the carbonate that formed after 30 h was 'stable' vaterite [2]. The presence of additive ions strongly influenced both the reaction kinetics and the nature of the crystalline end products. For example, using approach (*b*) but adding 1 mM Zn produced calcite (instead of vaterite) with Zn becoming incorporated into the calcite structure; conversely, with 100 mM Mg present in the initial solution, ACC transformed to aragonite after 12 h and calcite was not observed. These results revealed that aqueous additives play a fundamental role in controlling the nature and formation pathway of the end product and this has major implications for biomineralization, industrial applications, and CO₂ sequestration.

[1] Sanz-Rubio *et al.* (2001) *Sedim. Geology* **140**, 123–142.

[2] Bots *et al.* (2011) *Geology* **39**, 331–334.

Re-Os geochronology of the Neoproterozoic Coppercap and Twitya Formations: Implications for the Rapitan-Sturtian glaciation

A.D. ROONEY^{1*}, F.A. MACDONALD² AND D. SELBY¹

¹Earth Sciences Department, Durham University, DH1 3LE, UK (*correspondence: alan.rooney@durham.ac.uk)

²Department of Earth & Planetary Sciences, Harvard University, Cambridge MA, 02138

The late Neoproterozoic Windermere Supergroup of NW Canada is a ~7 km thick mixed carbonate-siliciclastic succession deposited on the margin of Laurentia. The Coppercap Formation of the Coates Lake Group consists of ~300 m of TOC-rich limestone that unconformably underlie glaciogenic deposits of the Rapitan Group. U-Pb zircon ages below and within the Rapitan Group in the Yukon constrain the onset of the Rapitan glaciation to ca. 717 Ma. The Rapitan Group is conformably overlain by the Twitya Formation, which is ~900 m thick and consists predominantly of carbonate and siliciclastic turbidites.

A 21 m interval of organic-rich carbonate of the Coppercap Formation yields a Model 1 depositional isochron age of 733 ± 4 Ma. Further Re-Os geochronology of a ~2 m interval of organic-rich carbonate of the Twitya Formation yield a Model 1 depositional isochron age of 655 ± 26 Ma. Combined with U-Pb zircon data, these ages constrain the minimum duration of the Rapitan glaciation to 36 Myrs.

Initial Os isotope composition (Os_i) derived from the Re-Os isotope data of the Coppercap Formation reveals an unradiogenic Os_i (0.14) for seawater prior to the Rapitan glaciation. This unradiogenic Os seawater signal may be derived from the erosion of basalts of the underlying Little Dal Group as well as the Gunbarrel magmatic events, and hydrothermal vents associated with rifting during the break-up of Rodinia. The Os_i data from the Twitya Formation yields a radiogenic composition (~0.83) suggesting that post-glaciation; the crustal Os flux from rivers exerted a strong influence on ocean Os composition. These data are consistent with Sr isotope data, which show a large increase to more radiogenic values across the Rapitan-Sturtian glaciation.

Both the Re-Os isochron age and the Os_i data for the Twitya are identical, within uncertainty, to that of the Aralka Formation, which overlies the glaciogenic Areyonga Formation of Central Australia suggesting that de-glaciation was broadly penecontemporaneous, and that the Sturtian and Rapitan glaciations are correlative. The Re-Os geochronology and Os_i data presented here has profound implications for our understanding of Late Proterozoic ocean chemistry and the Snowball Earth hypothesis.

Synchrotron XAS and XRF study of microbially reduced arsenic and iron in iron-based remediation media

ROBERT A. ROOT^{1*}, FERNANDO J. ALDAY², SAHAR FATHORDOOBADI², WENDELL P. ELA² AND JON CHOROVER¹

¹Department of Soil, Water and Environmental Science, University of Arizona, Tucson AZ, USA (*correspondence: rroot@email.arizona.edu)

²Department of Chemical and Environmental Engineering, University of Arizona, Tucson AZ, USA

Arsenic remediation technologies exploiting the high affinity of ferric (oxy)hydroxides for oxyanion sorption has resulted in a significant increase in the volume of arsenic-bearing solid residuals generated by drinking water utilities. These iron sorbents widely utilized for water treatment may be legally disposed in municipal solid-waste landfills if they pass the USEPA toxicity characteristic leaching procedure (TCLP). However, conditions in a mature landfill are biotic and generally suboxic where iron and arsenic may be reduced and released to the leachate; a consequence not simulated with the TCLP test. To examine the effect of biotically induced reducing conditions, controlled flow through column experiments were used to simulate conditions similar to those found in a landfill. Upflow 30 cm x 2.5 cm reactors were packed with 15 g (dry wt.) ferric arsenate sludge (Fe:As = 20:1; pH 7-8) and 73 g of 0.8 mm glass beads then reacted for 432 days (864 pore volumes) with a synthetic landfill leachate containing nutrients (e.g. components: $[SO_4] = 64 \mu M$, $[Na] = 12 \mu M$, $[CO_3] = 24 \mu M$ etc.) and a consortium of microorganisms from an anaerobic digester sludge collected from a water treatment plant.

Columns were sub-sectioned and investigated with Synchrotron X-ray absorption spectroscopy and fluorescence microprobe (μXRF) to determine the bulk As, Fe, and S speciation and to spatially resolve As and Fe species with energy difference μXRF mapping. Reducing conditions prevail at the inlet of the column and the primary iron phase there is siderite, whereas vivianite, green rust and ferric (oxy)hydroxide form as the conditions become more oxidic. Arsenic is present as As (III) and As (V) sorbed to ferric (oxy)hydroxide in suboxic and oxidic environments respectively. When the columns are run at sulfate influent concentrations increased from 64 μM to 2.1 mM, the primary iron and arsenic phases are amorphous iron sulfide (FeS) and realgar (AsS), indicating sulfate and iron concentrations are important for As sequestration in landfills.

Contaminated soil diagnosis by electrical resistivity tomography in underground storage tanks of different petrol stations in SE Spain

R.M. ROSALES*, P. MARTÍNEZ AND A. FAZ

Technical University of Cartagena, Cartagena 30203, Spain

(*correspondence: rosamaria.rosales@upct.es, p.martinez@upct.es, angel.fazcano@upct.es)

Introduction

Soil contamination could be produced by petroleum products spill and leaks related to activities of refinement and fuel dispensing in Service Stations. Although pipelines and Underground Storage Tanks (UST) are designed to avoid this kind of accidents, the large amount of fuel dispensed at petrol stations during years may cause a very important damage in the surrounding uncontaminated area. Through this research it has been made an environmental diagnosis to identify possible leaks in UST as plumes in the subsoil by applying Electrical Resistivity Tomography 2D (ERT 2D), a non destructive geophysical technique in three petrol stations located in Murcia Region, Spain. Three ERT profiles were carried out in each petrol station per campaign (wet and dry seasons).

Results and discussion

Figure 1 shows electrical pseudosections obtained by processing ERT data with PROSYS II and RES2DINV softwares corresponding to one petrol station in wet season. These results may define different confined zones in the subsoil with electrical resistivity values up to 2000 $\Omega\cdot m$, very high values for a natural soil. Hydrocarbons are excellent insulators and exhibit very high values of electrical resistivity [1] around 2500 $\Omega\cdot m$, values assigned to a possible fuel leak [2].

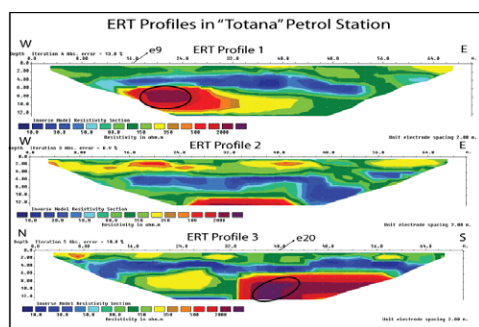


Figure 1: Processed pseudosection from ERT 2D profiles in "Totana" petrol station corresponding to wet season.

[1] Delaney *et al.* (2001) *Cold Reg. Sci. Techn.* **32**, 107–119.

[2] Znamensky (1980) *Field Geophysics. Nedra* **351**, 279–284.

On the variability of aerosol intensive optical properties over South America

N.E. ROSARIO^{1,2*}, M.A. YAMASOE¹ AND K.M. LONGO²

¹University of São Paulo, São Paulo, Brazil

(*correspondence: nrosario@model.iag.usp.br)

(akemi@model.iag.usp.br)

²National Institute for Space Research, São José dos Campos, Brazil (karla.longo@inpe.br)

The variability of aerosol intensive optical properties, specifically single scattering albedo (ω_{0s}) and asymmetry parameter (g_s), over South America have been analyzed using data from Aerosol RObotic NETwork [1]. The stations considered in the study are installed in distinct environment: Alta Floresta and Belterra are in the biomass burning regions of the southern and northeast of the Amazon basin, respectively, Cuiaba is in the *Cerrado* area, São Paulo is an urban center in the southeast of Brazil, and Arica and Surinam are coastal sites on the west and north coast of South America, respectively. The variability of aerosol optical properties inter and intra stations is significant, in particular for those located downwind of the biomass burning regions. Further differences emerge when the signal of smoke aerosols from the southern of Amazon basin are excluded from the mean calculation. For instance, São Paulo and Cuiaba locally produced aerosol is more absorbing than the indiscriminate average of optical properties suggests. The smoke transport from the southern Amazonia tends to reduce the heterogeneity that characterizes optical properties elsewhere. A clustering analysis based on the magnitude and spectral dependence of ω_{0s} and g_s was performed for each station. The factors associated with the occurrence of the identified clusters vary among the stations. For São Paulo and Cuiaba, as expected, the clusters occurrence are indeed correlated to the smoke transport. In Alta Floresta less absorbing clusters are in general associated with wetter and/or highly polluted conditions. Arica presents the lowest variability in optical properties, although a dependence on the wind diurnal cycle was observed. These results have been analyzed from the perspective of the representation of aerosol intensive optical properties in regional circulation models. Ongoing analysis evaluating the impact of the variability in optical properties on radiative balance using the Coupled Aerosol and Tracer Transport model to the Brazilian developments on the Regional Atmospheric Modelling System [2] are discussed.

[1] Holben *et al.* (1994) *Rem. Sens. Environ.* **66**, 1–16.

[2] Freitas *et al.* (2010) *Chem. Phys. Discuss.* **7**, 8525–8569.

Exploring the first steps of iron(III) oxyhydroxide nucleation using a competitive ligand kinetic approach

ANDREW L. ROSE

Southern Cross GeoScience, Southern Cross University,
Lismore 2480, Australia
(*correspondence: andrew.rose@scu.edu.au)

Under favourable conditions, nucleation of iron (III) oxyhydroxides (FeOx) is typically rapid compared to subsequent processes. To date, little work has been done to examine the first steps of FeOx nucleation, namely the initial polymerisation of dissolved monomeric iron (III) complexes, which may be rate-limiting in the nucleation process.

I have investigated the kinetics of iron (III) polymerisation over a wide range of pH values using a competitive ligand approach in which the complexation of monomeric iron (III) by desferrioxamine B (DFB) competes with iron (III) polymerisation when conditions conducive to nucleation are induced. Polymerisation was induced by the rapid (< 5 ms) mixing of acidified solutions of dissolved iron (III) with a pH-buffered DFB solution using a micromixer chip. Formation of the orange coloured iron (III)-DFB complex was quantified over time from 100 ms after mixing onwards at concentrations down to ~10 nM with a stopped-flow long (1 m) optical pathlength spectrophotometry system (Figure 1).

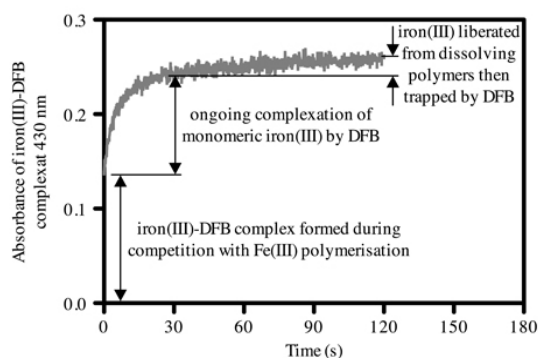


Figure 1: Kinetic traces reveal initial rapid partitioning of iron(III) between the iron(III)-DFB complex and iron(III) polymers, followed by the slow redissolution of polymers.

Kinetic parameters for FeOx polymerisation (obtained by simultaneously fitting data from multiple iron (III) and DFB concentrations at each pH) varied with pH in a manner consistent with control of the initial polymerisation step by the exchange of water bound to monomeric iron (III). The initial steps in FeOx nucleation can thus be interpreted in a similar context to other aquatic chemical processes.

