Cosmochemical Constraints on Asteroid Accretion

EBEL DENTON S [1,2], MICHAEL K. EISBERG [1,3]
AND ELLEN CRAPSTER-PREGONT[1,2]

[1]American Museum of Natural History, Central Park West at 79th St, New York, NY 10024. (*debel@amnh.org)
[2]Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York.
[3]Kingsborough College, City University of New York.

Multiple lines of chemical, isotopic and textural evidence constrain how kilometer-sized bodies accreted. Km-size chondrite parent bodies were likely precursors to planetesimals and the modern planets. **First**: Chondritic meteorites (~90% of known meteorites) contain widely variant modal abundances of their primary components: Chondrules, Ca-Al-rich inclusions (CAIs), and fine-grained matrix containing insoluble organic matter (IOM) and presolar grains (PSG) including graphite and SiC [1], yet are all "chondritic" in composition [2,3]. **Second**: Chondrules, themselves highly variable in Fe/Si, combine to make rocks with bulk chondritic Fe/Si [4]. **Third**: Chondritic meteorites contain most major elements (Si, Mg, Al, Ca, Ti) and rare earth elements (REEs) in solar proportions, with the most variation in Fe, yet CAIs have highly variable REE inventories [5]. **Fourth**: Oxygen isotopes, CAI abundances, and clast sizes suggest each chondrite group formed under locally distinct conditions. Variations in Fe do not affect the present argument. That extraterrestrial materials universally tend towards chondritic major and trace element abundances is, alone, a powerful constraint on disk processes, that has been dubbed "complementarity" [2-4]. That is, the primary components (chondrules, CAIs, matrix) complement each other to produce "chondritic" bulk meteorite composition. Why is this so?

We will present major and trace element (REE) evidence that the parent bodies of chondritic meteorites accreted from local, gravitationally unstable (overdense) accumulations of material of bulk solar or dust-enriched composition [6], subjected, prior to accretion, to varying degrees of highly local heating that produced melted objects (e.g., chondrules) with varying degrees of efficiency [7].

[1] Huss GR & Lewis RS (1994) MaP*S* **29**, 811. [2] Hezel DC & Palme H (2010) *EPSL* **294**, 85-93. [3] Bland PA *et al*. (2005) *Proc. Nat. Acad. Sci*. **102**, 13755-13760. [4] Ebel DS *et al*. (2008) *MaPS* **43**, 1725-1740. [5] Boynton WV (1975) GCA **37**, 1119-1140. [6] Alexander C.M.O'D. *et al*. *Science* **320**, 1617-1619. [7] McNally *et al*. (2013) LPS XLIV, Abs. #2844.

Deformation-related chemical alteration of meta-pegmatites

TOBIAS EBERLEI[1]*, GERLINDE HABLER[1],
RAINER ABART[1] AND BERNHARD GRASEMANN[2]

[1]University of Vienna, Department of Lithospheric Research (*correspondence to: tobias.eberlei@univie.ac.at)
[2]University of Vienna, Department of Geodynamics and Sedimentology

Deformation and chemical reactions often occur contemporaneously in nature and a proper understanding of the feedback between the two is required for correctly interpreting rock microstructures and evaluating the $P-T-t-d$ evolution of rocks. Permian meta-pegmatites from the Austroalpine Matsch Unit in the Eastern Alps were deformed at conditions close to the greenschist–amphibolite facies transition during the Cretaceous [1,2], locally producing proto-, meso- and ultramylonites with finite strain gradients at the cm- to m-scale.

We focus on the relation between the Cretaceous deformation and major element re-equilibration of the major metapegmatite phases. Several white mica and feldspar generations are recognised based on combined microstructural and microchemical characteristics. A spatial relationship between specific deformation-microstructures (kink bands, micro shear zones, cracks, strain shadows) and chemical alteration is reflected by cm-sized white mica and plagioclase clasts. A fine-grained phengitic white mica generation dominates mylonitic foliation domains and compressional quadrants of clasts. Primary K-feldspar (Kfs) shows deformation-related replacement by albite, whereas secondary Kfs together with fine-grained biotite, phengitic white mica, albite and quartz precipitated in micro-fractures and extensional quadrants of large albite and muscovite clasts. Fine-grained plagioclase aggregates in the strain-shadows of albite clasts indicate deformation by dissolution-precipitation creep (DPC). The mineral compositions of fine-grained phengitic white mica co-existing with secondary Kfs, biotite, quartz and albite are consistent with $P-T$ conditions of 480 ± 30 °C and 5 ± 1 kbar.

Our results document the correlation between deformation and chemical alteration and yield quantitative PT constraints on deformation based on syntectonic phase assemblages. The study will be further extended to examine the relationship between deformation and isotopic re-setting of the Rb-Sr system in white mica.

[1] Habler, Thöni & Grasemann (2009) *Mineral. Petrol*. **97**, 149-171. [2] Froitzheim, Conti & van Dalen (1997) *Tectonophysics* **280**, 267-297.

Quantitative analysis of high resolution isotope and concentration data from a toluene-pulse experiment by reactive transport modeling

DOMINIK ECKERT[1]*, SHIRAN QIU[2], MARTIN ELSNER[2] AND OLAF A. CIRPKA[1]

[1]Center for Applied Geosciences, University of Tübingen, Tübingen 72074, Germany (*Dominik.Eckert@uni-tuebingen.de)
[2]Institute of Groundwater Ecology, Helmholtz Center München, München 85764, Germany

A major challenge in the application of compound-specific isotope analysis (CSIA) to quantify biodegradation at contaminated field sites is the separation of microbial- and physical-induced effects on the measured isotope signal. In contrast to simple analytical tools, as the Rayleigh equation, reactive transport models can account for the complex interaction of different fractionating processes.

In this study, we analyze the high resolution toluene concentration and isotope ratio ($\delta^{13}C$) data set of a large-scale laboratory toluene pulse experiment by reactive transport modeling. We uniquely quantify degradation and sorption properties of the system, estimate the contributions of reaction-induced, sorption-induced and transverse-dispersion-induced isotope fractionation to the overall isotope signal and quantify the error introduced by neglecting individual processes (e.g. fractionation by physical processes, Michaelis-Menten degradation kinetics) in the analysis of the data. Our results show that highly resolved data of both concentration and isotope ratios are needed for unique process identification of reactive transport facilitating reliable model calibration and that the combined analysis of these highly resolved data demands reactive transport models with sufficient complexity.

Mantle control on eruption style at Kīlauea Volcano, Hawai'i

M EDMONDS[1], I SIDES[1], J MACLENNAN[1], D SWANSON[2] AND B HOUGHTON[3]

[1]Earth Sciences Department, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK
[2]Hawaiian Volcano Observatory, United States Geological Survey, Hawaii National Park, HI 96718, USA
[3]School of Ocean and Earth Science and Technology, University of Hawaii at Manoa, Hawaii, USA.

Ocean island volcanoes are associated with melting of a heterogeneous mantle source. Geochemical heterogeneity might be expected to influence the way in which melts ascend and are stored and erupted, with some melts inherently more enriched in incompatible trace elements, and hence volatiles, than others. Contrasts between effusive and explosive (fountaining) behaviour in basaltic magmas has previously been explained in terms of shallow melt-gas segregation, with little geochemical control. Here we present data from a suite of melt inclusions from 25 historical eruptions of Kīlauea Volcano over the last 500 years. The deposits were emplaced via a range of eruptive styles, from effusive lava flows, fissure eruptions, high fountains and transient subplinian (gas-rich) eruptions.

The data show that more explosive styles of eruption (high fountaining and fissure eruptions) are associated statistically with more enriched melts (with higher relative proportions of Light Rare Earth Elements) with higher volatile concentrations, which ascend faster, retain their primitive nature and interact only minimally with the summit magma reservoir. Effusive styles of eruption, on the other hand, are linked statistically with more depleted melts, with lower volatile concentrations, that tend to homogenise, cool and evolve in the summit magma reservoir before eruption.

The ranges in melt volatile concentrations between the "depleted" and "enriched" end member primary melts are approximately 0.28 to 0.87 wt% water respectively and 0.17 to 0.68 wt% carbon dioxide respectively. The more volatile-rich melts are considerably more buoyant, which has a dramatic effect on their transport, storage and eruption, owing to their higher vapour content at low pressure, increasing the likelihood of explosive high fountaining styles of volcanic activity. Over time, Kīlauea's style of eruption and magma supply rate are linked fundamentally to the geochemistry of primary melts: magma explosivity thus might be determined right at the point of separation from its mantle source region.

V.I Vernadsky: Holistic thinker and geochemical pioneer

W.M.EDMUNDS[1]* AND A A BOGUSH[2]

[1]School of Geography and the Environment, Oxford University, Oxford OX1 3GY, UK (correspondence: wme@btopenworld.com)

[2]Institute of Geology and Mineralogy of Siberian Branch of the Russian Academy of Sciences, pr.Koptyuga 3, Novosibirsk 630090. Russia (annakhol@gmail.com)

Vladimir Ivanovich Vernadsky has only recently become recognised internationally [1,2], despite being regarded as one of the greatest names in science of the 20th century in his homeland Russia. There are several reasons for his lack of renown in the west, but mainly that his most important work *"The Biosphere"* was only fully translated into English in 1997 [1,3]. This book and the ideas it contains are now becoming regarded as one of the seminal scientific works of the last century. It defines the biosphere as a unifying, holistic concept for the earth system at a time when reductionism was the driving motivation in scientific research. Above all, for earth scientists, Vernadsky regarded life as the driving geological force. He also adopted the concept of the 'Noosphere' (the evolution of human thought) to emphasis man's role as a geological agent. His publications foreshadow Gaia theory some half a century later.

This paper, coinciding with the 150th anniversary of his birth celebrates his achievements as a pioneering geochemist through his contribution in mineralogy and crystallography, geology and isotope geoscience, geochemistry and biogeochemistry, chemistry and biochemistry, pedology and hydrology, meteoritics and, the history of science and philosophy [4]. His was the first text on geochemistry [5] and also on hydrogeochemistry [2,6] published in three volumes. Vernadsky's ideas also led to the evolution of landscape geochemistry which was promulgated by his contemporaries and students (Polynov, Fersman, Perel'man *et al.*).

[1] Margulis *et al.*(1998) In: Vernadsky *The Biosphere* Nevraumont Books, New York, 14–19. [2] Edmunds & Bogush (2012) Appl Geochem **27**, 1871-1886. [3] Vernadsky (1977) The Biosphere (Trans. Langmuir DB) Springer NewYork. [4] Vinogradov (1963) Geokhimiya **3** 211-214. [5] Vernadsky (1924) La Géochimie, Paris. [6] Shavartsev *et al.* 2006 Geochem Int, **44** 619-634.

Water security in low rainfall areas

W M EDMUNDS[1]

[1]Oxford Water, School of Geography and the Environment, Oxford University, OX1 3GY

Humans have shown a capacity over millennia to adapt to living in water scarce areas under changing climatic conditions. Today the challenges of adaptation are still water-based, but more complex due in particular to energy requirements, food security and population growth. Renewable groundwater of adequate quality is the key to water resource security in arid and semi-arid areas. Excessive and uncontrolled abstraction of mainly fossil water has already led to massive depletion of valuable reserves of groundwater in major aquifers worldwide. Access to safe drinking water supplies however remains the primary issue for most of the world's poorest people.

Geochemistry plays a role in both the quantitative and qualitative aspects of water security. Physical parameters such as recharge estimation can best be estimated or validated using simple tools such as chloride mass balance; importantly such techniques are inexpensive and widely applicable. Residence times can be determined by a mix of radiometric and isotopic tracers as well as CFCs. Natural groundwater is widely recognised as the purest and most reliable water resource but its properties need assessment for harmful substances derived from geological sources. Above all, the needs of one quarter of the world's population with no access to safe drinking water and one third without access to sanitation can be addressed often using basic hydrogeology coupled with simple geochemical measurement.

It is argued that rural communities may have greater opportunities for developing water security as compared with many of those in urban areas. The key lies in creating self-sufficient and productive communities based on water prioritisation. This involves *inter alia*, careful conservation and management of renewable groundwater, rainfall harvesting, underground storage - combined with education and training initiatives benefiting rural society. Policies need to be adapted and implemented to ensure that development is based on water renewability.

Synchrotron X-ray fluorescence reveals the colourful chemistry of fossils

N.P. EDWARDS[1]*, P.L. MANNING[1], H. BARDEN[1],
W.I. SELLERS[2], U. BERGMANN[3] AND R.A. WOGELIUS[1]

[1]University of Manchester, SEAES, Williamson Research
   Centre for Molecular Environmental Science, Manchester,
   M13 9PL, UK (correspondance:
   nicholas.edwards@manchester.ac.uk)
[2]University of Manchester, Faculty of Life Science,
   Manchester, M13 9PT
[3]SLAC National Accelerator Laboratory, Linac Coherent
   Light Source, Menlo Park, CA, 94025, USA

Despite the widely accepted biogenic origin and composition of sedimentary organic matter, identification of endogenous chemical signals within intact fossil organisms is often met with scepticism. Fossilisation processes (both biological and geochemical) are widely believed to eradicate any original biochemical information, but many studies have identified endogenous chemistry within fossils. However, these studies have predominantly focused on biological structures composed of relatively geo-stable molecules (e.g., lignin and chitin) and have used techniques that have limitations with regards to maintaining sample integrity that preclude many fossils from analysis and provide only small scale or no spatial information. Synchrotron Rapid Scanning X-ray Fluorescence (SRS-XRF) is an advance in XRF imaging that provides decimeter scale, 2D maps of elements in ppm concentrations in large (100x100x30cm) fossils at rapid acquisition rates ($\sim$30 s/cm^2 at 100 micron resolution). This allows the non-destructive visualisation of chemical variation of entire fossil organisms and their enclosing matrices *in-situ*, allowing the identification of biologically and geologically derived phases. This technique has shown that certain elements correlate with, and can reveal, discrete biological structures in a range of fossil and extant organisms. Additionally, X-ray absorption spectroscopy shows that the chemical inventory of fossil tissues commonly consists of organo-metallic and organo-sulfur compounds coordinated in a manner similar to comparable extant organisms. These findings support an endogenous origin for the observed fossil chemistry and thus fossil tissues may retain useful biochemical information. For example, previously unknown remnant tooth chemistry (phosphorus) within a 50 Mya fossil reptile has been revealed, and elements (e.g., copper) associated with dark eumelanin pigmentation have been identified and mapped within feathers of an exceptionally preserved 120 Mya Chinese bird.

Coupled Fe-S-P cycling in sediments of an oligotrophic coastal basin and the role of anaerobic oxidation of methane

MATTHIAS EGGER, TOM JILBERT
AND CAROLINE P. SLOMP

Department of Earth Sciences, Utrecht University, The
Netherlands

Studies of phosphorus (P) dynamics in coastal marine sediments typically emphasize the role of coupled iron (Fe), sulfur (S) and P cycling for sedimentary P burial and release. Here, we present field results suggesting that this model may have to be extended to include interactions of reactive Fe(III) phases with methane (CH_4).

Using pore water and solid phase analyses for sediments from an oligotrophic coastal basin (Bothnian Sea) we provide evidence for the formation of Fe-bound P, possibly vivianite ($Fe_3(PO_4)_2 8H_2O$), below the sulfate/methane transition zone (SMTZ). Solid phase Fe and S profiles indicate that the SMTZ in these sediments has recently shifted upwards to its current position close to the sediment-water interface (< 10 cm). This upward shift is attributed to an enhanced rate of methanogenesis driven by an increased eutrophication over the past decades. Below the SMTZ, extremely high Fe^{2+} concentrations (> 2 mM) are observed, and supersaturation with respect to vivianite is reached. We suggest that the exceptionally high dissolved Fe^{2+} concentrations in this non-sulfidic zone may be explained by anaerobic oxidation of methane (AOM) coupled to the reduction of Fe-oxides. Dissimilatory iron reduction appears to be unlikely due to the presence of relatively refractory organic matter. Instead, the concurrent presence of both abundant CH_4 and reactive ferric Fe rather suggests Fe reduction coupled to AOM. The resulting release of Fe^{2+} into the pore water and subsequent formation of Fe(II)-P provides an important sink for P released during reductive dissolution of Fe-oxides within and below the SMTZ. If this P sink below the SMTZ would be absent this would likely lower the P burial capacity and enhance the diffusive P flux out of the sediment back into the overlying water column.

Thus, while AOM coupled to Fe reduction likely accounts for only a relatively small percentage of CH_4 removal, our study suggests that the impact on the sedimentary P cycle could be large.

Visualisation of detrital zircon age data relative to deposition age and identification of potential provenance regions

BRUCE EGLINGTON[1]*, SALLY PEHRSSON[2]
AND DAVE EVANS[3]

[1]University of Saskatchewan, Saskatoon, Canada;
   (*correspondence: bruce.eglington@usask.ca)
[2]Geological Survey of Canada, Ottawa, Canada;
   (pehrsson@nrcan.gc.ca)
[3]Yale University, New Haven, U.S.A.; dai.evans@yale.edu

Conventional probability function diagrams are routinely used to illustrate detrital zircon age data. Where numerous samples are available from stratigraphic successions, these probability plots require a lot of space and can not capture the link between zircon age and inferred stratigraphic (depositional) age. We present an alternative view of the probability plots which emphasise the relative stratigraphic age of different samples or lithostratigraphic units while illustrating which time intervals the majority of its detrital grains come from. In effect, one views the probability curves from above with the highest frequency sections of the curves plotted in emphasised ornament and colour relative to lower probability intervals in minimised ornament and shades of grey. This methodology has been built in to the DateView and StratDB online databases and into a standalone software package (FitPDF), all available from http://sil.usask.ca.

Once probability distributions have been associated with lithostratigraphic units in StratDB and DateView, the online software allows users to find all samples in the DateView geochron database which match detrital age peaks. These potential provenance localities may be further refined to take into account sediment transport directions and other geological constraints, after which it is possible to generate a probability plot for the most likely provenance localities for comparison with the actual (sample) detrital age distribution.

Locality information may also be illustrated on palaeogeographic reconstructions so as to enhance the regional provenance interpretation of detrital zircon data.

This approach is illustrated using data from the Kalahari and Pilbara cratons so as to assess different models for the Vaalbara hypothesis and of collision between the Zimbabwe and Kaapvaal cratons.

Geochemistry and the spatial patterns of water management are reflected in human hair

JAMES R. EHLERINGER[1], BRETT J. TIPPLE[1],
LESLEY A. CHESSON[1] AND LUCIANO O. VALENZUELA[1]

[1]IsoForensics Inc., 421 Wakara Way, Salt Lake City, Utah
   84108 USA (jim@isoforensics.com)

Element concentrations and isotopes of human tissues within urban regions are known to reflect human health, to provide diagnostic dietary information, and to provide region-of-origin information in a linear fashion. Here, we show the importance of isotopes of both oxygen in water and strontium within tap waters to the isotope ratios preserved within hair. We test the concept that oxygen isotopes in hair are predictable based of local drinking water values at the time that hair proteins (keratin) are initially produced within hair follicles, whereas strontium isotopes in hair reflect a progressive input from external tap waters after hair has emerged from the scalp. The contrasting inputs of oxygen and strontium isotopes to hair provide a predictable diagnostic tool that can be used in a wide array of forensics and region-of-origin studies. Since both oxygen isotope and strontium isotopes within drinking water are known to vary independently and spatially across continents in a predictable manner, the simultaneous measurement of both isotopes provides a new and powerful modern tool to reconstruct the region-of-origin of unidentified murder victims in forensic investigations.

Stable silicon isotopes in porewaters off Peru – diatom dissolution versus authigenic clay mineral formation

CLAUDIA EHLERT[12]*, KRISTIN DOERING[3],
KLAUS WALLMANN[1], PATRICIA GRASSE[1]
AND MARTIN FRANK[1]

[1]GEOMAR, Helmholtz Centre for Ocean Research, Kiel,
Germany (*correspondence: cehlert@mpi-bremen.de)
[2]Max Planck Research Group for Marine Isotope
Geochemistry, ICBM, University of Oldenburg, Germany
[3]Institute of Geoscience, University of Kiel, Germany

The stable silicon isotope compositions (δ^{30}Si) of dissolved silicic acid and of diatom opal have been used successfully to investigate changes in nutrient utilisation and biogeochemical cycling processes in the present and past ocean. Opal dissolution, however, might have an effect on the preserved δ^{30}Si signal of diatom opal in the sediment and therefore on the interpretation of paleo δ^{30}Si records.

To investigate the effects of dissolution processes on the preserved diatom δ^{30}Si signal we analysed the sedimentary biogenic opal content and dissolved silicic acid concentrations of the porewaters, as well as their δ^{30}Si signals in the upper 20-50 cm of three short sediment cores from different water depths within the Peruvian upwelling region. The cores show large variations in biogenic opal content ranging from 10-25% in the shallowest core to only 1-2% in the deepest one. The dissolved silicic acid concentration in all three profiles increases with sediment depth. The dissolved δ^{30}Si signature of the porewaters is unexpectedly high (+1.1‰ to +1.9‰) with the highest values occurring in the uppermost 5-10 cm of the deepest station. These δ^{30}Si signatures are significantly higher than the diatom opal (+0.6‰ to +1.0‰) and the seawater above (+1.0‰ to +1.5‰). In the shallowest profile the porewater δ^{30}Si does not show significant variations with profile depth, whereas the deepest profile is characterised by a pronounced decrease in the porewater δ^{30}Si with increasing profile depth.

Based on these results we suggest that the heavy δ^{30}Si signatures near the top of the profiles are the result of the precipitation of authigenic clay minerals with a very light Si isotope composition leaving the porewaters isotopically heavy. With increasing profile depth the effect of clay precipitation diminishes and the dissolution of diatom opal becomes dominant. So far we cannot unambiguously conclude on any significant effect of these processes on the preserved δ^{30}Si of the diatom opal itself and therefore on the interpretation of the downcore paleo records.

Early stage uptake of Se into rice (oryza sativa jap) seedlings depending on medium and Se concentration

E. EICHE*, A. NOTHSTEIN AND G. KONRAD

Institute for Mineralogy and Geochemistry, KIT, 76131 Karlsruhe, Germany (*elisabeth.eiche@kit.edu)

Selenium is a ubiquitously present trace element which is of interest because of its essentiality for human nutrition but also because of its toxicity in slightly elevated concentrations [1]. Various factors like pH-/ redox-conditions, organic matter content, microbial activity or competing ions can influence the Se cycling in the rhizosphere [1,2]. In order to investigate and quantify the influence of individual parameters on the Se uptake we carried out simple experiments in artificial and controlled systems.

The early stage uptake of Se into rice seedlings depending on the concentration was investigated in the range of 0 to 50 ppb Se using hydroponic systems. Selenium was added as Selenate (SeO_4^{2-}) to nutrient solution and to phytoagar (0, 20 ppb). The rice plants were grown in a climatic chamber and were harvested after 10 (1st harvest) and 17 days (2nd harvest), respectively.

The results show a linear increase of plant Se accumulation with increasing Se concentration in the nutrient solution. The Se enrichment was >3 times higher after the 2nd harvest compared to the 1st one. Also, 3.7 times more Se was taken up by shoots compared to roots. It is striking that already 50 ppb of Se in the nutrient solution lead to an accumulation of 10 ppm in the rice, a concentration that normally assigned to plants grown on seleniferous soils [3]. An even higher Se content of 17.1 ppm was reached (2nd harvest) if Se (20 ppb) was added to phytoagar. Generally, 6 to 8 times more Se was accumulated if the Se bearing medium was phytoagar and not the nutrient solution. This is probably due to interaction and competition of Se with other ions in the nutrient solution.