Environmental impact of engineered nanoparticles and nanomaterials through their life cycle

JÉRÔME ROSE^{1,2}, MÉLANIE AUFFAN^{1,2},
PERRINE CHAURAND^{1,2}, JÉRÔME LABILLE^{1,2},
DANIEL BORSCHNECK^{1,2}, ARMAND MASON^{1,2},
HELENE MICHE^{1,2}, CÉLINE BOTTA¹,
CHRISTOPHE GEANTET³, ERIC PUZENAT³,
PAVEL AFANASIEV³, EMMANUEL LECELRC³,
JEANNE GARRIC⁴, FOUQUERAY MANUELA⁴,
BERNARD VOLLAT⁴, PATRICE NOURY⁴, KHEDIDJA ABBA
CI⁴, KRZYSZTOF PIELICHOWSKIAZE⁵,
AGNIESZKA LESZCZYNSKA⁵,
SLAWOMIR MICHALOWSKI⁵, JAMES NJUGUNA⁶,
SOPHIA SACHSE⁶ AND JEAN-YVES BOTTERO^{1,2}

¹CEREGE UMR 6635- CNRS, Aix-Marseille Université,
13545 Aix-en-Provence France

²ICEINT: international Center for the Environmental
Implications of Nanotechnology, CNRS-CEA,
www.i-ceint.org

³IRCELYON, UMR 5256 CNRS/Université LYON 1, F-
69626 Villeurbanne France

⁴CEMAGREF Lyon UR MALY, Ecotoxicologie, F-69336
Lyon France

⁵Cracow University of Technology, Krakow, Poland

⁶Cranfield University, Bedfordshire MK43 0AL, United
Kingdom

Even though preliminary risk assessments of manufactured nanoparticles (NPs) are emerging, information on NPs bioavailability to aquatic biota and trophic transfer are largely lacking, and early studies have yielded incomplete and contradictory results. Moreover, a considerable confusion exists concerning the distinction between 'nanotechnology' and 'nanomaterial' which are most often considered to be synonymous of nanoparticles. But for most applications nanoparticles can be surface modified and generally are embedded in the final product and therefore do not come into direct contact with consumers or the environment. So what about their toxic effects when surface modified?

The aim of our study is to better constrain the transfer, transformation and ecotoxicity of by-products released from nanomaterials during their life cycle. Two examples will be detailed 1) nano-TiO₂ incorporated as UV filter in sunscreens ii) nano-SiO₂ based composite (polymeric matrixes including polyamides, polypropylenes and polyurethanes as bulk materials) to compare impact between by-products and bare nanoparticles. Methodology and experimental issues concerning durability characterisation using accelerated aging protocols, characterisation will be addressed.

The project is supported by the French national programs NANOALTER (INSU/EC2CO/CYTRIX), AGING NANO & TROPH (ANR-08-CESA-001) and the FP7 NEPHH project (CP-FP 228536-2).

Medically-derived ^{131}I as a tracer in aquatic environments

P.S. ROSE^{1,2*}, J.P. SMITH², J.K. COCHRAN¹,
R.C. ALLER¹, R.L. SWANSON¹ AND R.B. COFFIN²

¹SoMAS, Stony Brook University, Stony Brook, NY 11794-5000, USA

²Marine Biogeochemistry, Code 6114, US Naval Research Laboratory, Washington, DC 20375, USA
(paula.rose.ctr@nrl.navy.mil)

Iodine-131 ($t_{1/2} = 8.04$ d) has been measured in Potomac River water and sediments in the vicinity of Blue Plains, the world's largest advanced wastewater treatment plant. It serves all of Washington, DC, treats an average of 1.4×10^9 L d⁻¹ and has a maximum capacity of $>4 \times 10^9$ L d⁻¹. Concentrations of ^{131}I detected in sewage effluent and in the river suggest a continuous discharge of the isotope from Blue Plains. Surface water ^{131}I ranged from 0.076 ± 0.006 to 6.07 ± 0.07 Bq L⁻¹. Partitioning in sewage effluent and river water suggests that ^{131}I is associated with colloidal and particulate organic material. Iodine-131 was detected in sediments to depths of 5 cm with specific activities between 1.3 ± 0.8 and 117 ± 2 Bq kg⁻¹ dry weight. The behavior of ^{131}I in the Potomac River is consistent with the cycling of natural iodine in aquatic environments. It is discharged to the river via sewage effluent, incorporated into particulate matter and deposited in sediments where it is subject to diagenetic remineralization.

Additionally, dissolved ^{131}I showed a strong, positive correlation with $\delta^{15}\text{N}$ values of nitrate in the river. Surface water $\delta^{15}\text{NO}_3$ values ranged from 8.7 ± 0.3 to $33.4 \pm 7.3\%$ with dissolved inorganic nitrogen ($\text{NO}_3 + \text{NO}_2$) concentrations between 0.38 ± 0.02 and 2.79 ± 0.13 mgN L⁻¹. $\delta^{15}\text{N}$ in sediments ranged from 4.7 ± 0.1 to $9.3 \pm 0.1\%$. Sediment profiles of particulate ^{131}I and $\delta^{15}\text{N}$ indicate rapid mixing or sedimentation and in many cases remineralization of a heavy nitrogen source consistent with wastewater nitrogen.

Sewage effluent discharges of ^{131}I to surface water can be used to study the rates and mechanisms controlling natural iodine cycling. Iodine-131 coupled with $\delta^{15}\text{N}$ can be an excellent tracer for the short-term fate of wastewater nitrogen. The utility of ^{131}I is not limited to the Potomac River. The presence of medically-derived ^{131}I has been documented in several aquatic environments and is readily measurable in sewage effluent. Continuous discharges of this radioisotope in sewage effluent are likely to be widespread. Further study of ^{131}I in receiving waters can provide valuable insight into the fate and transport of this radioisotope in the context of large scale accidental releases.

Volatile abundances and Pb isotopes in melt inclusions from Iwate volcano, Japan

E.F. ROSE-KOGA^{1*}, K.T. KOGA¹, M. HAMADA²,
T. HELOUIS¹, M.J. WHITEHOUSE³ AND N. SHIMIZU⁴

¹Laboratoire Magmas et Volcans, Université Blaise Pascal, CNRS, UMR 6524, IRD, R 163, Clermont-Ferrand, France

(*correspondence: ekoga@opgc.univ-bpclermont.fr)

²Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Japan

³Swedish Museum of Natural History & Nordic Center for Earth Evolution, Stockholm, Sweden

⁴Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA

The pre-eruptive volatile content of magma is of fundamental importance for understanding melting processes, as well as eruption dynamics. However, since volatiles in magma are largely degassed during subaerial eruptions, it is difficult to estimate their pre-eruptive concentrations based on the measurements of volcanic whole rocks. Melt inclusions trapped in early crystallizing olivine retain dissolved volatiles of magmas at depth (e.g. [1]).

Iwate volcano is located on the volcanic front of the North-east Japan arc on the Honshu Island. The Iwate samples are one of the most undifferentiated rocks on the volcanic front of Japanese island arcs. The olivine hosted melt inclusions of the 1686 eruption of Iwate volcano are basaltic to basaltic-andesitic in composition.

The melt inclusions have Pb isotope compositions $^{207}\text{Pb}/^{206}\text{Pb}$ (0.836 to 0.850) and $^{208}\text{Pb}/^{206}\text{Pb}$ (2.079 to 2.094). These compositions are homogeneous and close to MORB values. The volatile contents (H_2O , S) are highly variable and reaches values comparable to that of Izu Oshima melt inclusions (up to 3.57 wt% and 1798 ppm, respectively; [2]). F and Cl concentrations are highly clustered between 113 and 183 ppm and 285 and 408 ppm, respectively. This low F and Cl magma, yet with arc H_2O content, may represent partial melting of a highly depleted mantle wedge with no or little metasomatism.

[1] Sobolev (1996) *Petrol.* 209–220. [2] Ikehata, Yasuda & Notsu (2010) *Miner. Petrol.* 143–152.

U/Pb age spectra of detrital rutile as a powerful tool for provenance analysis

DELIA RÖSEL¹, THOMAS ZACK¹, MATTHIAS BARTH¹,
ANDREAS MÖLLER² AND JEFFREY OALMANN²

¹Institut für Geowissenschaften, Universität Mainz, Becher
Weg 21, 55128 Mainz

(*correspondence: roeseld@uni-mainz.de)

²University of Kansas, Dept. of Geology, Lawrence, KS,
66045, USA

Compared with zircon, rutile is assumed to be unstable during low-grade metamorphic conditions, so that rutile grown under prograde metamorphic conditions should not contain inherited cores of older metamorphic events. Therefore rutile predominantly reflects the age of the latest metamorphic overprint. In general, metamorphic overprint is orogen-wide with similar ages in large areas. We therefore propose that detrital rutile age spectra can be utilized to distinguish between local sources (unimodal age distribution) and continent-wide catchment areas (several age peaks).

As part of a larger project aiming at detrital rutile of sub-greenschist facies meta-psammitic rocks, several samples from the Saxo-Thuringian Zone of the Variscan Orogen have been dated. All detrital rutiles from the Neoproterozoic to Lower Silurian depositional ages show pre-depositional ages indicating that the rutiles are detrital and that the Variscan overprint has not reset the ages. Most samples show an unimodal age distribution, with Pan African ages between 600 and 800 Ma. However, rutiles out of one meta-sandstone with Late Ordovician / Early Silurian depositional age show a multimodal age spectrum. 30 % of the ages are > 1000 Ma and reaching a maximal age of 2200 Ma. This age distribution suggests erosion of other metamorphic domains and transport of the eroded material at the same time and to the same sedimentary environment as those from the Pan African Orogen. The Late Ordovician of the Saxo-Thuringian strata characterizes the transition from rift basin to a passive margin setting on the northern periphery from Gondwana [1]. The age spectrum indicates a direct sedimentary connection between Saxo-Thuringia and Gondwana during that period, perhaps by a continent-wide river system.

Alternatively, another source of multimodal detrital rutiles can be deposits of the Late Ordovician Hirnantian glaciation of Gondwana, which are found stratigraphically below the meta-sandstones [1]. However, this possibility would still imply a sedimentary connection between Gondwana and Saxothuringia.

[1] Linnemann *et al.* (2004) *Int J Earth Sci* **93**, 683–705.

Reactivity of mafic and ultramafic rocks with CO₂-charged fluids and the autocatalytic reduction of CO₂ to form CH₄

R.J. ROSENBAUER^{1*}, C. OZE², L.C. JONES¹, B. THOMAS¹,
G.I. GOLDSMITH³ AND J.L. BISCHOFF¹

¹US Geological Survey, 345 Middlefield Rd., Menlo Park, CA
94025 (*correspondence: brosenbauer@usgs.gov)

²Department of Geological Sciences, University of
Canterbury, Christchurch, New Zealand

³Department of Chemistry, Bryn Mawr College, 101 N.
Merion Ave., Bryn Mawr, PA 19010

Mafic and ultramafic rocks are highly reactive to carbon dioxide (CO₂). They may be potential repositories for sequestering CO₂ because of their capacity for trapping CO₂ in carbonate minerals. They are also capable of reducing CO₂ to form CH₄ via molecular hydrogen (H₂) from serpentinization reactions. Geochemical laboratory experiments, reacting tholeite, picrite, and olivine with CO₂-charged fluids over a range of temperature (50 - 200°C) and pressure (100 - 300 bar) conditions, resulted in a high degree of rock alteration, secondary mineral formation and gas synthesis. In tholeite and picrite experiments, CO₂ is taken up from solution at all temperatures but the maximum extent and rate of reaction occurs at 100°C and 300 bar. The amount of CO₂ uptake at 100°C, 300 bar ranged from 8 wt% for a typical tholeite to 26 wt% for a picrite, where the amount of uptake coincides with the Mg content of the rock as a reaction limiting factor. Although geochemical modeling predicts an equilibrium carbonate alteration assemblage of calcite, magnesite, and siderite, only secondary ferroan magnesite was identified in the residual solids.

An alternate fate for CO₂ when reacted with ultramafic rocks is conversion to CH₄. In olivine hydrolysis experiments (200°C, 300 bar), Fe²⁺ from olivine is incorporated into carbonates more rapidly than Fe²⁺ oxidation (and concomitant H₂ formation) leading to diminished yields of H₂ and H₂-dependent CH₄ production. At carbonate equilibrium or under-saturated conditions, the experimental data suggest that produced magnetite catalyzes the reduction of CO₂ to form CH₄. Rate calculations suggest that the kinetic balance between the production of H₂ and CH₄ in natural systems undergoing serpentinization may serve to discriminate between abiotic and biotic processes.

The Co-precipitation of Ra in a large scale evaporitic system

Y.O. ROSENBERG^{*1}, V. METZ² AND J. GANOR¹

¹Dept. of Geological and Environmental Sciences, Ben-Gurion Univ., P.O.B. 653, Beer Sheva 84105, Israel
(*correspondence: yoavoved@gmail.com)

²Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, P.O.B. 3640, 76021 Karlsruhe, Germany

High concentrations of radium pose environmental and health concerns in natural and industrial aqueous systems. Co-precipitation of Ra²⁺ with barite is an effective process in decreasing its concentration, and was extensively addressed in laboratory experiments. The outcome of such small scale experiments often serves in theoretical risk assessments simulation, but was hardly validated over large field systems.

The co-precipitation of Ra²⁺ with barite was studied in a large scale field system, comprising 6 sequential evaporation ponds, having a total volume of 3.25·10⁵ m³, in which a rejected brine of a desalination plant is evaporated. The non evaporated brine has an ionic strength of 0.7 m, ²²⁶Ra concentration of 12 Bq kg⁻¹, and it is oversaturated with respect to gypsum, celestite and barite. Upon its evaporation the ionic strength increases up to 8.4 m, and a total amount of ~ 4·10⁶ kg year⁻¹ of sulphate minerals precipitates.