[1] Neal, R. H. 1995; in Heavy Metals in Soils, ed. Alloway, B. J. John Wiley & Sons Inc., 1995, 260-283. [2] Levander, O. & Burk, R.; in Selenium, eds. Hatfield, D. L.; Berry M. J. & Gladyshav, V. N. Springer US, 2006, pp. 399-410. [3] White et al., 2004. Interactions between selenium and sulphur nutrition in Arabidopsis thaliana. Journal of Experimental Botany 404, 1927-1937.

Isotopic anatomies of organic molecules

JM EILER[1] AND D KRUMWIEDE[2]

[1]Caltech, Pasadena, CA, USA (eiler@gps.caltech.edu)
[2] Thermo-Fisher Scientific, Bremen, Germany

Most organic molecules exist in an astonishingly large and diverse variety of isotopologues, i.e., considering all possible site-specific and multiple isotopic substitutions. These species are fractionated from one another by physical, chemical and biological processes. Thus isotopic variations of organics must involve an extraordinarily large number of independent compositional dimensions. Full analysis of even a fraction of this diversity presents a complex, challenging problem, but would potentially yield much new information about sources, conditions, reaction mechanisms and perhaps other variables.

Several emerging technologies make such measurements: chemical and/or pyrolytic preparations; IR spectroscopy, SNIF-NMR; and novel instruments and methods of mass spectrometry. Each has strengths and weaknesses, but none to date is capable of examining both site-specific and multiple-substitutions in small quantities (ng-mg) of species larger than ~C3 hydrocarbons. Most isotopic diversity of most organic compounds remains out of reach.

We describe instruments, methods and initial results of an experiment to expand this field to encompass the isotopic anatomies of organics up to ~300 amu, potentially bringing into play fatty acids, amino acids, isoprenoids, and similar sized compounds. The experiment uses the MAT 253 Ultra, a prototype high resolution (M/ΔM~25,000) multi-collector gas source mass spectrometer, and the Thermo DFS, a very high resolution (up to ~80-100,000) single collector gas source mass spec that is generally used for identification of organic compounds. We use the Ultra to precisely determine the intensity ratios of ion beams that include all isotopologues of a given compound (or its fragment ions), free from isobaric interferences by contaminant species, and then use the DFS to perform rapid scans over a narrow mass window, measuring relative proportions of isotopologues of that species at each cardinal mass. Combination of these data constrains proportions of each isotopologue at each cardinal mass. Initial experiments on butane indicate that this approach may be able to constrain $\delta^{13}C$ of ion fragments with precision of ±0.1-0.2 ‰ and δD with precision of ±2-3 ‰. We intend to combine this approach with recently invented methods for analysis of multiply substituted and position specific isotopologues of alkanes on the Ultra to create a set of techniques for characterizing proportions of a large number of isotopologues of moderate-sized organic molecules.

The impact of climate on land derived nutrient fluxes to the ocean

EYDIS SALOME EIRIKSDOTTIR[1], SIGURDUR REYNIR GISLASON[1] AND ERIC H. OELKERS[1,2]

[1]Institute of Earth Sciences, University of Iceland, Sturlugata 7, 101 Reykjavík, Iceland, (ese@raunvis.hi.is).
[2]GET, CNRS/URM 5563-Université Paul Sabatier, 14 ave. Edouard Belin,, 31400, Toulouse, France.

Weathering and denudation influence greatly the global elemental cycles. There are two main sources of nutrients in the oceans, recycling due to microbial degradation and influx of nutrients from terrestrial runoff [1]. Some elements are essential nutrients for photosynthesis (N, P, Si, Ca, Mg, etc) while other, such as Fe, V, and Mo catalyse biochemical transformations at key points in the carbon and nitrogen cycles. Chemical denudation is positively correlated with runoff and atmospheric temperature [2]. In this study, we demonstrate the different effects climate has on the individual elemental fluxes, derived from silicate weathering in six basaltic river catchments in NE Iceland, of which three are of glacial origin and three are non-glacial rivers.

Concentrations of suspended sediments, major dissolved elements, and some trace elements are discharge dependent while concentrations of most trace metals are discharge independent. Due to the distinct behavoir of the particulate and dissolved elements, some are more sensitve to climate change than others. The climate dependence of elemental fluxes is also different between the glacial and direct-runoff rivers.

Data regression of ~40 years of chemical and flow was used to determine the influence of temperature and runoff on the annual fluxes of elements transported to the oceans. The fluxes of the major elements, and Sr and Mo, depended less on the climate than those of the fluxes of trace elements, including the micro-nutrients Fe and V. A change of one °C changes 1) major element, Sr and Mo fluxes, and 2) micro-nutrient fluxes by 13 – 15%, and 15 – 19%, respectively in the non-glacial rivers and by 4 – 14% and 8 – 19% in the glacial rivers. A 10% incremental runoff increase, within the runoff range of the individual river, changed the same fluxes by 7 – 9% and 10 – 15% in the non-glacial rivers and by 2 – 8% and 9 – 16% in the glacial rivers. These results show that elemental fluxes of glacial rivers are more sensitive to climate change than those of non-glacial rivers.

[1] Falkowski (2004) Vol. 8. Treatise on Geochemistry (eds. H.D. Holland and K.K. Turekian), pp. 185 – 213. [2]. Eiriksdottir *et al*. (2013), *EPSL*, **107**, 65 – 81.

Metamorphic and magmatic overprint of garnet pyroxenites from the Beni Bousera massif (Northern Morocco): Mineralogical, chemical and textural records

FATIMA EL ATRASSI[1]*, FABRICE BRUNET[2], GILLES CHAZOT[3] AND CHRISTIAN CHOPIN[4]

[1]Laboratoire de G-Time, Université Libre de Bruxelles, Belgium (*Corresponding author : Fatima.El.Atrassi@ulb.ac.be)
[2]ISTerre, Université de Grenoble 1, CNRS, Grenoble, France
[3]Institut Universitaire Européen de la Mer, Brest, France
[4]Laboratoire de Géologie, Ecole normale supérieure, Paris, France

A detailed mineralogical and textural study of two garnet pyroxenites of the Beni Bousera massif, the garnet clinopyroxenite (GP) and the garnet clinopyroxenite containing graphite pseudomorphs after diamond (GGP), indicates a strong metamorphic overprint associated with the massif exhumation. In both pyroxenites, the primary assemblage [Cpx(I) + garnet +/- Opx] records temperatures in excess of 1200°C. Along the exhumation path, Cpx(I) has decomposed under sub-solidus conditions in at least two stages, which led first to pyroxene exsolution lamellae and second to garnet crystallization at the expense of the newly formed Cpx lamellae. These secondary garnets have grown in the 850-950°C temperature range. We show that these conditions are below the blocking temperature of the Mg-Fe exchange between garnet and pyroxene (ca. 1050°C) and above the blocking temperature of Mg-Fe interdiffusion in garnet. Consequently, the original composition of these secondary garnets has not been modified upon further cooling; equilibrium with the appropriate lamellar pyroxene can be used to retrieve meaningful P-T couples.

The late evolution of the Beni Bousera massif is recorded in the pyroxenites by the decomposition of primary garnet porphyroclasts into symplectite intergrowths at around 800-850°C below 10 kbar. These late conditions coincide with a major event: a temperature increase up to ca. 1050°C at most, which led to partial melting in both GP and GGP in the presence of water. The partial melting is evidenced by the presence of silicate films preserved in the graphite aggregates and the occurrence of interstitial amphibole and plagioclase.

Detailed chemical inspection of Gt–Cpx–Opx inclusions in the graphite pseudomorphs using LA-ICP-MS ablation, FEG-SEM and the electron microprobe indicates that (1) these silicates are genetically related to the same minerals in the bulk rocks and (2) they were chemically isolated from the bulk rock (included in diamond and/or graphite).

Ocean Geochemistry and Paleoproxies: Deep ocean carbonate ion through six glacial-interglacial cycles

H. ELDERFIELD

Department of Earth Sciences, University of Cambridge, CB1 1EE Cambridge UK; (he101@cam.ac.uk)

The presence of carbonate cycles in deep ocean sediments has been the subject of longstanding debate with much recent work supporting the view that changes in carbonate ion are responsible. Estimates of palaeo-carbonate ocean chemistry from boron incorporation in foraminifera provide important evidence. $[CO_3^{2-}]$ estimates also play a role in paleothermometry with debate as to the roles of ocean chemistry versus dissolution. Here we present data of behaviour of epifaunal and infaunal benthic species, factors influencing porewater $[CO_3^{2-}]$, and possibly boron coordination and emerging proxies. This is followed by evidence for elevated alkalinity in the glacial ocean with emphasis on sites within Circumpolar Deep Water.

Understanding D/H systematics of leaf wax *n*-alkanes in C₃ and C₄ plants at Stiffkey saltmarsh, Norfolk, UK

YVETTE ELEY[1]*AND NIKOLAI PEDENTCHOUK[1]

[1]School of Environmental Sciences, University of East Anglia, Norwich, UK (*contact: y.eley@uea.ac.uk)

D/H ratios of *n*-alkyl lipids are becoming increasingly popular as indicators of palaeohydrological regimes. The suitability of these compounds for such applications is dependent upon the precise nature of the information they are conveying. Current interpretations of this proxy are limited by an incomplete understanding of the mechanisms responsible for the variation in *n*-alkyl lipid δD values among plant species at individual locations.

To evaluate the relative importance of environmental, physiological and biochemical factors on the D/H composition of *n*-alkyl lipids, we sampled a range of C_3 and C_4 plants at Stiffkey saltmarsh throughout 2012. The results of δD analysis of soil, xylem, and leaf waters suggest that the bulk of interspecies variation in *n*-alkane δD values (>100‰) cannon be explained by environmental and plant physiological factors. Instead, we propose that species-specific D/H fractionation during lipid biosynthesis represents a fundamental control on *n*-alkane δD values of these plants.

Our ongoing work on starch δD will allow us to identify whether variation in carbohydrate recycling may explain the range of lipid δD in key species at our site. Furthermore, we are examining whether seasonal changes in leaf wax composition, including the nature and amount of precursor compounds, affect the *n*-alkyl D/H signal. Finally, our work on chloroplast-bound phytol will allow us to investigate whether the potential existence of different NADPH pools influences the δD of compounds biosynthesized in different plant compartments. Our results indicate an integrated physical and biochemical approach is required to interpret the D/H signals contained in the sedimentary record.

Isotope anomalies of Hf and W in chondrite leachates and residues

B.-M. ELFERS[1,2]*, S.T.M. PETERS[1,2], F. WOMBACHER[1,2] AND C. MÜNKER[1,2]

[1]Institut für Geologie und Mineralogie, Universität zu Köln, 50674 Köln, Germany (*correspondence: elfersb@uni-koeln.de)
[2]Steinmann-Institut, Universität Bonn, 53115 Bonn, Germany

The stepwise dissolution of primitive chondritic meteorites allows to reveal nucleosynthetic anomalies that are otherwise hidden in the bulk rock mix. Leaching experiments for Hf and W have previously been published, but in separate studies that did not include the rare p-process isotopes ^{174}Hf and ^{180}W [1, 2]. Here, we present for the first time combined Hf and W isotope data for acid leachates of several chondritic meteorites, including sufficiently precise analyses of p-process ^{174}Hf and ^{180}W for some chondrites (EET 96026 (R3), MAC 02839 (EL3) and WSG 95300 (H3.3)).

For leaching experiments, sample powders of the different meteorites were treated with 2M HCl and divided into a leachate and a residue fraction. Tungsten and Hf were separated from the same sample split using anion exchange chromatography. The W fraction was subsequently purified with TODGA resin, and Hf was further purified using Ln-Spec. Measurements were performed on a Neptune MC-ICP-MS. For the collection of the small ion beams, amplifiers with $10^{12}\Omega$ resistors were employed. Interferences from Yb, Lu and W, and Hf, Ta and Os isotopes, respectively, were sufficiently low to allow accurate interference corrections. The external reproducibilities on ^{174}Hf and ^{180}W were better than ±60 ppm and ±70 ppm, respectively, but significantly larger for small samples cuts <60 ng Hf and <150 ng W, respectively.