Brine and salt samples were collected and analyzed for their chemical composition and radium isotopes. Precipitation rate of the different ions was calculated by assuming a steady state at each pond. The *apparent* partition coefficient of Ra in barite for pond *n* was calculated as: $K'_{d,n} = \ln\{[Ra_n]/([Ra_{n-1}] \cdot EF)\} / \ln\{[Ba_n]/([Ba_{n-1}] \cdot EF)\}$, where *[i]* is the concentration of component *i* (mol kg⁻¹), and *EF* is the evaporation factor which corrects for concentration changes due to evaporation. Assuming that Mg is conservative, $EF = [Mg]_n/[Mg]_{n-1}$.

Preliminary results demonstrate that the increase in the amount of ²²⁶Ra and Ba in the solid is concurrent and is not correlated with the increase of neither Ca or Sr. This indicates that barite precipitates as a separate phase and that Ra co-precipitates with barite. On the average, $K'_{d,n}$ among all the ponds was calculated to be 1.1±0.1 in agreement with laboratory experiments carried out with the same brine (1.04±0.01). However, close examination reveals that $K'_{d,n}$ increases by a factor of ~2 from 0.7±0.3 to 1.5±0.1 as barite precipitation rate decreases ~20 fold. This trend suggests that similarly to laboratory observations, kinetic effect lowers Ra co-precipitation.

Constraints given by the above field observations support experimental data, and thus strengthen the validity of the parameters needed for risk assessments.

Solubility of carbon dioxide in aqueous fluids at subcritical pressure: Testing the models

JÖRGEN ROSENQVIST*, ANDREW D. KILPATRICK
AND BRUCE W.D. YARDLEY

School of Earth and Environment, University of Leeds, Leeds LS2 9JT, United Kingdom
(*correspondence: j.rosenqvist@leeds.ac.uk)

Modelling of CO₂ storage in geological reservoirs indicates that solution trapping will become significant with time. However, there is little direct experimental data for CO₂ solubility in aqueous fluids at subcritical and near-critical pressures. We have therefore performed CO₂ solubility experiments in an intermediate pressure range, and made comparisons with model predictions.

Experiments are conducted at temperatures from RT to 70°C, with absolute pressures ranging from 4 bar to tens of bars. Our experimental setup allows pH-measurements to be conducted at pressure, for pressures ≤ 10 bar. The solution phase can be sampled at any pressure and the CO₂ solubility is determined to within 1% using alkalinity titrations.

Figure 1 shows coupled pH – solubility data at a total pressure of 4 bar. At this pressure the agreement between experiment and PHREEQC modelling is generally good, but anomalously high solubilities are predicted for calcite-bearing assemblages giving relatively high pH fluids. If confirmed at higher pressures, this discrepancy will have important implications for modelling CO₂ storage.

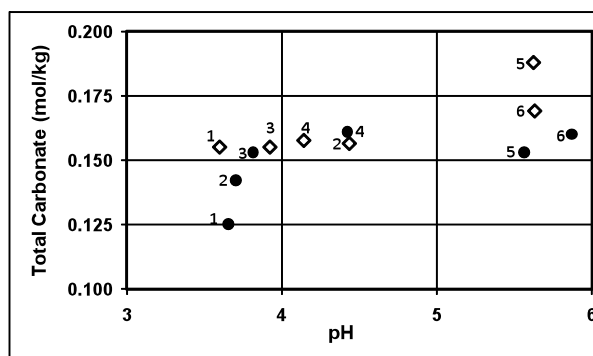


Figure 1: Solid symbols show experimental CO₂ solubility and pH, open symbols show results from PHREEQC calculations. Symbols numbered 1 are for pure H₂O - CO₂, while the others are for H₂O - CO₂ - mineral systems as follows: 2: K-feldspar 3: kaolinite 4: Na-montmorillonite 5: calcite 6: Na-montmorillonite + calcite.

New offset $\delta^{11}\text{B}$ isotope reference materials for geochemical and environmental boron isotope studies

M. ROSNER^{1,2*} AND J. VOGL²

¹IsoAnalysis UG, 10829 Berlin, Germany

(*correspondence: martin.rosner@bam.de)

²BAM Federal Institute for Materials Research and Testing, 12205 Berlin, Germany

The isotopic composition of boron is a well established tool in various areas of science and industries. Boron isotope compositions are typically reported as $\delta^{11}\text{B}$ values which indicate the isotopic difference of a sample relative to the internationally accepted isotope reference material NIST SRM 951. A significant drawback of all of the available boron isotope reference materials is that non covers a natural boron isotope composition apart from NIST SRM 951.

To fill this gap of required offset $\delta^{11}\text{B}$ reference materials we produced three new solution boric acid reference materials that cover two-thirds of the natural boron isotope variation (-20 to 40 ‰ $\delta^{11}\text{B}$) of about 100 ‰. The new reference materials are certified for their $\delta^{11}\text{B}$ values. The certified $\delta^{11}\text{B}$ values of -20.2 ‰ for ERM-AE120, +19.9 ‰ for ERM-AE121 and 39.7 ‰ for ERM-AE122 have been established by three independent analytical methods (gravimetric, TIMS Na_2BO_2^+ and Cs_2BO_2^+). The $\delta^{11}\text{B}$ reference materials are commercially available through European Reference Materials (<http://www.erm-crm.org>) or the webshop of the BAM Federal Institute of Materials Research and Testing (<http://www.webshop.bam.de>).

The newly produced and certified boron isotope reference materials will allow straight forward method validation and quality control of boron isotope data.

Micro-XRD and ICP-MS analysis of sub-milligram sized mineral samples

KIRK C. ROSS AND BALZ S. KAMBER

Laurentian University, Sudbury On Ca (kross@laurentian.ca)

We present a study that combined micro-analytical X-ray diffraction (XRD), employing the image plate - diffraction image integration software (IP-DIIS) method, with trace element analysis on the very same grain fragment via ultra-low blank solution inductively coupled plasma - mass spectrometry (ICP-MS). The experimental procedure involves three steps. First, trace element homogeneity in the mineral is studied via laser ablation ICP-MS by analysis of multiple spots. Subsequently, a very small fragment of material (typical edge length ~15-25 μm) is removed adjacent to the laser ablation pit. This is then mounted in a 114.6 mm Gandolfi camera. An IP is used to quantitatively record the diffraction inter-planar spacing (d-spacing) and intensity (I). The latent image on the IP is digitized through a proprietary IP scanner, after which the image plate can be erased and reused. The scanned image is then converted to a digital diffractogram using appropriate not-for-profit software. We demonstrate that simple XRD technique yields a fully quantitative digital diffractogram amenable to Rietveld structural refinement. The accurate and precise crystallographic parameters are thus known for the mineral fragment from the structural refinement. The final analytical step involves ultra-low blank miniaturized mineral acid digestion of the mineral fragments that typically weigh between 0.1 and 1 milligrams. The digests are subsequently analyzed for the trace element suite of interest by solution ICP-MS.

When crystallographic parameters and chemical information are combined in this fashion, it is possible to empirically test the control exerted by the crystal lattice on apparent trace element partition coefficients. In particular, this method allows a test of the theoretically derived and experimentally confirmed crystal lattice strain model (CLSM) [1, 2] for naturally occurring mineral phases. Namely, the fundamental premise of the CLSM is that isoivalent trace element distribution (D) in a mineral is controlled by the size (R_0) and elastic modulus (E) of the substituent crystallographic site. The XRD data can be used to compute R_0 while the trace element data can be used to calculate an independent value for R_0 from the strain-free admittance of a fictitious atom of radius R_0 .

[1] Brice J.C. (1975) *J Cryst. Growth* **28**, 249–253. [2] Blundy JD, Wood BJ (1994) *Nature* **372**, 452–454.

Thermodynamic properties of hydration layers on surfaces of metal oxide nanoparticles

N.L. ROSS^{1*}, E.C. SPENCER¹, B.F. WOODFIELD²,
A. NAVRTOSKY³, S.F. PARKER⁴ AND A.I. KOLESNIKOV⁵

¹VirginiaTech, Blacksburg, VA 24061, USA

(*correspondence: nross@vt.edu)

²Brigham Young University, Provo, UT 84602, USA

³NEAT, UC Davis, Davis, CA 95616, USA

⁴ISIS, RAL, Didcot, OX11 0QX, UK

⁵ORNL, Oak Ridge, TN 37831, USA

Water is ubiquitous on the surface of oxide nanoparticles and can exert a profound influence on the thermodynamic properties of the oxide [1]. We have measured inelastic neutron scattering (INS) spectra for several hydrated metal oxide nanoparticles systems, including 6nm SnO₂, 7nm rutile-TiO₂, 16nm Co₃O₄, and 10nm CoO, and determined the isochoric heat capacity and vibrational entropy of the water confined to their surfaces [2-4]. The results from these studies have been combined with complementary calorimetric data and show that the surface energy of the underlying metal oxide particles exerts a strong influence on the heat capacity of the hydration layers. The surface water adsorbed on metal oxide nanoparticles with higher surface energies have lower heat capacities and vibrational entropies. For example, isostructural SnO₂ and rutile-TiO₂ have surface energies of 1.72±0.01 and 2.22±0.07 Jm⁻², respectively, with S₂₉₈ values of their hydration layers equal to 37.17 and 32.34 JK⁻¹mol⁻¹, respectively [3, 5]. In addition, Co₃O₄ spinel and CoO rocksalt nanoparticles, although chemically similar, have surface energies of 1.96±0.05 and 3.57±0.20 Jm⁻², respectively, with S₂₉₈ values of their hydration layers equal to 38.13 and 37.03 JK⁻¹mol⁻¹, respectively [4, 5].

[1] Boerio-Goates *et al.* (2006) *Nano Lett.* **6**, 750.

[2] E.C. Spencer *et al.* (2009) *J. Phys. Chem. A*, **113**, 2796.

[3] E.C. Spencer *et al.* (2011) *J. Phys. Chem. A*, submitted.

[4] E.C. Spencer *et al.* (2011) *J. Phys. Condens. Matt*, in press.

[5] A. Navrotsky *et al.* (2010) *Science* **330**, 199.

The Late Jurassic Andean back-arc volcanism, Northern Chile (26-31°S)

P. ROSSEL¹, V. OLIVEROS^{1*}, M.N. DUCEA², M. LABBE¹
AND R. CHARRIER³

¹Departamento Ciencias de la Tierra, Universidad de Concepción, Casilla 160-C, Concepción, Chile

(*correspondence: voliveros@udec.cl)

²Univ. of Arizona, Dept. of Geosciences, Tucson, AZ, 85721, USA

³Departamento de Geología, Universidad de Chile, Casilla 13518, Correo 21, Santiago, Chile

The configuration of the Andes in southwestern Gondwana during the Jurassic and Early Cretaceous was characterized by abundant primitive arc magmatism, and marine to continental extensional back-arc basins controlled by hemigraben fault systems. Occasional effusion of volcanic material occurred along the eastern flanks of these basins. Between 26° and 31°, two parallel belts of volcanic rocks crop out to the east of the contemporary Upper Jurassic arc. The volcanic rocks located closer to the arc (G1), have a maximum age of 163.2 Ma, range from basaltic-andesite to andesite, with minor rhyolites, and have calc-alkaline affinities but with higher alkali content than the arc rocks. The more distant volcanics (G2) have a maximum age of ca. 153 Ma and are mostly alkaline basalts.

Spider diagrams show enrichment in LILE, usually not higher than 100, relative to the primordial mantle, and concentrations of HREE below 10. The rocks of G1 are characterized by Nb-Ta troughs and La_n/Nb_n ratios between 2.2 and 8.1, while G2 trace elements patterns have a concave-down shape, similar to that of the OIB, and La_n/Nb_n ratios between 1.8 and 2.5 or Nb-Ta anomalies commonly absent. Rocks from both groups have flat REE patterns, with minor negative Eu anomalies for G1, and positive Eu anomalies for some G2 lavas. The Ni concentrations (44-223 vs 20-130 ppm), Dy/Yb (1.8-2.8 vs 1.9-2.1) and La/Yb (7-23 vs 8-17) are higher for the G2 lavas, which is consistent with the greatest distance of this group from the trench, and lower degrees of partial melting of their mantle source. The lower Nb/Yb for the G1 lavas (2-37 vs 3-8) suggests a more depleted source than that of the G2 lavas, but more enriched relative to the source of the arc rocks (0.1-3). Isotopic ratios (⁸⁷Sr/⁸⁶Sr=0.7035-0.70501, ¹⁴³Nd/¹⁴⁴Nd=0.512455-0.512742, ²⁰⁶Pb/²⁰⁴Pb=18.4-19.34, ²⁰⁷Pb/²⁰⁴Pb=15.6-15.67, ²⁰⁸Pb/²⁰⁴Pb=38.43-39.0) are indicative of an enrichment in the magma source from the arc eastwards; the spatial and temporal geochemical variations suggest progressive increase of lithospheric contributions to the back-arc magmatism.