First data reveals that most of the Hf leachates and residues show anomalous s- and r-process patterns that are consistent with the results of [1]. First W isotope s- and r-process patterns are furthermore consistent with data reported by [2]. Neither leachates nor residues exhibit resolvable non-terrestrial ^{174}Hf, whereas both positive and negative ^{180}W signatures are resolved for almost all leachates and residues. The origin of the apparent decoupling between ^{180}W and ^{174}Hf is presently ambiguous, but possibly point towards different carrier phases for p-process Hf and W.

[1] Qin L. *et al*. (2011) *GCA, 75*, 7806-7828. [2] Burkhardt C. *et al*. (2012) *AJL, 753*, L6.

B and O isotopes as tracers of serpentinization along fossil oceanic detachments, Troodos ophiolite, Cyprus

BAR ELISHA[1], YARON KATZIR[1], MEIR ABELSON[2], SAMUELE AGOSTINI[3,] JOHN W. VALLEY[4] AND MICHAEL J. SPICUZZA[4]

[1]Ben Gurion Univ. of the Negev, Be'er Sheva Israel, (brelisha@gmail.com) (*presenting author)
[2]Geological Survey of Israel, Jerusalem, Israel;
[3]IGG-CNR, Pisa, Italy
[4]Univ. of Wisconsin, Madison WI 53706, USA

Serpentine lubricated detachment faults strike parallel to two segments of a paleo spreading center that are separated by the Arakapas transform in the Troodos ophiolite, Cyprus. To the north of the transform, serpentinite faulted against gabbro shows bimodal spatial distribution and covariance of B-O isotope ratios. These data indicate overprinting of fault localized, 'high temperature' oceanic serpentinization ($\delta^{18}O$=4 to 6‰; $\delta^{11}B$=-3 to 3‰) by widespread late hydration at lower temperatures, forming abundant chrysotile veins ($\delta^{18}O$=10 to 12‰; $\delta^{11}B$=7 to 13‰). At the Limassol Forest complex, south of the transform, extensive talc-amphibole-chlorite metasomatic zones and rodingitized gabbro boudins occur within strongly foliated serpentinite shear-zones separating an ultramafic section from sheeted dykes. $\delta^{18}O$ values of serpentine from shear-zones in the Limassol Forest have a narrow range and are invariably lower than mantle values(1 to 5.7‰; n=26), consistent with serpentinization during seafloor spreading. $\delta^{11}B$ (Srp) values are more scattered (5 to 27‰) and weakly correlate with boron contents (2 to 60 ppm), which might be accounted for by increase in pH of water as serpentinization progressed.

Absence of the lower crustal section above the mantle and injection of gabbroic magma followed by localized serpentinization, metasomatism and deformation along this discontinuity are major characteristics of oceanic detachments. Isotope systematics strongly resemble those of serpentine recovered from modern oceanic core complexes such as the Atlantis Massif. The mantle sequence of the Limassol Forest is thus suggested to have been exhumed at the footwall of an oceanic core complex. This scenario sheds light on the location of the spreading axis south of the transform and explains the highly complicated structure of the fossil ridge-transform intersection of the Limassol Forest.

Origins of anomalous ridge magmatism near Jan Mayen

L.J. ELKINS[1]*, E.R. RIVERS[1], K.W.W. SIMS[2], J. BLICHERT-TOFT[3], C. DEVEY[4], R. CHERNOW[1], R. DAVIS[1] AND K. MEISENHELDER[1]

[1]Bryn Mawr College, Bryn Mawr, PA, USA (*correspondence: lelkins@brynmawr.edu)
[2]University of Wyoming, Laramie, WY, USA (ksims7@uwyo.edu)
[3]Ecole Normale Supérieure de Lyon, Lyon, France (jblicher@ens-lyon.fr)
[4]GEOMAR, Kiel, Germany (cdevey@geomar.de)

The sustained volcanism at Jan Mayen Island, located immediately south of a major fracture zone (the Jan Mayen Fracture Zone) and adjacent to two slow-spreading mid-ocean ridges (the Kolbeinsey and Mohns Ridges), has been variably ascribed to a small, isolated plume, to material siphoned northward off the larger Icelandic plume, to convection-driven edge effects along a major compositional mantle discontinuity, and to the presence of highly fusable, wet, old, garnet-bearing material derived from veins or pockets of rift-faulted or delaminated Greenland sub-continental lithospheric mantle. The compositions of volcanic rocks from both Jan Mayen Island and the immediately adjacent segments of the Mohns and Kolbeinsey Ridges likewise support the long-term presence of mantle rocks enriched in incompatible elements. While the most recent work on long-lived radiogenic isotope compositions of Jan Mayen Island magmas has supported a complex model invoking several of the above scenarios of melting, no high-resolution sampling and analysis existed for the adjacent ridge segments.

We present geochemical data for new, precisely bathymetrically located volcanic samples from the Northern Kolbeinsey and Southern Mohns segments. Preliminary geochemical and bathymetric findings suggest that both segments host long-lived, localized sources of increased magma flux associated with the most geochemically enriched melt compositions hosted by those ridge segments, which decrease in indicators of geochemical enrichment with distance from Jan Mayen Island. The surface expressions of this high magma supply include large volcanic edifices straddling the axial valleys and walls, as well as evidence for ridge axis relocations in the direction of Jan Mayen Island. This supports a sustained point source of geochemically enriched magmatic activity beneath the region, consistent with a deep-seated mantle plume.

We further provide new U-series isotopic data for all three geographic areas, which place constraints on mantle source compositions and upwelling rates beneath the region.

Dripping, thinning, melt injection, metasomatism: Geochemical consequences of small-scale convection under continents

L. T. ELKINS-TANTON[1]*

[1]DTM, Carnegie Institution for Science, Washington DC 20015 (*correspondence: ltelkins@dtm.ciw.edu)

Through a variety of physical mechanisms, the lower lithosphere is thought to be recycled into the mantle, thinning the lithosphere and creating compositional differentiation. Lithospheric thinning has been inferred from increases in crustal heat flow in specific regions, rapid regional uplift, and from the appearance of signature high-potassium magmas [*e.g.* 1-5]. Seismic studies also support ductile delamination in specific areas [*e.g.*, 6].

Geochemical arguments appear to require foundering of crustal and mantle lithospheric materials to balance elemental budgets. Though continental crust and mantle are complementary reservoirs with respect to most trace elements, the continental crust is too felsic to be derived directly from the mantle [7,8]. A possible solution is the loss from the continental lithosphere through delamination of mafic residues from fractionation of mantle melts. The same process would explain the significant fractionation of thorium and lanthanum in continental crust, when they are unfractionated during the processes of subducting sediments and producing arc magmatism [9].

A spectrum of physical mechanisms have been proposed for this small-scale convection. The greatest discriminator among them appears to be rheology, that is, how ductile is the material that is sinking away? The most brittle material might sink away in the shape of a plate, while the most ductile drip off as fluids. The feasibility of these processes depends upon composition, pressure, and temperature, and all these combine to affect the surface expression and compositional ramifications, from recycling differentiated compositions back into the mantle, to producing melt that might erupt.

[1] Kay & Kay (1993) *Tectonophysics* **219**, 177-189. [2] Ducea & Saleeby (1998) *Int'l Geology Rev*. **40**, 78-93. [3] Schott & Schmeling (1998) *Tectonophysics* **296**, 225-247. [4] Lustrino (2005) *Earth Sci. Rev*. **21**. [5] Hoernle *et al*. (2006) *Earth Planet. Sci. Lett*. **248**, 335-352. [6] Jones & Phinney (1998) *J. Geophys.l Res*., **103**, 10,065 – 10,090. [7] Rudnick R.L. (1995) *Nature* **378**, 571-578. [8] Lee *et al*. (2006), *Contrib. Mineral. Petrol*. **151**, 222-242. [9] Plank (2005) *J. Petrology*.

Origin and evolution of volatiles in rocky airless bodies

L. T. ELKINS-TANTON[1]*

[1]DTM, Carnegie Institution for Science, Washington DC 20015 (*correspondence: ltelkins@dtm.ciw.edu)

Large planetesimals or asteroids, the Moon, and Mercury form a size continuum of airless bodies, but their formation histories are thought to be significantly different. While planetesimals formed from relatively lower energy accretionary impacts, they themselves continued to accrete gravitationally in more and more energetic impacts to build larger planets such as Mercury, and finally to produce the giant Moon-forming impact on the young Earth that resulted in the Moon. Despite the significant impact energy that went into producing the Moon, it was not completely dried and devolatilized during its formation [e.g., 1-3].

Part of the original evidence for a dry Moon, overturned by these recent measurements of volcanic materials, was the depleted K/U ratio compared to the Earth [4]. In contrast, Mercury shows a K content similar to the Earth and Mars, and thus may not be as depleted in volatiles as the Moon [5]. Similarly, measurements of meteorite compositions [6] indicate that neither primiive nor differentiated planetesimals were completely dried. Thus, the building blocks (planetesimals), the final planets (Mercury), and their impact debris (the Moon) all retained some fraction of their original volatile content.

In differentiated planetesimals and in the Moon and Mercury the silicate portions of the bodies were likely processed through a magma ocean stage [7]. Retention of volatiles is less likely in a planetesimal interior than it is in a planetary magma ocean. Internal heating from short-lived radiogenic aluminum 26 in small early planetesimals drives off volatiles from planetesimals above a certain size [8].

Factional solidification in a planetary-sized magma ocean, in contrast, can retain some volatile fraction inside the planet through partitioning with solid phases and sequestration of interstitial melts. Model results for these processes will be compared with measurements from the Moon.

[1] Saal *et al*.. (2008) *Nature* **454**, 193-195. [2] Boyce *et al*.. (2010) *Nature* **466**, 466-470. [3] McCubbin *et al*.. (2010), *PNAS* **107**, 11223-11228.. [4] Tera *et al*.. (1974) *EPSL* **22**, 1-21. [5] Peplowski *et al*.. (2011) *Science* **333**, 1850-1852. [6] Jarosewich (1990) *MAPS* **25**, 323-337. [7] Elkins-Tanton (2011) *Ann.Rev. Earth Planet. Sci*. **40**, 113-139. [8] Young *et al*.. (2003) *EPSL* **213**, 249-259.

The Global U Isotopic Cycle

TIM ELLIOTT[1], MORTEN ANDERSEN[2]*
AND HEYE FREMUTH[1]

[1]Bristol Isotope Group, School of Earth Sciences, University of Bristol, Bristol, BS8 1RJ, UK (tim.elliott@bris.ac.uk)
[2]Institute of Geochemistry and Petrology, ETH Zürich, CH 8092 Zürich, Switzerland (*correspondence: morten.andersen@erdw.ethz.ch)

The mobility of U under oxic conditions and its enrichment in the oceanic crust has long led to speculations about the importance of these low tempeature processes in the global distribution of U [e.g. 1]. Notably, the return flux of U from surface to mantle, via subduction, is potentially sufficient to perturb the mantle U abundance. This mechanism has been used as a means to explain puzzling features of mid-ocean ridge basalt (MORB) U-Th-Pb systematics [e.g. 2]. Advances in muti-collector inductively coupled plasma mass-spectrometry (MC-ICPMS) allow the hiterto presumed invariable $^{238}U/^{235}U$ ratio to provide new constraints on this cycle. Recent work has shown that the U in the near surface environment can be fractionated by about 1‰ [e.g. 3,4]. Therefore, recyling of significant amounts of isotopically fractionated U from the surface to the mantle has the potential to perturb not only its U abundance but also its isotope ratio.

In order to exploit this potential we have had to tune our torch. Using a ^{233}U-^{236}U double spiking approach and by measuring intense U beams (>1nA), we have obtained precisions of ~0.02‰ on $^{238}U/^{235}U$ ratios of mantle derived samples. This provides sufficient resolution to detect the influence of recyled U in the mantle.

We have determined that the net effects of alteration and subduction leave deep recycled slab with isotopically heavy U [5]. The preferential return of this U into the upper mantle, as invoked to explain the anomalously low Th/U ratio of MORB [e.g. 2], predicts that MORB should be ~0.1‰ heavier than pristine mantle. We show that this prediction is realised in our measurements of MORB glasses relative to ocean island basalts and chondritic meteorites. Thus we provide striking, independent confirmation of the importance of recyling in shaping the U budget of the mantle courtesy of the capabilities of modern MC-ICPMS.