Large-scale simulation of molecular structure and electron transfer in microbial cytochromes

KEVIN M. ROSSO^{1*}, PIOTR ZARZYCKI¹,
 MARIAN BREUER², JOCHEN BLUMBERGER², LIANG SHI¹,
 DAVID J. RICHARDSON³, THOMAS A. CLARKE³,
 MARCUS EDWARDS³, JULEA BUTT³, JOHN M. ZACHARA¹
 AND JIM K. FREDRICKSON¹

¹Pacific Northwest National Laboratory, Richland
 Washington, USA

(*correspondence: kevin.rosso@pnl.gov)

²University College London, London, UK

³University of East Anglia, Norwich, UK

This research seeks to understand rates and molecular mechanisms used by microbial multiheme c-type cytochromes (c-Cyts) for mediating extracellular Fe valence transformation, an important biogeochemical process affecting the availability and supply of reactive Fe (II) in subsurface environments. The structure of MtrF, an outer-membrane decaheme c-type cytochrome from an iron-reducing bacterium, has been determined by synchrotron diffraction measurements. Results show that the ten hemes of MtrF are organized into a unique 'wire cross', in which a staggered 65 Å octa-heme chain transects the length of the protein and is crossed at the middle by a 45 Å tetra-heme chain. Each heme is within 7 Å of its nearest neighbors, in principle permitting rapid interheme electron transfer.

Large-scale molecular dynamics simulations are being carried out to understand the free energy landscape for electron hopping along various trajectories of the wire cross. Using the technique of thermodynamic integration, relative redox potentials of all possible intraprotein electron transfer steps have been computed, which shows that upon possible electron entry into heme 5, only a 0.84 kcal/mol (1.4 kT) activation free energy barrier for electron transfer to heme 4 opposes otherwise net thermodynamically downhill heme-to-heme conductance to hemes 2, 7, and 10 at the protein-environment interface. It is therefore proposed that heme 5 is the input site of electrons from partner proteins MtrDE up the electron transport chain, and that MtrF transfers electrons down the chain directly to Fe (III)-oxides via highly solvent-exposed heme 10. The combined experimental and computational simulation activity is collectively providing a comprehensive understanding of bacterial outer-membrane c-Cyt functioning at the level of individual heme redox potentials, heme-to-heme electron transfer rates across the protein, and insights into dynamical effects of protein fluctuation and solvent reorganization on overall electron transfer conductance.

Reactive Fe(II) and electron exchange dynamics in iron oxides

K.M. ROSSO^{1*}, P. ZARZYCKI¹, C.I. PEARCE¹, J. KATZ²,
 B. GILBERT², R.M. HANDLER³, M.M. SCHERER³
 AND P. MEAKIN⁴

¹Pacific Northwest National Laboratory, Richland WA, USA
 (*correspondence: kevin.rosso@pnl.gov)

²Lawrence Berkeley National Laboratory, Berkeley, CA, USA

³University of Iowa, Iowa City, IA, USA

⁴Idaho National Laboratory, Idaho Falls, ID, USA

Ferrous-ferric electron exchange is central to the biogeochemical cycle of iron and determines iron forms and availability in the subsurface. For most environmentally relevant conditions this exchange involves interaction between soluble ferrous iron and solid-phase iron oxides and oxyhydroxides, with complex involvement of solid-state charge migration. Examples include Fe (II)-catalyzed transformation of Fe (III)-oxides and oxyhydroxides, and spinel ferrite nanoparticles acting as a mineralogic source and sink for reactive Fe (II) due to their topotactic solid-solution property and stable multi-valent nature. This presentation focuses on the interdependence of Fe (II) fluxes at these mineral-water interfaces with structural and electronic properties of mineralogic iron oxide forms. Using combined experiment and computational molecular simulation, we examine the underlying mechanisms of observed complete iron atom exchange without change in mineralogy, crystallinity, crystal size or shape between an aqueous Fe (II) pool and well-defined goethite (FeOOH) crystallites, the accessibility of solid-state Fe (II) in titanomagnetite (Fe_{3-x}Ti_xO₄) nanoparticles in which the structural Fe (II)/Fe (III) ratio is intentionally tuned by the Ti (IV) content, and the highly time-resolved dynamics and fate of Fe (II) electrons photoinjected into maghemite (Fe_{8/5}O₄) nanoparticles. Aspects covered will include thermodynamic energy requirements for bulk crystal conduction and possible free energy sources sustaining bulk currents, ferrous iron adsorption energies at iron oxide surfaces and the kinetics of interfacial electron exchange, the structural dependence of ferrous-ferric electron exchange in the solid, and internal charge compensation mechanisms. These lines of research are collectively converging on a picture of rapid electron exchange dynamics between aqueous ferrous iron and iron oxides, with broad-reaching implications for the biogeochemistry iron in the subsurface.

New approaches to assess the responses of phytoplankton to ocean acidification

BJÖRN ROST

Alfred Wegener Institute for Polar and Marine Research,
Bremerhaven, Germany (Bjoern.Rost@awi.de)

Global Change will affect phytoplankton in many ways, altering the complex balance of biogeochemical cycles and climate feedback mechanisms. Hence, predictions of how phytoplankton may respond to these perturbations at the cellular and ecosystem levels are a major challenge in global change research. In this presentation, I will outline the expected physico-chemical changes in the marine environment (e.g. ocean acidification, light regime, nutrients supply) and describe how these may affect different phytoplankton groups. Focusing on coccolithophores, diatoms, dinoflagellates and cyanobacteria, results from laboratory and field studies will be analyzed in view of the overall sensitivity (e.g. elemental composition, growth rate, productivity) to ocean acidification. To go beyond this descriptive level, methods on cellular processes are increasingly applied in the context of global change research. They yield information about underlying mechanisms causing processes like photosynthesis, calcification or N₂ fixation to be responsive to ocean acidification.

Overall results indicate major species- and taxa-specific differences in the sensitivity towards ocean acidification. While some species are not responsive at all, others will clearly benefit or have to face detrimental effects. The presented data will stress, however, that responses to ocean acidification are strongly modulated by other environmental conditions, such as light or nutrient levels. As these factors are also influenced in the framework of global change, the combined effects have to be considered. Some of the observed responses can meanwhile be related to species- or taxa-specific physiological traits. Next to *direct* CO₂ effects (e.g. on processes like the CO₂ concentrating mechanism), the aspect of energy allocation between physiological processes seems to play an crucial role in causing *indirect* CO₂ effects (e.g. on processes like N₂ fixation). As the cellular changes imposed by ocean acidification likely influence the competitive abilities of species, implications for the natural phytoplankton communities and biogeochemical cycling may be even be larger than indicated from results obtained in mono-specific incubations.

Wetland extension on the Russian Plain over the past 40 kyr: A biomarker approach from the Black Sea

F. ROSTEK* AND E. BARD

CEREGE, Univ. Aix-Marseille, CNRS, IRD & College de France, Technopole de l'Arbois BP 80 13545 Aix-en-Provence Cedex 04, France
(*correspondence: rostek@cerege.fr, bard@cerege.fr)

The Black Sea is a catchment basin for large areas of the European Russian Plain, the Alps and southeastern Europe. In order to study the hydrological changes in this basin over the last 40 kyr, we measured a continuous series of terrestrial long-chain *n*-alkan-2-ones and *n*-alkanes as paleoclimate proxies in well dated glacial lacustrine to Holocene marine sediments from the NW Black Sea.

Two specific molecules of these homologous series are normalized to total organic carbon (TOC), respectively Ket27/TOC for *n*-alkan-2-ones and C23/TOC for *n*-alkanes and interpreted as characteristic biomarkers for *Sphagnum* mosses, a dominant vegetation component in wetlands. Decreased concentrations of *Sphagnum* biomarkers are found for the North Atlantic icebergs surges and cooling events known as Heinrich Events, the Last Glacial Maximum and the Younger Dryas. These drops are pointing to low erosional input to the Black Sea with cold and dry climate conditions. Increased biomarker inputs characterize the mild climate phases known as Dansgaard/Oeschger Interstadials, pointing to increased erosion due to permafrost degradation and/or wetland extension on the Russian Plain.

The final retreat of the Fennoscandian ice sheet is concomitant with Heinrich Event 1 and expressed by increased biomarker concentrations in the so-called Red Layers, a typical series of deglacial clay layers. The two biomarker signals are decoupled at the start of the Bølling/Allerød: C23/TOC is decreasing whereas Ket27/TOC variations are in phase with the major climate events like the Bølling/Allerød, the Younger Dryas event and the early Holocene. The paleoclimatic record is interrupted by the final reconnection of the Black Sea with the Mediterranean Sea which led to marine conditions.

Halogen composition of the early Solar System inferred from meteoritic apatites

J. ROSZJAR^{1*}, T. JOHN², M. WHITEHOUSE³, G. LAYNE⁴
AND A. BISCHOFF¹

¹Institut für Planetologie, WWU Münster, Germany

(*correspondence: j_rosz01@uni-muenster.de)

²Institut für Mineralogie, WWU Münster, Germany

³Laboratory for Isotope Geology, Naturhistoriska Riksmuseet
Stockholm, Sweden

⁴Department of Earth Sciences, Memorial University, St.
John's, NL Canada

The volatile halogens are important tracers in constraining Solar System processes, such as degassing, and as abundant anionic components in fluids they are also useful in deciphering fluid-rock interactions. So far, there is limited information about halogen ratios and the $\delta^{37}\text{Cl}$ isotope composition of planetary reservoirs, such as the chondritic reservoir, depleted Earth mantle or bulk silica Earth.

The halogen budget of individual meteorite samples appears dominantly controlled by apatites that preferentially incorporate halogens. To constrain the halogen budget of the early Solar System planetesimals we determined F, Cl, Br, and I concentrations, and the $\delta^{37}\text{Cl}$ of individual apatite grains in meteoritic materials - including ordinary and Rumuruti chondrites, primitive achondrites, eucrites, and iron meteorites. Phosphate grains were documented by SEM and their mineral chemistry was determined by EPMA. Halogen concentrations and $\delta^{37}\text{Cl}$ were determined using a Cameca IMS 1280 (NORDSIMS). Mass balance calculations were carried out to evaluate the potential of apatite to act as a probe for the halogen chemistry.

$\delta^{37}\text{Cl}$ values of different meteorite groups span a range from about -1 ‰ to +1 ‰ [1; this study]. We found an evolutionary trend in $\delta^{37}\text{Cl}$ from chondritic through differentiated material, with the latter probably being balanced by silicate-bearing iron meteorites, such as Campo del Cielo. This trend is also seen for F/Cl of apatites from different meteorite groups, which ranges from $\sim 100 \times 10^{-3}$ in chondritic material to $\sim 32, 500 \times 10^{-3}$ in differentiated meteorites. I/Cl range from $\sim 0.6 \times 10^{-6}$ to 6×10^{-6} , - except for eucrites, which have I/Cl two orders of magnitude higher. Br/Cl vary from $\sim 0.02 \times 10^{-3}$ in ordinary chondrites to $\sim 1.7 \times 10^{-3}$ in iron meteorites. This implies discernible variation of halogens among different meteorite groups but, compared to Earth's halogen reservoirs, a relatively homogeneous halogen composition for the early Solar System.

(1) Sharp *et al.* (2007) *Nature* **446**, 1062-1065.

Inherited ^{142}Nd anomalies in the Nuvvuagittuq supracrustal belt

A.S.G. ROTH¹, B. BOURDON², T. KLEINE³, S.J. MOJZSIS⁴
AND M. TOUBOUL⁵

¹Institute of Geochemistry and Petrology, ETH Zurich, 8092
Zurich, Switzerland (antoine.roth@erdw.ethz.ch)

²ENS Lyon, UMR 5276, CNRS, France

³Institut für Planetologie, Universität Münster, 48149 Münster,
Germany

⁴Department of Geological Sciences, University of Colorado,
Boulder, CO 80309-0399, USA

⁵Department of Geology, University of Maryland, College
Park, MD 20742, USA

The short-lived ^{146}Sm - ^{142}Nd chronometer is a sensitive tool to trace early silicate Earth differentiation. Mantle depletions prior to ~ 4.2 Ga are documented as positive ^{142}Nd anomalies in Eoarchean rocks [e.g. 1]. O'Neil *et al.* [2] reported evidence for an early enriched reservoir from negative ^{142}Nd anomalies in pre-3750 Ma rocks of the Nuvvuagittuq supracrustal belt (NSB) in Québec. These authors derived a ^{146}Sm - ^{142}Nd isochron with a 4.28 Ga age and concluded that the NSB may be the oldest crust.