[1] Albarède & Michard (1986) *Chem Geol* **57** p1-15 [2] Elliott, Zindler & Bourdon (1999) *EPSL* **169** p129-145 [3] Stirling, Andersen, Potter & Halliday (2007) *EPSL* **264** p208-225 [4] Weyer *et al*. (2008) *GCA* **72** p345-359 [5] Freymuth, Andersen & Elliott this volume

Tracing changes in the biogeochemical cycling of iron during the annual subtropical spring bloom east of New Zealand

M.J. ELLWOOD[1]*, P.W. BOYD[2], S. NODDER[3],
D.A. HUTCHINS[4], S.W. WILHELM[5], A. MILNE[6]
AND M. LOHAN[6]

[1]Research School of Earth Sciences, Australian National University, Canberra, Australia, (*correspondence: michael.ellwood@anu.edu.au)
[2]Centre for Chemical and Physical Oceanography, NIWA, University of Otago, Dunedin, New Zealand
[3]NIWA, Wellington, New Zealand
[4]Marine Environmental Biology, University of Southern California, Los Angeles, California, USA
[5]Department of Microbiology, The University of Tennessee, Knoxville, USA
[6]School of Geography, Earth and Environmental Sciences, University of Plymouth, UK

The turnover time of iron in the surface ocean can vary from days to weeks and months, while within cells the turnover time can be on the order of hours to days. Accordingly, the iron isotope ($\delta^{56}Fe$) composition of particulate organic matter should be sensitive to changes in the cycling of iron in the surface ocean and immediately below. Here we present data showing a dynamic change in the $\delta^{56}Fe$ composition of particulate organic matter during the development and subsequent export of phytoplankton bloom material. Our results, obtained from two FeCycle voyages in 2008 and 2012, suggest that before the onset and development of the phytoplankton bloom iron regeneration dominates the dissolved iron signal with lighter dissolved $\delta^{56}Fe$ valves (-0.14‰ at 100 m to 0.07‰ at 500 m) relative to particulate iron (-0.02‰ at 60 m to 0.13‰ at 300m). In contrast, during the development and export phase of the bloom, iron scavenging and/or iron consumption by heterotrophic bacteria community appears to dominate the dissolved iron isotope signal with heavier dissolved $\delta^{56}Fe$ values (0.15‰ at 30 m to 0.16‰ at 500 m) relative to particulate $\delta^{56}Fe$ valves (-0.11‰ at 30 m to -0.33‰ at 300 m). A strong relationship was also observed between particulate $\delta^{56}Fe$ and Fe/Al ratios with lighter values. The dissolved and particulate $\delta^{56}Fe$ results were modelled with Rayleigh-type functions and produced the following fractionation factors: 1.00015 prior to the onset and development of the bloom and 0.99945 during the subsequent export of the bloom material to depth. Taken together our results show that the iron isotope composition of dissolved and particulate material can be used to monitor changes in the biogeochemical cycling of iron in the marine realm.

Crystal chemistry and magnetism of Fe-serpentines based on XMCD

A. ELMALEH[1]*, M.-A. ARRIO[1], A. JUHIN[1],
P. SAINCTAVIT[1], S.C. TARANTINO[2], M. ZEMA[2],
A.-L. AUZENDE[1], A. SMEKHOVA[3,4] AND A. ROGALEV[3]

[1]IMPMC-UPMC/CNRS, Paris, France (*correspondence: Agnes.Elmaleh@impmc.upmc.fr)
[2]Dep. of Earth & Environ. Sciences, University of Pavia, Italy
[3]ESRF, Grenoble, France
[4]now at Faculty of Physics, Moscow State University, Russia

Fe-rich layer silicates are rare on Earth, but are a major component of CM2 carbonaceous chondrites. They formed during early aqueous alteration events that affected CM2s' asteroidal or cometary parent body [1]. Bulk magnetometry (300-2 K) has proven useful for characterizing Fe-serpentines' mineralogy, close to the pole cronstedtite in CM2s [2]. Comparison with results from single crystals supports the hypothesis of a variable Fe content of serpentines along the alteration sequence of CM2s [2], similarly to terrestrial serpentinization. Site distribution and valence of iron in serpentines would directly be linked to their growth conditions (T, water-rock ratio or duration [3]). Understanding the conditions in which the reactions occurred on the parent body of CM2s thus relies on a thorough characterization of their crystal chemistry.

Here we present the results of a X-ray Magnetic Circular Dichroism study at the Fe K-edge of oriented single crystals of cronstedtite, showing a strong planar anisotropy. We measured XMCD at various angles between the **c** axis and the applied field. We will show how ligand field multiplet calculations [4] allow one to separate various contributions to the pre-edge. This would yield an estimate of the crystal chemistry of Fe in this multisite (octahedral, Oh, and tetrahedral) and multivalent ($Fe^{2+,3+}$) mineral, allowing for a fine characterization of this alteration mineral in meteorites. Also, XMCD suggests that the anisotropy of cronstedtite originates from the strong single ion anisotropy of Fe^{2+} in distorted Oh sites. Finally, exploring the variations of XMCD with substitutions (mostly Fe-Si) would clarify which parameters control the disruption of a long-range magnetic order in Fe-serpentines, from AF, when only Fe^{2+} is present, in Oh sites [5], to spin-glass like, in cronstedtite [2].

[1] Zolensky, Krot & Benedix (2008) *Rev. Miner. Geochem.* **68**, 429-462. [2] Elmaleh, Tarantino, Zema, Devouard & Fialin (2012) *Geochem. Geophys. Geosyst.*, **13**, Q05Z42. [3] Marcaillou, Muñoz, Vidal, Parra, & Harfouche (2011) *EPSL*, **303**, 281-290. [4] Arrio, Rossano, Brouder, Galoisy & Calas (2000) *Europhys. Lett.*, **51**, 454. [5] Coey, Ballet, Moukarika & Soubeyroux (1981) *Phys. Chem. Miner.* **7**, 141-148.

Estimating the Potential Evapotranspiration by using Landsat imagery

M. EL MOULAT[1], M. HAKDAOUI[1], F. T.-C. TSAI[2]
AND A. M. MILEWSKI[3]

[1]Department of Geology, University Hassan II Mohammedia-Casablanca Faculty of Sciences Ben M'sik B.P 7955, Sidi Othmane. Casablanca, Morocco. (Email: m.elmoulat@gmail.com and hakdaoui@gmail.com)
[2]Department of Civil and Environmental Engineering, University of Louisiana State, 3418G Patrick F. Taylor Hall, Baton Rouge, LA 70803-6405. (ftsai@lsu.edu)
[3]Department of Geology, University of Georgia, Athens, GA 30602. (milewski@uga.edu)

Freshwater resources are becoming increasingly limited in many parts of the world, and decision makers are demanding new tools for monitoring water availability and rates of consumption. Remotely sensed data and especially Landsat imagery provides an estimate of land-surface temperature that allow mapping of evapotranspiration (ET) at the spatial scales. This work presents the utility of satellite imagery in water resource management. General modeling techniques for using land-surface temperature in mapping the surface energy balance are described, including methods developed to safeguard ET estimate. Examples are provided of how remotely sensed maps of ET derived from Landsat thermal imagery are being used operationally by water managers today: in monitoring water rights, negotiating, estimating water-use by invasive species, and in determining allocations for agriculture, urban use, and endangered species protection. To better address user requirements for high-resolution, time-continuous ET data, novel techniques have been developed to improve the spatial resolution of Landsat thermal-band imagery and temporal resolution between Landsat overpasses by fusing information from other wavebands and satellites.

Interactions between Fe(II) and arsenic species during co-sorption onto aluminum oxide and clay mineral substrates under anoxic conditions

EVERT J. ELZINGA*AND YING ZHU

Rutgers University, Department of Earth & Environmental Sciences, Newark, New Jersey, USA. (*correspondence: elzinga@andromeda.rutgers.edu)

Reductive dissolution of Fe(III)-oxides and hydroxides in suboxic and anoxic soils and sediments leads to substantial changes in aqueous geochemical conditions, including a strong increase in the aqueous concentrations of Fe(II) and trace metal(loid) species released during dissolution of Fe(III)-oxide sorbents. The fate of released Fe(II) and trace metal(loid)s is likely to be at least partially controlled by sorption reactions with mineral constituents remaining in the soil matrix, and may further be influenced by redox reactions between Fe(II) and redox-sensitive elements including As. While there have been quite a few studies addressing sorption of Fe(II), As(III) and As(V) onto common soil minerals in binary systems, very little is known about the interactions between these species in ternary systems involving co-sorption.

Here, we use a combination of batch experiments and X-ray absorption spectroscopy to study the co-sorption of Fe(II) with As(V) and As(III) onto aluminum-oxide and clay surfaces under anoxic conditions and at near-neutral pH values typical of reduced geochemical environments. We observe notable differences between the ternary and binary systems as to the extent and mechanisms of Fe(II) and As sorption. The XAS results indicate the operation of several processes, including formation of monomeric surface complexes and precipitation of Fe(II)-Al(III)-layered double hydroxides. Interactions among these processes and the significance of redox reactions in the ternary systems will be discussed.

Co-benefits of tackling poor air quality and regional climate: A focus on ecosystems

LISA EMBERSON[1], KEVIN HICKS[1] AND PATRICK BÜKER[1]

[1]Stockholm Environment Institute, Environment Dept. University of York, York, YO10 5DD, U.K.. (e-mail: l.emberson@york.ac.uk)

A substantial body of experimental evidence exists describing the impacts of ozone (O_3) and aerosols on important ecosystems (agro-, forest and grassland ecosystems). Much of this empirical data has been collected from co-ordinated studies conducted in North America and Europe; and more recently in Asia. Pooling these data allows the development of risk assessment methodologies which can be used to assess the benefits of emission reductions over regional to global scales. This talk describes these risk assessment methodologies focussing both on their strengths (in relation to providing estimates of a variety of ecosystem damage) as well as weaknesss and limitations (primarily associated with limited data availability for key global regions such as Asia, Africa and Latin America).

Within this context results are presented that describe benefits of emission reductions of O_3 and aerosol forming species for crop yields, forest productivity and grassland biodiversity along with benefits for near term climate. Examples of indirect benefits are also given by showing the importance of ecosystems acting as sinks for atmospheric pollution; alterations to this sink under extreme climates (e.g. heatwave type conditions) are exemplified through their influence on net atmospheric pollution concentrations and subsequent human health impacts.

Finally, the importance of considering ecosystem damage and feedbacks to the climate system within a new generation of Earth System Models, currently being developed to understand the implications of climate change, is advocated based on the evidence presented.

Characterization of the effects of grain size to mine water quality and Acid Rock Drainage (ARD) production in Kinetic Testing

R. EMBILE JR.[1,2,3,] I.F. WALDER[1], F. MADAI[2],
F. MORICZ[2], P. WALDER[1] AND P. RZEPKA[1]

[1] Kjeoy Research and Education Center, Kjeoy 8412
Vestbygd, Norway (*correspondence:
rodrigofembilejr@gmail.com)
[2] University of Miskolc, Miskolc H-3515 Hungary
[3] Camborne School of Mines, University of Exeter

The quality of mine drainage from sulfide containing waste dumps is controlled by several factors and surface area (grain size) exposed to weathering conditions is important. However, the textural variation may control the main driving mechanisms for an acid generating or neutralizing reactions. Depending on their rates and intrinsic properties, leachate chemistry for a certain grain size can be characterized through different types of tests and analysis.

Kinetic test using humidity columns is performed on five different grain size ranges of waste rocks from the Recsk porphyry copper-skarn deposit in Hungary. Water leachate quality is analysed on a weekly basis for their pH, alkalinity, conductivity, anions, cations and dissolved metal concentrations. Results showed that finer grains produced near neutral to neutral pH and higher sulfate production rates unlike for coarser grains. This indicates that the rate of sulphide oxidation and neutralization may be only partly controlled by grain size as well as a number of interrelated factors.