We present new coupled ^{147}Sm - ^{143}Nd systematics for six different NSB lithotypes. Samples yield a range of $^{147}\text{Sm}/^{144}\text{Nd}$ ratios from about 0.07 to 0.17. Nd data were collected on a Triton (TIMS) at ETH; repeat measurements of the JNdi-1 standard yield an external precision of ± 4 ppm (2 SD) for the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio (n=39). We reproduced negative ^{142}Nd anomalies for sample powders reported in [2], and for a cummingtonite amphibolite from the mapped area in [3]. A mafic (tonalitic) gneiss and a quartz-biotite schist from an Inukjuak supracrustal enclave NE of the NSB show $^{142}\text{Nd}/^{144}\text{Nd}$ ratios lower than the terrestrial standard ($\epsilon^{142}\text{Nd} = -0.08$ to -0.13). Taken together, these negative ^{142}Nd anomalies are uncorrelatable with $^{147}\text{Sm}/^{144}\text{Nd}$ for mafic or felsic lithologies and do not produce a ~ 4.28 Ga isochron as in [2]. In ^{147}Sm - ^{143}Nd isochron diagrams our NSB whole rock samples define an array with an imprecise age of ~ 3.75 Ga similar to ages from U-Pb ion microprobe zircon geochronology [3]. Data indicate that the NSB rocks suffered a complex protracted history and that the Sm-Nd system is disturbed. We conclude that the absence of concordant ages in the ^{143}Nd - ^{142}Nd system suggests that the negative ^{142}Nd anomalies were inherited from an early enriched reservoir and do not represent the age of the formation of the NSB rocks.

[1] Caro *et al.* (2006) *GCA* **70**, 164-191. [2] O'Neil *et al.* (2008) *Science* **321**, 1828-1831. [3] Cates and Mojzsis (2007) *EPSL* **255**, 9-21.

Use of TGA/DSC-IR to assess the effect of Cr on struvite stability

ASHAKI A. ROUFF

School of Earth and Environmental Sciences, Queens College,
CUNY, Flushing NY 11367, USA
(Ashaki.Rouff@qc.cuny.edu)

A TGA/DSC-IR hyphenated technique was used to evaluate the effect of sorbed Cr on the thermal properties of struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$, MAP). MAP occurs in guano deposits, peat, and lake sediments [1, 2]. It is also found in agroecosystems as a fertilizer decomposition product, and as a component of animal manure and poultry litter [3]. These systems can have high metal content, including Cr, which may substitute for P in MAP. Simultaneous thermal analysis has been used to determine the effect of Cr on the thermodynamic properties and stability of phosphate minerals [3, 4]. Addition of IR spectroscopy allows direct identification and quantification of decomposition products. Cr-MAP solids were generated from solutions with 0-100 μM Cr (III) and Cr (VI). DSC indicated an endothermic peak for all solids at 127 ± 0.5 °C, accompanied by >50% sample weight loss based on TGA, due to evolution of H_2O (g) and NH_3 (g) as identified by IR. The enthalpy, weight loss, and moles of evolved gases varied with initial Cr oxidation state and concentration. This was suggestive of diverse sorption complexes and mechanisms, further investigated using FT-IR and XAFS. The overall effect of sorbed Cr was to increase the structural H_2O content of MAP and to reduce the enthalpy of the endothermic transition. This indicates that Cr reduces the stability of MAP, increasing susceptibility to decomposition and thus release of the metalloid. This has implications for cycling of Cr, P and N in MAP-bearing natural and agricultural systems.

- [1] Abdelrazig & Sharp (1988) *Thermochim. Acta* **129**, 197–215. [2] Donovan *et al.* (2007) *The Holocene* **17**, 1155–1169. [3] Hunger *et al.* (2008) *J. Environ. Qual.* **37**, 1617–1625. [3] Wakamura *et al.* (1997) *Polyhedron* **16**, 2047–2053. [4] Yasuda & Hishinuma (1995) *Solid State Ionics* **78**, 109–114.

Identification of geochemical processes in groundwater at the Chernobyl Pilot Site and preliminary contamination characterization with $^{36}\text{Cl}/\text{Cl}$ ratios

C. ROUX^{1,2*}, C. LE GAL LA SALLE¹, C. SIMONUCCI²,
S. BASSOT², J.-L. MICHELOT³, K. FIFIELD⁴,
N. VAN MEIR², D. BUGAI⁵ AND J. LANCELOT

¹GIS/CEREGE, UMR 6635, CNRS/University of Nîmes and Aix-Marseille, F-30035, Nîmes cedex 1, France

(*correspondence: celine.roux.1@etu.univ-cezanne.fr, corinne.legallasalle@unimes.fr)

²IRSN, POB 17, F-92262 Fontenay-aux-Roses, France (caroline.simonucci@irsn.fr)

³IDES, UMR 8148, CNRS/University of Paris 11, F-91405, Orsay, France

⁴Department of Nuclear Physics, Australian National University, Canberra ACT 0200, Australia

⁵IGS, National Ukrainian Sciences Academia, U-01054 Kiev, Ukraine

After the accident at the Chernobyl Nuclear Power Plant in april 1986, $12 \cdot 10^{18}$ Bq of radionuclides (RN) were released in the atmosphere and most of them were redeposited around the facility. To prevent atmospheric resuspension, about 800 trenches were dug on site to dispose contaminated material (debris, organic matter, topsoil containing reactor fuel particles). Since 1999, the EPIC (Experimental Platform In Chernobyl) project has been set to study migration of radionuclides from one of these trenches, the trench T22, through the unsaturated and saturated zone. A plume of ^{90}Sr was identified downstream from the trench. The aim of this study is to contribute to the understanding of the migration of ^{90}Sr and other RN in groundwater. Water stable isotopes indicate winter recharge and groundwater stratification. Major elements show an increase in concentration with depth, linked to mixing and/or water-rock interaction processes. Preliminary results in $^{36}\text{Cl}/\text{Cl}$ show ratios in the order of those observed in concrete of proton-accelerator facilities [1] and 2 to 3 orders of magnitude higher than the theoretical ratio in precipitation. The source of this contamination may be contaminated particles released during the explosion and/or background activity and/or waste buried in the trench. Characterization of transport processes will be further investigated based on $^{235}\text{U}/^{238}\text{U}$, $^{86}\text{Sr}/^{88}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and additional $^{36}\text{Cl}/\text{Cl}$ measurements.

- [1] Bessho (2007) *Nucl. Instr. & Meth. in Phys Research B* **259**, 702–707.

Energy content of soil organic matter as studied by bomb calorimetry

PERE ROVIRA* AND RITA HENRIQUES

Forest Sciences Center of Catalonia (CTFC), Solsona, Spain
(*correspondence: pere.rovira@ctfc.cat)

Calorimetry has been applied to the study of soil organic matter for decades. Differential scanning calorimetry (DSC) has been the most widely used technique: this method submits the soil sample to a controlled temperature increase (often, 10°C per minute), and records the energy released by the combustion of organic matter. The components of organic matter (cellulose, lignin, polyphenolics, etc) have contrasting ignition temperatures; thus the graph of energy released *versus* temperature characterizes a given substrate [1]. In spite of the obvious attractive of this technique, it has the problem that during the temperature increase (and as a consequence of it) some components of the sample may volatilize before being affected by combustion, a fact that may result in underestimations of the amount of energy stored within the structure of the organic matter under study.

Bomb calorimetry is an alternative procedure. This technique does not allow a detailed study of the release of energy along a range of temperatures, because it gives just a single value, the total energy released by the combustion of the sample. Nevertheless, since the combustion occurs within a closed vessel, no losses of material occur. Therefore, the recorded release of energy reflects the amount of energy stored in the sample probably better than DSC techniques.

We applied bomb calorimetry to quantify the energy stored in soil organic matter in a set of mediterranean forest soils, under *Pinus halepensis* and over calcareous substrates (limestones, marls, etc). Methodological problems were observed; for instance, for soil samples below 7% of OC it was not possible to start a combustion by the standard method (electrical flash in the O₂-saturated vessel), and a comburent was needed.

The amount of energy released was linearly related to the organic carbon content. The relationship was very close, with r^2 values higher than 0.9. Translated to stored energy per unit of organic matter, the obtained values were around 34 Joules per mg C. This ratio, however, was not constant, for it increased with the total organic matter of the sample. In soil horizons very rich in organic matter (some OH horizons) it can reach almost 40 Joules per mg C, whereas it may drop down to less than 30 in mineral soil horizons. The relationships between energy stored and characteristics of the soil organic matter are under study.

[1] Rovira *et al.* (2008) *Soil Biol. Biochem.* **40**, 172–185.

Basaltic magmatism and mantle metasomatism in the Rio Grande Rift

M.C. ROWE^{1*}, J.C. LASSITER² AND B.M. SCHMANDT³

¹Washington State University, School of Earth and Environmental Sciences, Pullman, WA 99164, USA
(*correspondence: mcrowe@wsu.edu)

²University of Texas at Austin, Jackson School of Geosciences, Austin, TX 78712, USA

³University of Oregon, Department of Geological Sciences, Eugene, OR 97403, USA

The Rio Grande Rift in the southwest United States provides an excellent opportunity to investigate temporal and spatial variations in mantle sources and basaltic magmatism in an active continental rift setting. The Rio Grande Rift, extending from northern Mexico to northwest Colorado, has undergone varying amounts of extension, with extension decreasing to the north. Prior rheological studies have indicated that metasomatism and hydration may have a significant effect on the strength of the lithospheric mantle. Here we combine primitive melt inclusion geochemistry (major-, trace-, and volatile elements), whole rock Sr-Nd-Pb isotopic analysis, and tomographic imaging to examine potential mantle metasomatism and its effects on basaltic magma compositions in the Rio Grande Rift.

Melt inclusions and whole rock compositions are screened for potential crustal contamination based on negative correlations between Cl/K and Ba/Nb as described by Rowe & Lassiter [1]. Here we focus on Cl variations in melt inclusions, specifically variations in Cl/Nb, to identify mantle metasomatism. The only significant temporal variation along the rift in Cl/Nb is in the southernmost region where the highest Cl/Nb ratios are observed in olivine-hosted melt inclusions from a ~37Ma basalt (~150 Cl/Nb) compared to melt inclusions from a young (<50ka) basalt (~10 Cl/Nb). Correlations between age of magmatism, Cl/Nb, and whole rock ¹⁴³Nd/¹⁴⁴Nd, particularly in the southern rift segment, indicates changes in Cl/Nb are likely related a transition from lithospheric to asthenospheric melting over time.

For basaltic volcanism younger than 5 m. y. the highest Cl/Nb ratios are in the central Rio Grande Rift, suggesting little systematic Cl/Nb fluctuations along the rift (N to S). However, for young volcanics, tentative correlations between whole rock Pb isotopes and mantle seismic velocity models (Vs/Vp at 60-100km depth) may further support diverse mantle sources for basaltic magmatism.

[1] Rowe & Lassiter (2009) *Geology* **37**, 439–442.

The Fe L₃-edge as a probe for Fe oxide speciation

A.N. ROYCHOUDHURY^{1*}, B.P. VON DER HEYDEN¹,
M. FRITH² AND S.C.B MYNENI²

¹Dept. of Earth Sciences, Stellenbosch University,
Stellenbosch 7602, South Africa
(*correspondence: roy@sun.ac.za)

²Dept. of Geosciences, Princeton University, Princeton, NJ
08544, USA

L-edge XANES spectroscopy has been used to identify the speciation of Fe in natural samples. The majority of previous analyses are limited to the identification of Fe (II) versus Fe (III) speciation in complex natural samples however, these spectra are rarely used to identify different mineral phases in soils and sediments. Using the fine spectral variations between different crystalline and amorphous Fe phases, we developed a technique to evaluate the local co-ordination environment of Fe in natural samples. The technique makes use of splitting of the main electronic transitions in the L₃ edge (ΔE) region, and the ratio of their peak intensities. These spectral parameters are sensitive to the valence state, electronegativity of the coordinated ligands and the degree of distortion of the polyhedra of Fe. We collected L-edge XANES spectra of several synthetic Fe-oxides and oxyhydroxides, and also compiled the spectra of several published spectra in the literature.

When compared for the characteristic ΔE values and intensity ratio values; the common Fe (III) minerals, goethite, akaganeite, lepidocrocite, amorphous Fe, hematite, and maghemite fall within their own discreet oblong fields, with minor overlap between some of the phases. Similarly, the Fe (II) rich phases occupy their own positions on the plot characterized by greater intensity ratios. The differences in the characteristic intensity ratio values of the fields for the ferric standards is defined predominantly by the number of hydroxyls co-ordinating, and the characteristic ΔE values are governed predominantly by the magnitude of the ligand field splitting. The arrangement of the fields is also a function of the polyhedral linkages and this is reflected in the average metal-metal distances. However, this analysis is limited by the saturation effects, an artifact of the XANES analysis of thicker and Fe-rich particles.

Details of these spectral analyses, the effects of cation substitution in Fe-oxides that influence these spectral parameters, and an application of this technique to study the natural samples will be presented.