Global variability of the ocean's biological pump from *in situ* measurements of the air-sea oxygen flux: A status report

STEVEN EMERSON*, SETH BUSHINSKY
AND STEPHEN RISER

School of Oceanography, University of Washington, Seattle,
WA, 98195 (*correspondence: emerson@uw.edu;
smbush@uw.edu; riser@uw.edu)

The ocean's biological pump is the process by which biological production exports carbon and oxygen from the ocean's euphotic zone. The geographic variability of the biological pump, along with ocean mixing and air-sea exchange, strongly influences the pCO_2 of the atmosphere and maintains the oxygen distribution below the surface ocean. We propose to determine the global variability of the biological pump by measuring the air-sea oxygen gradient using oxygen sensors on profiling floats. Oxygen mass balances at ocean time-series sites indicate the connection between net annual air-sea oxygen flux and biological carbon export and suggest a biological pump of $2 - 4$ mol C m^{-2} yr^{-1} with little global open-ocean variability; however, there are only about five locations where there is sufficient data to do this calculation. Global Circulation Models and Satellite color measurements predict the biological pump varies by as much as a factor of four among the equatorial, subtropical and subarctic oceans. A better global coverage of the annual air-sea oxygen flux would provide critical calibration for the predictions based on satellite color. To accomplish this we calibrated the Aanderaa oxygen sensors in our laboratory and modified the Argo profiling instrument package so that the oxygen sensors continue recording when they surface (every five days). The oxygen sensors on our special floats are positioned well above the float body so they are in the air when the float surfaces providing a measure of the air-sea pO_2 gradient. We deployed ten of these floats in March 2013 in the Western North Pacific across the Kuroshio extension. Winkler oxygen measurements were made near the floats after deployment to calibrate them in situ. This abstract was written only two weeks after successfully deploying and calibrating the floats in situ. We will report the results of the first three months of measurements to assess how accurately it is possible to determine the air-sea oxygen flux using *in situ* oxygen measurements on Argo floats. We believe this is the next step in using oxygen mass balance to determine the global distribution of the marine biological carbon pump.

How surface heterogeneity impacts reaction rates in carbonate rocks

SIMON EMMANUEL[1]* AND YAEL LEVENSON[1]

[1]The Hebrew University of Jerusalem, Jerusalem, Israel, (simonem@cc.huji.ac.il)(* presenting author)

Due to the ubiquitous nature of calcite in natural systems, much research has focused on determining the reaction kinetics of calcite dissolution. However, the empirical rate laws derived in such studies assume that the reactivity of calcite crystals typically used in laboratory experiments is the same as the reactivity of natural carbonate surfaces that have been exposed to fluid during diagenesis. In this study, we demonstrate that the difference between polished calcite surfaces and naturally-aged calcite surfaces is significant. Atomic force microscopy (AFM) measurements show that the rate of calcite dissolution within micron-size pores of a limestone sample is much lower than the rate of dissolution in the surrounding calcite surface. In addition, we use numerical simulations to show that this difference cannot be explained using a diffusion - surface reaction model. Instead, we attribute the heterogeneous reaction rates to the high density of tiny asperities on the polished surface surrounding the pore which increase the overall reactivity of the surface. We suggest that the range of reaction rates we observe could be representative of real geological systems, helping to explain the widely reported discrepancy between laboratory and field rates. The implications for weathering, dissolution in carbonate reservoirs, and carbon sequestration are also discussed.

Tracking stable CO_2 isotopes with laser spectroscopy at Jungfraujoch

LUKAS EMMENEGGER, BÉLA TUZSONAND, PATRICK STURM AND STEPHAN HENNE

Empa, Laboratory for Air Pollution / Environmental Techology, CH-8600 Dübendorf, Switzerland (lukas.emmenegger@empa.ch)

Isotope ratios of trace gases contain highly valuable information about their sources, sinks and transport processes from the local to the global scale. While isotope ratio mass spectrometry (IRMS) has been the method of choice, laser spectroscopy is rapidly gaining importance because it can deliver real-time data with unprecedented temporal resolution at moderate cost and instrument size.

We employ a quantum cascade laser absorption spectrometer (QCLAS) and perform continuous monitoring of the stable CO_2 isotopes in the free troposphere since December 2008 at the High Altitude Research Station Jungfraujoch (3580 m a.s.l.), Switzerland [1].The instrument is based on differential absorption technique in the 4.3 μm spectral range. Being a fully cryogen-free setup, it is well suited for unattended field applications, delivering both $\delta^{13}C$ and $\delta^{18}O$ of CO_2 at atmospheric abundance with a precision of 0.02 ‰ for both $\delta^{13}C$ and $\delta^{18}O$-CO_2 at 10 minutes integration time [2].

The high temporal resolution of the $\delta^{13}C$ time series allows the detection of pollution events and the application of the Keeling plot method for source signature identification. Backward Lagrangian particle dispersion simulations are used to determine the spatial origin of these CO_2 emission sources. Furthermore, the long data series permits the analysis of yearly, seasonal and daily patterns. Footprint clustering shows significantly different wintertime $\delta^{13}C$ and $\delta^{18}O$-CO_2 values depending on the origin and surface residence time of the air masses.

We present the development of the instrumental set-up, the improvements of the most critical parts and the resulting performance. Then, we discuss methodologies for calibration and data treatment and illustrate the advantages of measuring high time resolution isotopic signatures of CO_2 in the atmosphere with exemplary results.

[1] Tuzson, B. *et al*., ACP, 2011, 11, 1685–1696. [2] Sturm, P. *et al*., AMTD, 6, 423-459, 2013.

Temperature-induced phase transitions in Pb/Sr-lawsonites

M. ENDE[1], B. WUNDER[2], M. KOCH-MÜLLER[2] AND E. LIBOWITZKY[1]

[1]University of Vienna, 1090 Vienna, Austria
[2]Helmholtz Centre Potsdam, GFZ (German Research Centre for Geoscience), 14473 Potsdam, Germany

Pb-lawsonite and itoigawaite $(SrAl_2[(OH)_2|Si_2O_7]\cdot H_2O)$ were synthesised using either oxides [1,2], spinel phases with quartz, feldspars or glasses with stoichiometric compositions. The achieved crystal sizes reached 20 μm in maximum for the Pb-lawsonite and about 60 μm for itoigawaite.

For the syntheses a piston cylinder press at GFZ Potsdam, Germany was used. Experimental conditions were 600°C and 3-4 GPa for Pb-lawsonite and 700°C and 4 GPa for itoigawaite. Using Raman spectroscopy temperature-induced shifts of different bands were analysed. For Pb-lawsonite the most interesting one was a band at about 860 cm^{-1}, which probably arises from an AlO_6 stretching vibration [3]. It shows a minimum of two discontinuities, which could be interpreted as phase transitions at about 350 and 445 K (Fig. 1). Analyses of a band arising from a ν_{as} SiO_3 stretching vibration [3] reveal a minimum of one phase transition for itoigawaite at about 225 K.

These reversible phase transitions are comparable to those of lawsonite and are mainly caused by changes of OH$^-$ and H_2O groups from disordered, apparently highly symmetric positions to ordered ones at lower temperatures [4].
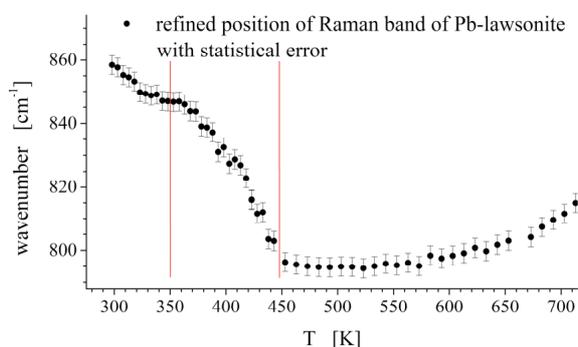

Figure 1: Raman band positions vs. temperature for Pb-lawsonite. Discontinuities probably reveal phase transitions.

[1] Dörsam et al.. (2011) N. Jb. Miner. Abh. **188/2**, 99-110 [2] Liebscher et al.. (2010) Am. Mineral. **95**, 724-735 [3] Le Cléac`h & Gillet (1990) Eur. J. Mineral. **2**, 43-53 [4] Libowitzky & Armbruster (1995) Am. Mineral. **80**, 1277-1285

Pressure-dependent change of ultraviolet absorption cross section of SO_2 isotopologues and S-MIF

YOSHIAKI ENDO[1], SEBASTIAN O. DANIELACHE[2], YUICHIRO UENO[1,3], SHOHEI HATTORI[4], MATTHEW S. JOHNSON[5] AND HENRIK G. KJÆRGAARD[5]

[1]Earth & Planetary Sciences. Tokyo Institute of Technology, Japan (endo.y.ac@m.titech.ac.jp)
[2]Faculty of Science & Technology, Sophia University, Japan
[3]Earth-Life Science Institute (ELSI), Tokyo Institute of Technology, Japan
[4]Environmental Chemistry and Engineering, Tokyo Institute of Technology, Japan
[5]Department of Chemistry, University of Copenhagen, Denmark

Photolysis of SO_2 is known to produce anomalous sulfur isotope fractionation (S-MIF). The mechanism of the photochemical S-MIF is important for reconstructing chemistry of paleoatmosphere, though has been still poorly understood. It is important to determine isotopologue-specific UV absorption cross section accurately for estimating fractionation factor of the SO_2 photolysis. We used a dual beam monochromator in order to obtain higher accuracy cross section that is complementary to high spectral resolution Fourier transform spectrometer [1]. The results show the peak position for heavier isotopologue is red shifted relative to the lightest $^{32}SO_2$ isotopologue, though rotational structures cannot be seen due to low spectral resolution. The observed cross sections systematically changed depending on the gas pressure at certain specific wavelengths. This may suggest that S-MIF can occur when SO_2 is photolyzed even under optically thin condition and thus not by self-shielding effect in the Archean atmosphere. Also, the observed pressure dependence of cross sections may indicate S-MIF can be changed as a function of atmospheric pressure.

[1] Danieleche et al.. (2008) J. Geophys. Res. **113**, 1-14.

Viruses outnumber prokaryotes in marine subsurface sediments

TIM ENGELHARDT[1], JENS KALLMEYER[2], HERIBERT CYPIONKA[1] AND BERT ENGELEN[1]*

[1]Carl-von-Ossietzky University of Oldenburg, Institute for Chemistry and Biology of the Marine Environment, Carl-von-Ossietzky Straße 9-11, D-26129 Oldenburg, Germany (*correspondance: Engelen@icbm.de, Tim.Engelhardt@icbm.de, Cypionka@icbm.de)

[2]Deutsches GeoForschungsZentrum GFZ, Telegrafenberg, 14473 Potsdam, Germany, Sektion 4.5 Geomicrobiology (kallm@gfz-potsdam.de)

The marine subsurface comprises nutrient-depleted and energy-limited environments, exhibiting a high microbial abundance and diversity. Sources of organic carbon in deeply buried sediments are vanishingly small and the long-term survival of indigenous microorganisms is still enigmatic. Cells are capable to live under energy-limited conditions but controlling factors for cell death in marine subsurface environments remain largely unidentified. Here, the question arises if viruses are controlling prokaryotic mortality. For this habitat, the general role of bacteriophages as a potential driver of microbial ecology was barely addressed so far [1, 2, 3]. Phages are known to contribute to carbon cycling and to control microbial communities in various marine habitats. Furthermore, they mediate horizontal gene transfer and thus, supporting the adaptation of host organisms to environmantal conditions.

We found phages to be highly abundant even in deep, ancient (~14 Ma old) and the most oligotrophic subsurface sediments of the world´s oceans (South Pacific Gyre). The number of viruses always exceeded that of prokaryotic cells and varied by several orders of magnitude within a comprehensive set of globally distributed subsurface sediments. Abundances of phages and cells generally decreased with sediment depth. However, an increasing virus-to-cell ratio is constituted in deeper and more oligotrophic layers, exhibiting values of up to 225 in the deep subsurface of the South Pacific Gyre. The presence of phages in enormous numbers suggests their impact on prokaryotic communities as controlling factor for cell abundance, diversity and life in the marine deep biosphere.

[1] Engelhardt et al. (2011) Environ Microbiol Rep **3**, 459-465. [2] Engelhardt et al. (2013) ISME J **7**, 199-209. [3] Middelboe et al. (2011) Aquatic Microb Ecol **63**, 1-8.

Analysis of internal dynamics in a deep subduction channel

MARTIN ENGI[1], DANIELE REGIS[1,2] AND DANIEL RUBATTO[3]

[1]Inst. of Geological Sciences, Univ. of Bern, Baltzerstrasse 3, 3012 Bern, Switzerland. (engi@geo.unibe.ch)

[2]Dept. of Environment, Earth & Ecosystem, The Open Univ., Milton Keynes, MK7 6AA, UK (daniele.regis@open.ac.uk)

[1]Research School of Earth Sciences, Australian National University, Mills Road, Canberra 0200, Australia

The spatial-temporal scales of tectonic fragmentation and mixing during the evolution of subduction channels need to be resolved. Current thinking nourished by numerical models requires critical testing against data on HP-terrains. However, deciphering natural archives of the time-integrated record of structural and metamorphic processes demands an approach that combines observations from μm- to km-spatial scales.

Our approach is shown for a case study in the Sesia Zone, a classic eclogite facies terrain in the Western Alps, Italy. The control provided by regional structural maps was extended from the meso- to the microscopic scale. Painstaking petrographic documentation was required to recognize the several generations of HP-assemblages, mineral inclusions, textural and chemical domains and to relate these in (relative) time. *in situ* dating by robust Th-U-Pb mineral chronometry was combined with thermobarometry; this allowed several stages of HP-tectonics to be discerned and metamorphic reactions to be related to the polyphase deformation. PTDt-sequences thus derived were mutually consistent for individual sample suites, but substantial differences emerged for different parts of the Sesia Zone. Their regional distribution indicates that tectonic slices (previously unrecognized) exist. Differential mobility between these lasted >20 Myr and one terrane experienced pressure cycling (ΔP ~5 kbar). These dynamics had escaped the many previous studies and predate what has until recently been accepted as "the age" of the Sesia HP-belt, i.e. ~65 Ma.

The major challenge remains to quantify the typical mobility of fragments within this subduction channel. In the Sesia Zone fragmentation at micro- to mesoscopic scale is very common in the eclogitic micaschists; in gneissic parts mylonites are not rare. Yet estimating the total amount of strain or the magnitude of displacements between adjacent units is difficult beyond the deca- to hectometer scale of outcrops. Our ongoing regional work aims to provide better constraints on the geometry and size of mobile tectonic slices, again using the petrochronological approach described.

At this stage of our study, it is clear that (km-size) tectonic fragments were independently mobile within the subduction channel, with vertical cycling rates of 2-3 mm/a.

Challenges connected with experimental upscaling of flow and transport in porous media

A. ENGLERT*, T. VAITL, S. FRANK AND T. GOEKPINAR

Hydrogeology Department, Ruhr-University Bochum, 44801, Germany (*correspondence: andreas.englert@rub.de)

Column and sandbox experiments have a long and successful tradition in estimating flow and transport parameters of porous media. A recently developed methodology based on the combination of column and sandbox experiments might be even capable for upscaling flow and transport as follows: In a first step, a cubic Darcy cell of 0.1 m x 0.1 m x 0.1 m is used to experimentally estimate flow and transport characteristics of an unconsolidated sediment, means flow and transport is experimentally upscaled from the pore-scale to the 0.1 m- scale. In a second step, the sediment filled Darcy cell is frozen and the frozen sediment cube is extracted from the Darcy cell. In a third step, nine frozen sediment cubes are composed in a sandbox model such that a sediment body of 0.3 m x 0.3 m x 0.1 m is formed. Finally the flow and transport characteristics of the sediment body are estimated based on flow and transport experiments. Such procedure could allow for successive experimental upscaling from the pore- to the 0.1 m- to the 1 m-scale of flow and reactive transport.

First tests of the recently developed setup for experimental upscaling showed that it is feasible to form sediment cubes, extract them from the experimental apparatus and assemble them in a sandbox model. It could also be shown that the developed experimental set up is well suited to study flow and transport in single sediment cubes and sediment bodies consisting of assembled sediment cubes. Our ongoing experiments focus on improving the accuracy of the developed set up. So far, we found hydraulic conductivities (Ks) of fine gravel sediment cubes rather constant, and Ks of coarse and middle sand sediment cubes slightly changing pre- and post freezing. We also found from sandbox experiments that sediment bodies formed based on fine gravel or coarse sand sediment cubes to be rather insensitive, but sediment bodies formed based on middle sand cubes to be prone to the formation of preferential flowpath. Through procedures such like tuning of the sediment structure in sediment cubes and bodies, but also optimized drainage of sediment cubes before freezing, we are confident to enhance the developed methodology to reach an accuracy needed for proper experimental upscaling.

Cretaceous Large Igneous Provinces: the effects of submarine volcanism on calcareous nannoplankton

ELISABETTA ERBA*, CINZIA BOTTINI AND GIULIA FAUCHER

Department of Earth Sciences, Università degli Studi di Milano, 20133 Milan, Italy. (*correspondence:elisabetta.erba@unimi.it)

During the Cretaceous the construction of Large Igneous Provinces (LIPs), forming gigantic oceanic plateaus, affected ecosystems at global scale. LIP volcanism was coeval with episodes of oxygen depletion in the oceans with consequent burial of massive amounts of organic matter known as Oceanic Anoxic Events (OAEs). Under these conditions, biota were forced to face excess CO_2 and global perturbations in the ocean-atmosphere system.

In the open ocean, coccolithophores are important carbonate rock-forming organisms, extremely sensitive to changes in physical-chemical parameters of surface waters. They are an ideal tracer for detecting the direct/indirect impacts of submarine volcanism on transient responses and evolution of calcifying biota.

We investigated calcareous nannoplankton assemblages across the early Aptian OAE1a and the latest Cenomanian OAE2, associated to the Ontong Java Plateau (OJP) and the Caribbean Plateau (CP), respectively. Massive submarine volcanism of OJP triggered a disruption in the oceanic carbonate system: excess CO_2 arguably induced ocean acidification that was detrimental to marine calcifiers, with temporary failure, but no extinctions, of rock-forming nannoconids and production of dwarf and malformed coccoliths. Similarly, during OAE2 the excess CO_2 from CP volcanism affected nannoplankton calcification inducing some coccolith dwarfism. Hydrothermal plumes during construction of both OJP and CP introduced biolimiting metals that fertilized the global ocean. However, some toxic metals might have disturbed the functioning of some intolerant coccolithophorid species.

There is a causal link between intervals of LIP submarine volcanism and changes in nannoplankton composition, abundance and biocalcification through OAE1a and OAE2. Changes in ocean chemistry, structure, and fertility during formation of oceanic plateaus might explain observed tempo and mode of nannoplankton evolution: major origination episodes might result from magmas especially enriched in biogeochemically important elements from the mantle.

Some Organic Geochemical Characteristics of Oil Shale Deposits in the Ereğli-Bor Basin, (Konya-Niğde), Central Turkey

M.S. ERDOĞAN[1]*, S. KORKMAZ[1], G. KADıNKıZ[2]
AND R. KARA-GÜLBAY[1]

[1]Karadeniz Technical University, Trabzon / Turkey
(*correspondence: mserdogan@ktu.edu.tr)
[2]General Directorate of MTA, Ankara / Turkey

Upper Miocene-Pliocene aged oil shale sequence, with an average thickness ranging between 72 and 160 m, has been cross-cut during the drilling studies at Ereğli-Bor basin, Central Turkey. In addition, the live oil show has also been observed in this oil shale sequence.

Paleocene-Eocene aged volcanic, volcano-clastic, clastic and carbonate rocks form the base of this basin. This basin is overlain unconformably by the Oligocene-Middle Miocene aged evaporatic rocks, carbonates and clastic rocks. The upper Miocene-Pliocone aged oil shale bearing sequence overlie this unit. The Kızılbayır formation, is overlain by the Katrandedetepe formation which is composed of claystone, sandstone, siltstone, gypsium, anhidrite and oil shale. Sandstone and claystone alternations, known as Beştepeler formation, form the upper part of the sequence. All these units are overlain unconformably by Upper Pliocene-Holocene aged clastic sediments and volcanic rocks.

According to the Pyrolysis analyses results of the selected oil shale samples, total organic carbon contents (%TOC) of the oil shale range between 1.21 and 13.98, with an average TOC value of 4.75. Hydrogen index (HI) and oxygen index (OI) values, ranging between 127-664 and 7-50 respectively, suggest that oil shales are formed by Type II kerogen. Tmax values (ºC) range between 332 and 419. Considering the Tmax values, oil shales are considered to represent the immature stage, although some of them reflect the early mature stage. Pyrolysis data suggest no oil generation in the basin. The live oil show in the basin has probably formed due to the young volcanic rocks cross-cutting the oil shale which resulted oil shales to reach the thermal maturity.

Characterizing the Pb isotopic contribution of dust to seawater

A.M. ERHARDT[12], C-T. CHEIN[2], A.D. JACOBSON[3], C. M. MOY[4] AND A. PAYTAN[2]

[1]Stanford University, Stanford, CA 94305
(*correspondence: erhardt@stanford.edu)
[2]University of California Santa Cruz, Santa Cruz, CA 95064
[3]Northwestern University, Evanston, IL 60208
[4]University of Otago, Dunedin, New Zealand

Different sources of dust to the open ocean have varying effects on seawater chemistry, productivity and plankton community structure due to the release of various amounts of nutrients and trace metals. Pb isotopes in marine sediments have been used to reconstruct these dust sources (provenance). This is typically done by comparing the isotopic signature in the detrital fraction of sediments to the Pb isotope ratios of bulk dust or loess samples from dust source regions. What is missing in these studies is the isotopic composition of the seawater soluble fraction of the dust and its role in the seawater Pb isotope budget.

In this study, we characterized the Pb isotopic contribution of dust to seawater from select source regions to the Pacific Ocean through a direct simulation of dust solubility in seawater. We found that the readily leachable fraction of dust from multiple source regions to the Pacific Ocean is less radiogenic than the bulk source sample or that of the detrital fraction of sediments. Clear differences in the soluble and bulk Pb isotopic ratios of dust between the different source regions were also observed.

Knowing the true dust isotopic contribution to seawater allows for more accurate Pb mass balance calculations and clearer identification of dust sources and/or fluxes. We show preliminary results linking seawater, dust, ferromanganese, and detrital Pb isotope signatures in the Eastern Equatorial Pacific and generate a potential framework for future Pb mass balance calculations.

A comparison of shocked zircon and quartz from the Reis impact structure, Germany

TIMMONS M. ERICKSON*, STEVEN M. REDDY, NICHOLAS E. TIMMS AND ALEXANDER A. NEMCHIN

Department of Applied Geology, Curtin University, GPO Box U1987, Perth, WA 6945, Australia (*timmons.erickson@gmail.com)

Shock metamorphism is well established within the zircon and quartz mineral systems. Shocked quartz has been documented in a number of impact locations on the Earth and the shock deformation mechanisms have been identified, allowing for a well constrained thermobarometer of shock conditions to be developed [1]. Zircon is an important mineral in crustal studies and also records shock metamorphism through crystallographic deformation.

Shocked zircon has been identified from a number of impact structures, however development of a thermobarometer for shock metamorphism in zircon has been limited to one emperical study [2] and work on naturally shocked zircons from the Earth [3, 4, 5] and the Moon [6]. The work of Leroux et al. (1999) have determined that zircon exhibits planar microstructures >20 GPa, begins to transform to reidite >40 Gpa, completing conversion >60 GPa. Timms et al. (2012) further documented shock metamorphism of zircon and began to develop a shock deformation mechanism map. The aim of this study is to further constrain the development of shock features in zircon through the careful comparison of shocked zircon and quartz from the Reis impact structure.