Redox stratification of the White Sea sediments

ALEXANDER ROZANOV

P.P. Shirshov Institute of Oceanology, Russian Academy of
Sciences, Moscow (rozanov@ocean.ru)

Redox stratification is formed by the consequence of biogeochemical reactions of oxidation and reduction of organic and inorganic components of the sediments. Organic matter on the surface of the White Sea sediments is oxidized by oxygen dissolved in bottom water. However, in the subsurface horizons the oxygen is rapidly disappearing and other carriers of oxygen, namely, oxygen compounds of nitrogen, manganese, iron and sulfur serve as oxidants. The most striking manifestation of diagenesis is an extremely high content of Mn²⁺ in the pore water (sometimes more than 500 μ M), which determines its flux from the sediments to the bottom water and oxidation at the contact with oxygen to form oxyhydroxides MnO₂, enriching the surface layers of the sediments. In lesser extent, migration and oxidation are characteristic of iron. After exhaustion of oxygen in the surface layer at the stage of anaerobic diagenesis newly formed oxyhydroxides (MnO₂ and FeOOH) themselves become oxidants of organic matter. Estimation of the diffusion flux of manganese from the sediments (280 μ M/(m²day) and the corresponding amount of MnO₂ formed, compared with the opposite flux of oxygen to the sediments (1-10 mM/(m² day), shows that over 10% of the organic matter of the surface layer of the sediments can be oxidized with MnO₂. The role of other oxidants of organic matter (FeOOH and SO₄²⁻) is prominent in the deeper horizons. In the upper package of sediments (0 - 100 cm) 61% of the anaerobic oxidation of Corg accounted for MnO₂, the proportions of FeOOH and SO₄²⁻ are 14 and 25% respectively. At the same time in the topmost surface layer (0-5 cm) MnO₂ is practically 100 per cent oxidant agent, and at 100 cm the 100-percent oxidizer is SO₄²⁻. A detailed calculation of the balance of reduction process shows the higher consumption of organic matter in diagenesis of surface sediments than gives a direct determination of Corg. The most active processes of redox diagenesis end at 25-50cm. Layers of manganese enrichment in the deeper horizons are in the nature of metastable relics of the surface accumulation (probably, manganese nodules), subject to gradual dissipation within the sediment column.

Core formation in the Earth and the terrestrial planets

D.C. RUBIE^{1*}, D.J. FROST¹, D.P. O'BRIEN², F. NIMMO³,
A. MORBIDELLI⁴ AND H. PALME⁵

¹Bayerisches Geoinstitut, Univ. Bayreuth, D-95440 Bayreuth, Germany (*correspondence: dave.rubie@uni-bayreuth.de)

²Planetary Science Institute, Tucson, AZ 85719, USA

³Dept. of Earth and Planetary Sciences, University of California, Santa Cruz, CA 95064, USA

⁴Observatoire de Nice, F-06304 Nice Cedex 4, France

⁵Forschungsinstitut und Naturmuseum Senckenberg, D-60325 Frankfurt am Main, Germany

Accretion of the terrestrial planets occurred through a series of impacts/mergers with smaller differentiated embryos and planetesimals (e.g. [1]). In addition to adding Fe metal to proto-planets, impacting bodies provide sufficient energy to cause large scale melting, the establishment of deep magma oceans and therefore episodes of metal-silicate segregation. In our recent model of multistage core formation [2], collisions result in an impactor's core partially or fully equilibrating in a magma ocean before merging with the planet's proto-core. Compositions of metal and silicate that result from the equilibration process are determined from the bulk composition by a novel approach involving mass balance combined with element partitioning. In the case of the Earth, model parameters (e.g. metal-silicate equilibration pressures) are determined by a least squares regression based on constraints provided by the concentrations of major and trace elements in the Earth's mantle. Results show that accretion of the Earth was heterogeneous: early accreting material was highly-reduced and volatile-poor and later accreted material was more oxidized and volatile-rich. This is consistent with dynamical simulations which suggest that late-accreting material originates from greater heliocentric distances and should thus be more volatile rich [1]. Oxygen fugacity and the FeO content of the mantle both increase during accretion due to (a) the dissolution of Si into the core by a reaction that releases oxygen and (b) the late addition of oxidized material. In contrast to early models of heterogeneous accretion, equilibration at pressures up to 60-80 GPa and a significant degree of disequilibrium both play a critical role.

The model is currently being integrated with N-body accretion simulations [1] in order to investigate the chemical evolution of all the terrestrial planets simultaneously. Some simulations suggest an increase in mantle FeO contents (e.g. from 4 to 14 wt%) and a decrease in mantle Mg/Si ratios and core mass fractions as heliocentric distance increases from 0.5 to 2 AU [3]. Finally, the model is used to investigate the causes of ¹⁸²W anomalies in planetary mantles.

[1] O'Brien *et al.* (2006) *Icarus* **184**, 39–58. [2] Rubie *et al.* (2011) *EPSL* **301**, 31–42. [3] Rubie *et al.* (2011) *42nd LPSC*, Abstract #1061.

Do erupted mafic lavas accurately reflect mantle magmatic timescales?

K.H. RUBIN

Dept. of Geology & Geophysics, Univ. of Hawaii, Honolulu, HI 96822 USA (krubin@hawaii.edu)

Mantle melting and melt transport encompass a range of processes that vary in duration, magnitude and length scale, and depend upon variables such as tectonic setting, volcano maturity, volcano spacing, and mantle physical characteristics (e.g. thermal state, composition, lithology, upwelling rate). Multiple compositional attributes of mantle derived magmas provide information on melting processes and conditions. The U-series nuclides are nearly unique in their ability to provide information about rates of such processes because chemical fractionation creates radioactive disequilibria between decay chain nuclides, which then decay away on characteristic timescales once fractionation ceases. Some surprising results from this literature suggest that the duration of melting is highly variable over short temporal and spatial scales in the mantle, and that melt transport is generally quite fast. But how trustworthy are these interpretations? Early studies were content to use the presence or absence of radioactive disequilibria in magmas to crudely estimate the duration of magma generation and transport in the mantle. Yet since the 1970s, development of much more sophisticated melting models and of analytical methods for nuclide activity measurements with 100-fold precision improvements have led to more specified time scale assessments in the U-series literature. Despite these refinements, the geological errors introduced by the melting and melt transport processes in the mantle place severe and often underestimated limits on our ability to tell time with these tracers in erupted magmas. Situations such as multiple melting lithologies, magma mixing, fluid-addition (at convergent margins) and reactive transport create a large amount of non-uniqueness to the way U-series data sets can be interpreted. Add crustal/magma chamber processes to this list and the challenge of deriving a unique temporal solution to the duration of magmagenesis and transport using a combined U-series, major/trace element and radiogenic isotope data set is nearly insurmountable. Nevertheless, results from U-series studies have much to tell us about magmatic timescales so long as data are not over-interpreted or modeled with a false sense of precision to the parameterization. This presentation will discuss the current state of the art and successful strategies for limiting the uncertainty of timescale assessments from magma chemistry, and present examples where results are generally consistent with independent geological and geophysical observations.

Local and regional magmatic modulators to mantle signatures in erupted mid-ocean ridge lavas

K.H. RUBIN^{1*}, JOHN MACLENNAN², JOHN SINTON¹
AND ERIC HELLEBRAND¹

¹Dept. of Geology & Geophysics, Univ. of Hawaii, Honolulu, HI 96822 USA (*correspondence: krubin@hawaii.edu)

²Department of Earth Sciences, University of Cambridge, CB2 3EQ, UK

Although nearly all mid-ocean ridge magmas are formed in the mantle and inherit local compositional characteristics of the mantle source, a range of processes that occur between melt generation at depth and eruption on the sea-floor modulate the chemical signals of mantle heterogeneity that is sampled by ridge volcanoes. Increased time-integrated magma supply from mantle to crust is one characteristic that dramatically impacts (reduces) true mantle compositional variance in MORB by promoting coupled magma mixing and differentiation in the crust (e.g. [1]). Studies at local and regional spatial scales underscore the importance of geological conditions for interpreting mantle signatures in erupted lavas and provide a means for studying non-steady-state aspects of magma transport and crustal construction on decadal to millennial timescales. The inherent complexity in MORB compositions reflects the processes and rates of magma delivery to and accumulation in the crust, as well as the extent of mixing and heat loss prior to eruption, with implications for the spatial scales of mantle compositional variation thereby recorded in MORB. This talk will discuss global variations in MORB compositions and new results of recently conducted local/regional studies at a range of spreading rates where there are melt supply 'anomalies' along axis (e.g. from hot spots) and clear short-term differences in magma supply and eruptive activity at neighboring ridge segments. In general, these studies demonstrate that short term fluctuations in magma supply are driven by mantle heterogeneity, and that globally inferred linkages between magma supply, mantle compositional variance, and differentiation degree hold at these shorter spatial and temporal scales as well. They also demonstrate the importance of understanding geological context of lava samples, the need to have a sufficiently well sampled eruptive unit, and the preference for less differentiated (generally, high MgO) lavas in order to begin to decipher mantle compositional variation patterns in MORB.

[1] Rubin & Sinton (2007) *EPSL* **260**, 257–276.

Intermediate water $\Delta^{14}\text{C}$ off Brazil between 3-40 ka BP

M. RUCKELSHAUSEN^{1*}, R. KOWSMANN², J.M. GODOY⁴,
G.M. SANTOS³ AND A. MANGINI¹

¹Heidelberger Akademie der Wissenschaften, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany (*correspondence: mario.ruckelshausen@iup.uni-heidelberg.de)

²Petrobras-CENPES, Cidade Universitaria, Quadra 7, Ilha do Fundao, CEP 21949-900, Rio de Janeiro, RJ, Brazil

³Keck-CCAMS Facility, Earth Systems Science, B321 Croul Hall, Univ. of California, Irvine, CA 92697-3100, USA

⁴Instituto de Radioprotecao e Dosimetria, Barra da Tijuca, CEP 22643-970, Rio de Janeiro, RJ, Brazil

The Southern Ocean is thought to play a key role in understanding the atmospheric rise of CO_2 at the end of the last glacial period accompanied by a decline of atmospheric $\Delta^{14}\text{C}$. Here we present reconstructed marine $\Delta^{14}\text{C}$ activities from corals of intermediate depth off Brazil. The corals stem from two new sediment cores in the direct vicinity to our cores already reported in [1]. This new dataset expands the older one and encompasses now the ages from 3-40 ka BP. First measurements validated our $\Delta^{14}\text{C}$ findings already published in [1]. The new data show that the continuous $\Delta^{14}\text{C}$ decline starting in our previous study with the Younger Dryas (YD) extends to 5 ka BP reaching an absolute minimum with an apparent ventilation age of over 6200 ^{14}C years. These observations are compatible with the scenario suggesting the existence of an abyssal reservoir in the Pacific Ocean that was isolated for several thousand years from the atmosphere before deglaciation. The observed continuous $\Delta^{14}\text{C}$ decline during Heinrich Stadial 1 (HS1) and the YD would then suggest a further weakening of ventilation of the deep water and the injection of this old carbon dioxide signature from the deep Pacific reservoir into the Circumpolar Water around Antarctica that is the source of Atlantic Intermediate Water. This follow-up study also attempts to trace back the history of the $\Delta^{14}\text{C}$ activity beyond HS1 (HS2, HS3 and HS4). First results lead to the conclusion that even during HS4 (38-35 ka), the water on the continental shelf off Brazil was highly depleted in ^{14}C with apparent ventilation ages of 4.84 ± 1.35 ka (2σ). Recurring events of old water masses advance at intermediate depth off Brazil indicate a coupling between the intensity of deep water formation in the North Atlantic and the ventilation of the deep Pacific Ocean.

[1] Mangini *et al.* (2010) *EPSL* **293**, 269–276

Statistical sampling of mantle heterogeneity

JOHN F. RUDGE^{1*}, JOHN MACLENNAN²
AND ANDREAS STRACKE³

¹Bullard Laboratories, Department of Earth Sciences,
University of Cambridge, Madingley Road, Cambridge,
CB3 0EZ, UK (*correspondence: rudge@esc.cam.ac.uk)

²Department of Earth Sciences, University of Cambridge,
Downing Street, Cambridge, CB2 3EQ, UK
(jcm1004@cam.ac.uk)

³Institut für Mineralogie, Westfälische Wilhelms-Universität
Münster, Corrensstraße 24, 48149 Münster, Germany
(stracke.andreas@uni-muenster.de)

The Earth's mantle is chemically, isotopically, and perhaps even lithologically, heterogeneous. This heterogeneity provides key information on Earth's evolution through time. Unfortunately much of this information is destroyed and overprinted by the melting and melt mixing processes that occur during the formation of basalt, which is then sampled at the Earth's surface.

The aim of this study is to better understand how mantle heterogeneity is filtered to produce the heterogeneity we observe in basalts. Since the physical processes of melting, melt mixing, and melt extraction are complex and still poorly understood, we focus here on developing simple statistical models of the sampling process. In these models we consider the melting of a two lithology source consisting of an enriched, more fusible, lithology (e.g. pyroxenite), and a more depleted, less fusible, lithology (e.g. peridotite). We fractionally melt these two lithologies, and then mix the resultant fractional melts together to form a sample, i.e. an erupted basalt.

There are many different ways in which the fractional melts can be mixed together to produce a sample, and we compare a number of different models for this mixing process. We focus in particular on the effects of biasing the mixing according to the different depths at which the fractional melts are generated. To constrain our models we compare the results with isotopic, major, and trace element observations of both whole rocks and melt inclusions from tightly constrained regions (e.g. Theistareykir, NE Iceland [1, 2]). Models in which deep melts mix more thoroughly than shallow melts can account for several key characteristics of these geochemical observations. We suggest that mixing of deep melts occurs during melt generation and migration in the mantle, prior to extensive mixing in lower crustal magma chambers.

[1] Stracke *et al.* (2003) *Geochem. Geophys. Geosyst.* **4**, 8507.

[2] MacleNNan *et al.* (2003) *Geochem. Geophys. Geosyst.* **4**, 8624.

A novel proxy links CAMP volcanism with end-Triassic mass extinction and early Jurassic evolution

M. RUHL*, C.J. BJERRUM, R. FREI AND C. KORTE

Nordic Centre for Earth Evolution, University of
Copenhagen, Oester Voldgade 10, DK-1350 Copenhagen
K, Denmark (*correspondence: micharuhl@gmail.com)

Phanerozoic mass extinctions are marked by global marine and terrestrial biodiversity loss and often linked to the formation of large igneous provinces (LIPs). Large-scale greenhouse gas release during these major volcanic events had a profound impact on the global exogenic carbon cycle, initiating strong perturbations in $\delta^{13}\text{C}$ records. Hence, they can be regarded as natural deep-time analogues of global environmental change. However, high resolution stratigraphic correlation between LIP formation, biotic crises and isotopic perturbations are poorly constrained. Here we present a novel proxy for volcanic activity, based on relative abundance changes of Lu, Hf, Y and Nb trace elements (ratio: $(\text{Lu}/\text{Hf})_{\text{Y/Nb}}$), in a marine sedimentary record across the Triassic-Jurassic boundary. We show that peak $(\text{Lu}/\text{Hf})_{\text{Y/Nb}}$ values exactly match up with consecutive continental flood basalt emplacements in the Central Atlantic Magmatic Province (CAMP). The observed $(\text{Lu}/\text{Hf})_{\text{Y/Nb}}$ -peaks also coincide with the end-Triassic mass extinction, one of the largest Phanerozoic extinctions (at ~201.38 Ma), and with early Jurassic recovery patterns, suggesting that volcanism also governs (the speed of) early Jurassic evolution. Hence, this proxy for the first time allows very detailed causality studies on increased volcanic activity, disruption of global geochemical cycles and global biodiversity/ ecosystem turnovers, in unprecedented stratigraphic resolution. We furthermore test this method on the end-Permian mass extinction, the largest extinction event in earth history. Furthermore, the abundance of these trace elements in different CAMP basalt units, suggests a transition in magmatic source for the flood basalts. Lu/Hf and Y/Nb values in the oldest CAMP units are similar to the upper crust and gradually change (within ~600 kyr) to MORB values in the youngest CAMP units. In addition, highly reactive iron and trace element (Mo, U etc.) data allow interpretation of water column conditions in terms of oxic vs. anoxic and ferruginous vs. euxinic conditions. Periods of ocean anoxia/ euxinia (based on increased Fe-HR/Fe-T, Fe (Py)/Fe-HR, Mo values) coincides with the CAMP volcanic phase, but a direct link to individual CAMP pulses is yet less clear.

Reduction of biogenic uranyl phosphate nanoparticles by three metal-reducing bacteria

X. RUI¹, M.I. BOYANOV², M.J. KWON²,
E.J.O'LOUGHLIN², S. DUNHAM-CHEATHAM³, J.B. FEIN³,
B.A. BUNKER¹ AND K.M. KEMNER²

¹Department of Physics, University of Notre Dame, Notre Dame, IN 46556 (xrui@nd.edu)

²Bioscience Division, Argonne National Laboratory, Argonne, IL 60439

³Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, IN 46556

The transformations of U in subsurface environments are controlled by a number of bacterially-driven precipitation and redox reactions. We examined the ability of three dissimilatory metal-reducing bacteria (*Anaeromyxobacter dehalogenans* strain K, *Geobacter sulfurreducens* PCA, and *Shewanella putrefaciens* CN32) to reduce U (VI) in three forms: hydrogen uranyl phosphate (HUP) nanoparticles on the cell wall of *Bacillus subtilis* bacteria precipitated by passive cell wall biomineralization; abiotically precipitated HUP; and aqueous uranyl ion. The reduction experiments were conducted at pH=6.8 with presence and absence of bicarbonate and phosphate. X-ray Absorption Fine Structure spectroscopy (XANES and EXAFS) showed varied reduction extent of U (VI) by the three bacteria. The biogenic HUP mineral was consistently more easily reduced than the abiotic HUP under the same experimental conditions. Higher extent of reduction was observed in the presence of bicarbonate. Reduction experiments under conditions that inhibited the HUP dissolution (i.e. high phosphate concentrations) showed smaller extents of U (VI) reduction. These results indicate reduction of the dissolved U (VI) species in the system, as opposed to direct electron transfer to the HUP mineral. EXAFS analysis shows that the reduced U (IV) species are consistent with mono- and bi-dentate phosphate complexation of the U (IV) atoms, as found in the U^{IV}Ca (PO₄)₂ mineral ningyoite.

Radioactive element abundances, paleo-heat flows, and the internal evolution of Mars

JAVIER RUIZ^{1*}, ALBERTO JIMÉNEZ-DÍAZ¹,
VALLE LÓPEZ^{2,3}, PATRICK J. MCGOVERN⁴,
JEAN-PIERRE WILLIAMS⁵, BRIAN C. HAHN⁶
AND ROSA TEJERO^{1,3}

¹Departamento de Geodinámica, Universidad Complutense de Madrid, Madrid, Spain

(*correspondence: jaruiz@geo.ucm.es)

²Instituto de Geología Económica, CSIC-UCM, Madrid, Spain

³Instituto de Geociencias, CSIC-UCM, Madrid, Spain

⁴Lunar and Planetary Institute, Houston, USA

⁵Department of Earth and Space Sciences, University of California, Los Angeles, USA

⁶Department of Earth and Planetary Sciences, University of Tennessee, Knoxville, USA

Lithospheric strength, crustal and mantle lithosphere composition and orbital measurements of radioactive element abundances can be used together to estimate paleo-heat flows for Mars (e.g. [1]), which help us to constrain the thermal evolution of this planet. In this work we present estimates of paleo-heat flow for several martian regions of different periods and geological context, derived from lithospheric strength and regional radioactive element abundances obtained with the *Mars Odyssey* Gamma Ray Spectrometer. The obtained surface heat flows are in general lower than the equivalent radioactive heat production of Mars in each time, suggesting a limited contribution from secular cooling to the heat flow during the majority of the history of Mars. This is contrary to the predictions from the majority of thermal history models [2], but it would be consistent with an inefficient cycling of volatiles to and from the mantle [3], as might be expected for Mars, which has lacked a plate tectonic cycle.

[1] Ruiz *et al.* (2008) *EPSL* **270**, 1–12. [2] Hauck & Phillips (2002) *JGR* **107**, 5052. [3] Sandu *et al.* (2011) *JGR*, submitted.

Dissolution/precipitation processes during low-temperature mineral weathering

E. RUIZ-AGUDO^{1*}, M. UROSEVIC¹, C.V. PUTNIS²,
C. CARDELL¹, C. RODRIGUEZ-NAVARRO¹
AND A. PUTNIS²

¹Dept. Mineralogy and Petrology, University of Granada, Spain (*correspondence: encarui@ugr.es)

²Institut für Mineralogie, Universität Münster, Germany

Low-temperature weathering of rock-forming minerals is critical for understanding earth-surface geochemical processes. Many of these minerals are reported to dissolve non-stoichiometrically, i.e. the elemental ratios in the solid are different to those in the fluid. This phenomenon is commonly called *incongruent dissolution*, and it is attributed to the preferential release of certain cations to the solution (due to differences in the bonding strength of the mineral components), leading to the formation of the so-called *leached layers* [1]. In this study, chemical analysis of the output solutions during mineral dissolution (dolomite, as an example of a mineral that reportedly dissolves 'incongruently' [2]) and in situ, nanoscale observations of the reacting surfaces using AFM are combined with the aim of establishing a realistic mechanism for the reaction. From our observations of the reacting surface we found no experimental evidence that supports the hypothesis of a preferential release of any of the cations. Moreover, our AFM results clearly indicate that the 'incongruent' behavior is the result of a dissolution-precipitation process, with the formation of a Mg-rich precipitate on dolomite dissolving surfaces. This process seems to be controlled by the composition of a boundary layer at the carbonate-fluid interface. Dissolution of the carbonate causes this fluid boundary layer to become supersaturated with respect to the secondary phase, which then precipitates.

[1] Busenberg E. & Plummer L.N. (1982) *Am. J. Sci.* **282**(1), 45–78. [2] Casey *et al.* (1993) *Nature* **366**, 253–256.

Optimized hydrofluoric acid demineralization for quantitative isolation of soil organic matter

M. RUPPENTHAL^{1*}, Y. OELMANN¹ AND W. WILCKE²

¹Institute of Integrated Natural Sciences, Department of Geography, University of Koblenz, Germany

(*correspondence: ruppenthal@uni-koblenz.de)

²Soil Science Group, Geographic Institute, University of Berne, Switzerland

Many analytical methods for chemical characterization of soil organic matter (SOM) require a precedent separation of SOM and soil mineral matrix [1]. For example, $\delta^2\text{H}$ measurements of SOM are hampered by the interference of constitutional water of clay minerals [2]. During demineralization of soil samples with hydrofluoric acid (HF), the hydrolyzed fraction of SOM is frequently discarded. Moreover, neoformed fluorides after HF treatment are often removed with highly concentrated acids resulting in additional SOM hydrolysis. Particularly from subsoil horizons considerable amounts of SOM are lost because of demineralization (losses of organic carbon [C_{org}] up to 70%).

In order to increase the C_{org} -recovery after HF treatment of soil samples and to minimize chemical alterations of SOM induced by the acid attack, we demineralized soil samples from three depth profiles. We used a new method involving density fractionation or dilute acid washings to reduce the amount of neoformed fluorides in SOM concentrates. Furthermore, we recovered the SOM dissolved in HF via precipitation of dissolved metals as hydroxides in the presence of sodium pyrophosphate to avoid coprecipitation of dissolved organic matter, followed by desalting the supernatant by means of dialysis.

Our results show that the new method allows for a better demineralization compared to established procedures, especially for subsoil horizons. We were able to minimize hydrolysis of SOM, double the C enrichment factors (ratio of C_{org} concentration after to that before treatment) and reduce C_{org} -losses to below 15%. We will discuss potential effects of the demineralization method on $\delta^2\text{H}$ values of SOM.

[1] Gélinas *et al.* 2001 *Organic Geochemistry* **32**, 677–693.
[2] Ruppenthal *et al.* 2010 *Geoderma* **155**, 231–241.

Magma mixing and the assembly of complex eruption sequences

PHILIPP RUPRECHT AND TERRY PLANK

Lamont-Doherty Earth Observatory, Columbia University,
61 Route 9W, Palisades, NY 10964, USA
(*correspondence: ruprecht@ldeo.columbia.edu,
tplank@ldeo.columbia.edu)

Elemental diffusion in plagioclase and olivine [1, 2] can provide an integrated timescale of the sequence of magma mixing until eruption. For example, at Quizapu volcano (Chile) textural observations and Mg diffusion in plagioclase constrain a succession of magma recharge, mixing and eruption to a few days to three weeks [3]. One major caveat in using elemental diffusion, however, is the potential competing effect of crystal growth, which may lead to similar normal zoning patterns when magma mixes, cools and crystallizes with more evolved compositions.

In order to deconvolve crystal growth from diffusion, we have obtained by LA-ICPMS multi-element zoning patterns for olivines from the 1963-5 eruption of Irazu volcano (Costa Rica) for elements that span a wide range of diffusivities (Fe-Mg, Mn, Li, Ca, P, Sc, Ti, V, Cr, Mn, Fe-Mg, Co, Ni, Zn). The 1963-65 eruption is characterized by phreatomagmatic deposits of basaltic andesites (54-57 wt% SiO₂, [4]). In three samples spanning a large sequence of the eruption we identify olivines of different origin (Fo70-91, crustal olivine cumulates and mantle-derived recharge olivines). Some olivines are dominated by growth signatures (primarily based on P profiles) and others record the timing of magma mixing through their diffusion profiles (Fe-Mg, Ni). The initial phase is dominated by mantle-melt derived olivines with a thin low Fo growth rim consistent with decompression growth over a few weeks in a mixed magma and a slightly normal zoned interior (Fo84-90) resulting from an extended time of diffusive exchange (months to years) at evolving but still mafic compositions. The later eruptive sequence shows much larger variety of olivines that records the syn-eruptive addition of distinct magmas that wax and wane through the eruption, though olivines still present from the early stage have much thicker growth rims indicating longer residence prior to eruption. Thus, multi-element zonation profiles record crystal growth during magma ascent and diffusive exchange during crystal storage, as an eruptive system evolves.

[1] Costa F *et al.* (2003) *GCA* **67**, 2189–2200. [2] Martin VM *et al.* (2008) *Science* **321**, 1178. [3] Ruprecht P (2009) PhD thesis, Univ. of Washington. [4] Alvarado GE *et al.* (2006) *GSA Spec. Paper* **412**, 259–276.

A complex network analysis of growth and mixing dynamics in natural metal-silicate systems

TRACY RUSHMER^{1*}, ANTOINETTE TORDESILLAS²
AND DAVID M. WALKER²

¹GEMOC/Department of Earth and Planetary Sciences,
Macquarie University, NSW 2109 Australia
(*correspondence: Tracy.Rushmer@mq.edu.au)

²Department of Mathematics and Statistics, University of
Melbourne, Victoria 3052 Australia

Core Formation in Partially Molten Planetesimals

The segregation of metallic cores from silicate mantles is one of the earliest, and most important, differentiation process involved in the evolution of terrestrial planetary bodies and reconciling our estimates of primary bulk silicate mantle with candidate planetary bulk compositions requires an understanding of the different regimes in which core forming material may have been mobile. This includes regimes that are dynamic and may result in transient states of high stress due to impact. Recent scenarios of core formation in planetesimals using calculations from extinct radionuclides (e.g. ²⁶Al, ⁶⁰Fe) call for segregation of a metal liquid (core) from partially molten silicate – a silicate mush matrix. This segregation scenario requires growth of molten core material into blebs large enough to overcome the strength of the mush matrix so that separation can occur. However, currently there is no satisfactory explanation as to how or why metallic liquid blebs in the presence of silicate melt actually grow. Experimental work has suggested deformation and shear can help coalesce metallic blebs. Here, we have developed an innovative approach that combines textures in experimental deformation experiments on a partially molten natural meteorite with complex network analyses. This approach can elucidate and quantify the growth of metallic blebs in regions where a silicate mush matrix is present and help predict separation.

Fate of nutrients in the fresh-saline water interface in coastal aquifers

A. RUSSAK^{1,2*}, O. SIVAN¹, Y. YECHIELI², B. LAZAR³
AND B. HERUT⁴

¹Department of Geological and Environmental Sciences, Ben Gurion University of the Negev, Beer Sheva, Israel
(*correspondence: russak@bgu.ac.il, oritsi@bgu.ac.il)

²Geological Survey of Israel, Jerusalem, Israel
(yechieli@gsi.gov.il)

³Institute of Earth Sciences, Hebrew University, Jerusalem, Israel (boaz.lazar@huji.ac.il)

⁴Israel Oceanographic and Limnological Research, National Institute of Oceanography, Haifa, Israel
(barak@ocean.org.il)

The fresh-saline water interface (FSI) is the transition zone between fresh and saline groundwater in coastal aquifers. Major ions composition indicate if the FSI deviates from conservative mixing between fresh and saline end-members, mainly attributed to cation exchange.

This study aims to quantify the changes in nutrient concentrations (NH_4^+ , NO_3^- , NO_2^- , PO_4^{3-} and $\text{Si}(\text{OH})_4$) across the FSI at the Israeli coastal aquifer due to freshening and salinization processes. In addition to field sampling in boreholes at the coastal aquifer, experimental studies were conducted to simulate salinization and freshening events using sediment columns and a flow-through system.

The field results show that the FSI acts as a redoxcline. The oxidized fresh groundwater zone is characterized by relatively high NO_3^- and low NH_4^+ and NO_2^- concentrations, while the saline groundwater is almost anoxic with high NH_4^+ and low NO_3^- and NO_2^- . Within the FSI NO_2^- was enriched.

During the experiments the nutrients behavior was not conservative as well. This was attributed to denitrification, adsorption/desorption and dissolution processes, similar to the field observations.

$\delta^{18}\text{O}$ zoning in eclogite garnet

A.K. RUSSELL*, K. KITAJIMA, A. STRICKLAND,
L.G. MEDARIS JR., M.J. SPICUZZA AND J.W. VALLEY

Department of Geoscience, Univ. of Wisconsin, Madison, WI
53703, USA (*correspondence: akrussell@wisc.edu)

Metamorphic garnets record history and can preserve evidence, through chemical zoning, of chemical changes and fluid interactions. O isotope ratios in minerals are valuable as monitors of fluid interactions. Secondary Ion Mass Spectrometry (SIMS) allows the measurement of $\delta^{18}\text{O}$ at 10 μm scale in garnet with a precision of $\pm 0.3\text{‰}$ (2sd) [1].

Nine garnets from eight different eclogite localities across Europe were analyzed for $\delta^{18}\text{O}$ zoning. Samples are from the Saxothuringian and Moldanubian Zones of the Variscan Bohemian Massif; Trescolmen, Alps, and the Scandian-age Nordfjord region, Norway. Analyzed by laser fluoination, eight garnets had bulk $\delta^{18}\text{O}$ values between -0.41 and 3.75‰ , and the ninth, 8.18‰ [2].

This first detailed study of $\delta^{18}\text{O}$ zoning in eclogite garnet reveals a common pattern: low $\delta^{18}\text{O}$ in the core with higher $\delta^{18}\text{O}$ rims (Figure). Seven out of nine garnets analyzed have this type of zoning, independent of garnet size, geological setting, peak metamorphic conditions, age, and garnet composition.

Our results are consistent with an inherited low $\delta^{18}\text{O}$ core derived from hydrothermally altered mafic protoliths formed at an oceanic spreading center. Due to small oxygen fractionations at high T between garnet and other minerals [3], and the refractory nature of garnet, we conclude that the increase of $\delta^{18}\text{O}$ toward the rims represents interaction with a high $\delta^{18}\text{O}$ reservoir at high pressures.

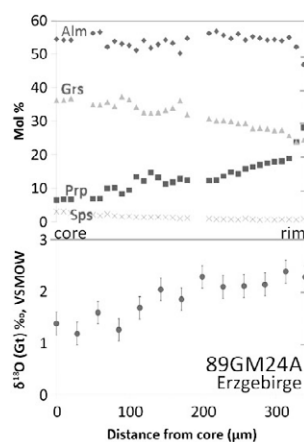


Figure: $\delta^{18}\text{O}$ and major element zoning from core to rim in garnet from the Erzgebirge[4].

- [1] Page *et al.* (2010) *Chem. Geol.* **270**, 9–19. [2] Wiesli (2002) *Geochem. ecl. & metapel. Adula Nappe, Central Alps, Switzerland. PhD thesis*, University of Tennessee at Knoxville. [3] Eiler (2001) *Rev. Min & Geochem* **43**, 319–359. [4] Klápová *et al.* (1998) *J. Geol. Soc.* **155**, 567–583.

Comparing ambient and generated marine particle composition, size, and production

L.M. RUSSELL^{1*}, A.A. FROSSARD¹, R. MODINI¹,
G.B. DEANE¹, M.D. STOKES¹, W.C. KEENE²,
P.K. QUINN³ AND T.S. BATES³

¹Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093-0221, USA

(*correspondence: lmrussell@ucsd.edu)

²Department of Environmental Science, University of Virginia, Charlottesville, VA 22904, USA

³Pacific Marine Environmental Laboratory, NOAA, Seattle, WA 98115, USA

Oceans cover two-thirds of the Earth's surface, and the particles emitted by waves breaking on the ocean surface provide an important contribution to the planetary albedo. The contribution of sea salt particles to atmospheric aerosol has been recognized and qualitatively understood for almost a century. The quantity, size distribution, and composition of submicron particles released into the atmosphere from bubble bursting remains unknown because measurements of particle production in controlled conditions have never fully explained open ocean observations. This presentation compares ambient-observed and artificially-generated composition, size, and production of marine particles.

In addition to physical measurements of particle number distributions, chemical analyses are used to illustrate the important role of surface seawater composition in forming particles. Filter samples were analyzed using Fourier transform infrared (FTIR) spectroscopy to determine the functional group composition and total organic mass (OM) of the ambient and generated marine particles. Positive matrix factorization (PMF) of the ambient particle FTIR spectra was used to separate the marine and anthropogenically-influenced sources of OM in ambient observations. Samples from marine aerosol bubbling generation showed similar organic compositions to those determined from ambient marine factors, all showing high fractions of hydroxyl functional groups. Number concentrations of artificially-generated particles were also related to the properties of the seawater from which they were generated.

To evaluate the role of organic and inorganic components of seawater in forming particles, we also investigated particle production from laboratory bubbling in controlled conditions with simple seawater model solutions. These experiments serve to illustrate the important role of sea surface components in the film bursting process that leads to particle production.

Magma degassing processes during Plinian eruptions of La Montagne Pelée (Martinique, F.W.I.)

LORRAINE RUZIÉ* AND MANUEL MOREIRA

Équipe de Géochimie et Cosmochimie, Institut de Physique du Globe de Paris, Sorbonne Paris Cité, Univ. Paris Diderot, UMR 7154 CNRS, F-75005 Paris, France
(*correspondence: ruzie@ipgp.jussieu.fr)

Magma degassing process is the driving force behind explosive eruptions. To assess our knowledge on this phenomena, we have measured noble gas abundances and isotopic ratios in pumices produced by fragmentation of volatile-enriched magma.

Ruzié et Moreira (2009) [1] conducted analyses on pumice samples coming from worldwide Plinian eruptions. All samples are characterized by a systematic enrichment in neon over argon, a depletion of krypton relative to argon and an isotopically fractioned ³⁸Ar/³⁶Ar ratio. These features do not depend on geological setting, or on pumice age, or eruption intensity. However, they are similar for pumices from the same eruption. A correlation is observed between ⁸⁴Kr/³⁶Ar and ³⁸Ar/³⁶Ar ratio. This illustrates that only one physical process is at the origin of the fractionation. We therefore proposed a model of kinetic magma degassing before fragmentation to explain the elemental and isotopic fractionation. Noble gases diffuse in a magma shell surrounding a preexisting bubble with constant radius. The model explains measurements and shows the rapidity of the magma degassing process in the conduit (few hundreds of seconds).

We apply a more elaborate model taking into account bubble growth in pumices coming from La Montagne Pelée volcano (Martinique), which produced Plinian eruptions with various intensities. A detailed stratigraphic study for the last three Plinian eruptions is still in progress.

[1] Ruzié et Moreira (2009) *JVGR* **192**, 142–150.

Regime of volatile components in magmatism of LIP (Siberian traps)

I.D. RYABCHIKOV

Institute for Geology of Ore Deposits, Russian Academy of Sciences, 119017, Moscow, Russia (iryab@igem.ru)

To assess the formation conditions of Siberian traps we investigated melt and fluid inclusions in the phenocrysts of these rocks, which were analyzed for major and trace elements (EMPA and SIMS methods).

Ion microprobe data for reheated melt inclusions show relatively low concentrations of water by comparison with non-volatile components of comparable incompatibility ($H_2O/Ce=4.5$ vs 170 for MORB). Similar decoupling of H_2O and light REE was found for OIBs which belong to EM2 mantle reservoir. This has been interpreted as diffusive dehydration of the EM2 source during its storage in a drier ambient mantle (Workman *et al.* 2006). Similar mechanism of diffusive loss of water to the surrounding mantle may be proposed for magmas in Siberian Trap Province. Fluorine whose partition coefficients for major minerals of mantle rocks are similar to those of water is characterized in the investigated melts by close correlation with its non-volatile analogue ($F/Nd=17$ vs 21 for MORB+OIB). Concentrations of volatiles other than water in the mantle source of Siberian magmas are similar to the estimates for the sources of OIB magmas.

Low concentration of H_2O and moderate contents of other volatiles imply that the estimates of near-solidus temperature based on comparison with volatile free systems would not be changed significantly. Comparison of the estimated from melt inclusion data pressures with experimental data shows that the temperature of rising plume material was ca 400°C higher by comparison with the convecting upper mantle at the same depth. This proves that plume material arrived from deep levels in the mantle below certain thermal boundary layer.

Predicting the properties and behavior of multiphase materials in disposal environments

J.V. RYAN*, C-W. CHUNG, R.E. WILLIFORD,
L.A. TURO, N.M. WASHTON AND A.L. WARD

Pacific Northwest National Laboratory

(*correspondence: joe.ryan@pnl.gov)

Multiphase materials such as cement, ceramics, metals, glasses, and glass-ceramics, are being considered for stabilization of primary and secondary radioactive wastes. These materials are hydrophysically, chemically, and structurally complex with properties varying across multiple length scales. Hydrophysical properties exert control over percolation processes that help to define the relationship between microstructure and transport properties. Chemically, each form contains several components and phases, some of which can be amorphous or poorly crystalline with metastable solid-solution compositions varying over a fairly wide range. Transport properties are generally not well understood; their dependences on microstructure are non-unique such that empirical relations cannot be universally applied with confidence and modeling of interactions is under-constrained. In addition, the characteristics, and thus performance, of multiphase materials will change as the system evolves and degrades. Prediction of these changes is necessary for an improved understanding of service life in the disposal environment. A direct consequence of this complexity is that the evolution and degradation of waste form systems (comprised of the waste form and the near-field environment) are difficult to measure and, consequently, long-term performance is difficult to predict.

This research uses an integration of computational materials science, multiphase hydraulics, and geophysical techniques with careful experimentation to develop the tools necessary for analyzing and predicting the changes accompanying the evolution and degradation of multiphase waste form systems. Two waste form systems have been chosen for analysis: corroded HLW glass and cementitious cast stone. Both subject materials are multi-scale in their heterogeneity, with variations in microstructure from nanometers to millimeters. Inverse modeling techniques are coupled with physically-realistic composite physico-chemical models to determine critical parameters. These are then investigated with targeted experiments utilizing a suite of experimental techniques covering the range of scales of interest to these particular problems, including nuclear magnetic resonance, electron microscopy, x-ray tomography, and impedance spectroscopy.