We have therefore analyzed a suite of thin sections from the 14.4 Ma Reis impact structure in Germany from samples collected between 300 and 1204 m depth in the Nördlingen 1973 borehole. Previous work by Wittmann et al. (2006) determined shocked zircons in suevites from Reis exhibit planar microstructres, granular texture and reidite indicating samples were shocked >40 GPa, while other mineral systems indicate pressures >60 GPa. In this study shocked zircon and quartz have been analyzed petrographically and by SEM including EBSD to further resolve the correlation of shock deformation within these two mineral systems.

[1] Stöffler and Langenhorst 1994 MAPS [2] Leroux et al. 1999 EPSL [3] Wittmann et al. 2006 MAPS [4] Moser et al. 2011 CJES [5] Erickson et al. 2013 Am Min [6] Timms et al. 2012 MAPS

Petrology, mineral chemistry and Sr–Nd−Pb isotopic compositions of granitoids in the central Menderes metamorphic core complex: Constraints on the evolution of Aegean lithosphere slab

F. ERKÜL[1]*, S.T. ERKÜL[2], E.Y. ERSOY[3], İ. UYSAL[4] AND U. KLÖTZLI[5]

[1]Akdeniz Univ., Vocational School of Technical Sciences, 07058, Antalya, Turkey (*correspondance: fuaterkul@gmal.com)
[2]Akdeniz Univ., Department of Geological Engineering, Dumlupınar Bulvarı, Campus, 07058, Antalya, Turkey
[3]Dokuz Eylül Univ., Department of Geological Engineering, 35160, Izmir, Turkey
[4]Karadeniz Teknik Univ., Department of Geological Engineering, Trabzon, Turkey
[5]Center for Earth Sciences, Department of Lithospheric Research UZA II, Vienna, Austria

Salihli and Turgutlu granitoids in the central Menderes metamorphic core complex are most suitable rocks in order to understand the magma forming processes in extended terrains. They are granodiorite in composition and contain monzonitic and monzodioritic microgranular enclaves. Host rocks are geochemically similar to each other while their enclave chemistry is in contrast with low SiO_2 and high Mg≠ values. Mineral chemistry data confirm a chemical equilibriation of distinct magma batches. Geochemical modelling suggests that these granitoids were derived from mixing of mantle and lower crustal components, which were finally modified by upper crustal contamination and fractional crystallization processes. Early-Middle Miocene syn-extensional granitoids across the Aegean region form a magmatic belt associated with roll-back of the Aegean lithosphere slab. Roll-back induced magmatism together with ductile deformation in western Turkey ceased after cooling of the Salihli granitoids at 12.2 Ma as defined in previous geochronologic work. But core-complex related magmatism was continuous in the Cycladic metamorphic core complex during Late Miocene and was followed by an active arc volcanism in the southern Aegean. Such abrupt change in the geodynamic setting of western Turkey can be explained by opening of a slab window on the Aegean lithosphere slab, which would lead to upwelling of fertile subslab asthenospheric mantle, forming transitional and finally OIB-type basalts.

Molybdenum isotopic composition of pre-GOE tidal carbonates

S. EROGLU[1]*, R. SCHOENBERG[1,] N. BEUKES[2]
AND M. WILLE[1]

[1]University of Tuebingen, Wilhelmstraße 56, 72074
Tuebingen, Germany
(*correspondence: suemeyya.eroglu@uni-tuebingen.de)
[2]University of Johannesburg, Auckland Park Kingsway
Campus, 2006, South Africa

The Transvaal Basin in South Africa contains one of the best preserved carbonate platforms of the Archaean. This platform was deposited between ~2.58 and 2.50 Ga [1], shortly before the 2.40-2.32 Ga great oxidation event (GOE) and is composed of alternating stromatolithic carbonates and shales. The depositional environment of the Transvaal Basin is very similar to modern tidal areas.

Variations in the isotopic abundance of the redox-sensitive transition metal molybdenum have been used in the past few years to constrain the redox conditions of Earth's atmosphere-hydrosphere system in the present and the past [2, 3]. Interestingly, carbonates and black shales from the slope of the Griqualand West Basin in South Africa, which can be well-correlated to the Transvaal Basin, shift towards heavy $\delta^{98/95}$Mo values, which might indicate an oxygenation of the atmosphere-hydrosphere system some 100 Ma before the GOE [4, 5]. In our study we determine the Mo content and $\delta^{98/95}$Mo composition of tidal carbonates from the platform of the Transvaal Basin, which precipitated in shallow waters and compare them to the contemporaneous deeper platform deposits of the Griqualand West Basin, in order to investigate the influence of sedimentary settings on Mo isotopic signatures. The very low Mo concentration of the carbonates generally lies around 20 ppb and most of our data cluster from +0.2 to +0.6‰ $\delta^{98/95}$Mo, but our preliminary results also reveal highly variable $\delta^{98/95}$Mo signatures between -0.7 and +1.4‰ and indicate an influence of the depositional environment of the stromatolites on their Mo isotopic composition. This observation might be an important aspect for future interpretation of Mo isotopic compositions of chemical sediments.

[1] Sumner & Beukes (2006) *SAJG* **109**, 11-22. [2] Barling *et al*. (2001) *EPSL* **193**, 447-457. [3] Siebert *et al*. (2003) *EPSL* **211**, 723-733. [4] Voegelin *et al*. (2010) *Precambrian Res*. **182**, 70-82. [5] Wille *et al*. (2007) *GCA* **71**, 2417-2435.

Geotechnical assessment of the rock masses in Düzyurt area (Trabzon, NE Turkey)

HAKAN ERSOY[1] AND M. OĞUZ SUNNETCI[2]

[1]Karadeniz Technical University, Department of Geological
Engineering, Trabzon, Turkey, ersoy@ktu.edu.tr
[2]Karadeniz Technical University, Department of Geological
Engineering, Trabzon, Turkey, moguzsunnetci@ktu.edu.tr

In this study, geological, hydrogeological, geotechnical properties of the rock masses in the Düzyurt Area (Trabzon, NE Turkey) were investigated. Engineering properties of geotechnical units were determined in two stages; surface and subsurface studies. Borehole applications, *in situ* testing, scan-line surveys (discontinuity direction, persistence, spacing, opening, roughness infilling material and RQD) and seismic surveys were conducted for description of geotechnical units and determination of vertical and horizontal homogeneity of these units in the site. *in situ* lugeon tests were applied for determination of bedrock permeability. During core drilling, lugeon tests were conducted and permeability of the rock masses is calculated. A total of 16 pumping tests were performed at the site in 5 boreholes. Based on the lugeon test results, permeability coefficients were calculated about 1.88×10^{-8} m/s for whole bedrock consisting of mainly limestone. According to the results, 1/2000 scaled engineering geological map was prepared. In the laboratory studies, physical and strength properties were determined on the samples collected from the boreholes and rock blocks in the geotechnical units. Rock mass strength was calculated with Hoek-Brown empirical approach using by data obtained from laboratory studies and scan-line surveys. Engineering properties of rock masses were performed with RMR system and durability of slopes in the area was investigated using kinematic analysis. GSI value for rock masses were calculated as 50. Based on the excavatability analysis of the rocks using seismic wave velocity and geotechnical properties of the rock mass, the excavatability category of rock masses is moderate-hard ripping.

A second rapid sea-level fluctuation during Termination II at Barbados

TEZER M. ESAT[1]* AND ERDEM BEKAROĞLU[2]

[1]Australian Nuclear Science and Technology Org., Kirrawee, Australia (*correspondence: tezer.esat@anu.edu.au)
[2]Ankara University, Sihhiye 06100, Ankara, Turkey

Rapid, centennial or shorter timescale, climate variations are often superimposed over thousands of year duration orbital insolation driven climate cycles. Fast paced Heinrich events of the last glacial period are associated with ice-berg discharges and sea-level oscillations that periodically have triggered changes in the North Atlantic Ocean's thermohaline circulation. The resultant severe climate shifts have been recorded in numerous climate proxies. Such climate variability is not confined to glacial periods but extend through degalciations and possibly into interglacial periods [1]. A definite pattern of climate change is discernible for the last six glacial terminations (T1, TII etc.) each of which appears to have gone through two major and distinct climate events. For T1 these are the Younger Dryas cold period and Henrich event H-1 during the so-called Mystery Interval [2]. Similar features are present at T3 and T4. At T2, there is a very large >60 m sea-level oscillation called the Aladdin's Cave (AC) transition first documented at Huon Peninsula that peaks around 135.3 ka, approximately 10 m below last interglacial sea levels [3,4,5,6]. A number of marine proxy climate records of the time as well as descriptions of European lacustrine deposits of the Saalian period indicate the presence of at least two climate oscillations which would be consistent with similar climate events during TI and TIII [2,6,7]. Along the Gordon Cummins Highway, adjacent to the West Indies University at Barbados, the road cut follows the rising sea-level during TII and there are deposits of fossil coral reefs that grew at the time in response to the rise in sea-level. Here, we have discovered a second peak in sea level at 133.5 ka, distinct from the timing of the original AC transition. The sea-level high-stand is close to the peak of the last interglacial relative sea levels at this location. However, its magnitude cannot be precisely quantified from the available data but may be as much as 90 m.

[1] Yokoyama & Esat (2011) *Oceanography* **24**, 54-69. [2] Broecker *et al.* (2010) *QSR* **29**, 1078-1081. [3] Thomas *et al.* (2009) *Science* **324**, 186-189. [4] Siddall *et al.* (2006) *Geology* **34**, 817-820. [5] Esat *et al.* (1999) *Science* **283**, 197-201. [6] Andrews *et al.* (2007) *EPSL* **259**, 457-468. [7] Risebrobakken *et al.* (2006) *EPSL* **241**, 505-516.

High frequency network sensors for integrating biogeochemical processes in the Seine River and quantifying the impact of Paris Megalopolis

N. ESCOFFIER[1], N. FLIPO [2], L. VILMIN[2], N. BENSOUSSAN[3], A. LAVERMAN[4], M. RAIMONET[4] AND A. GROLEAU[1]

[1]Géochimie des Eaux. Univ Paris Diderot, Sorbonne Paris Cité, IPGP, UMR 7154, CNRS , F-75205 Paris, France
[2]Centre de Géosciences. Systèmes Hydrologiques et Réservoirs. Mines ParisTech. 77305 Fontainebleau
[3]IPSO FACTO. 4, rue de Tilsit, F-13006 Marseille
[4]CNRS-UPMC UMR 7619 Sisyphe, Boite 125, 4 place Jussieu, 75005 Paris

The CARBOSEINE program, inititated in 2011, focuses on the urban part of the Seine river (Paris, France). It develops an integrated approach based on *in situ* sensors network in order to determine the main parameters controlling the biogeochemical carbon dynamics in the river. To do so, three on-line high frequency (every 15 min) multi-probe stations are devoted to the monitoring of the main hydrogeochemical parameters (weather, CTD, pH, phosphate, O_2, turb., chla) for the River downstream Paris (54 km long).

Carbon dynamics based on diel oxygen concentration variations allow the quantification of river metabolism processes over time. During algae blooms, river ecosystem shifts from heterotrophic to autotrophic on daily periods according to Net Ecosystem Production calculations. Combining Gross Primary Production and chlorophyll biomass leads to quantify the productivity of the autotrophic component, which can heavily differ from one bloom to another. Phosphate *in situ* measurements (4h freq.) demonstrates nutrient depletion without reaching the limitation level. They document the diffusive sources coming from watershed alteration, that allow algae growth upstream Paris. Moreover, these P measurements highlight the human impact variability. Comparison between probes located upstream and downstream the largest European Waste Water Treatment Plant allows to calculate the mass budget resulting from Paris megalopolis activity.

As a generic result, this high frequency observation approach constitutes a powerful tool for understanding and managing aquatic biogeochemistry in anthropic ecosystem. A challenge consists in developing an accurate data treatment strategy to segregate natural variations from human impact, with respect to different observation time scales. Finally, the generated dataset, allows to develop new modelling techniques to better define the processes representation in river numerical models.

Using textural data and fractal analysis to infer crystallization of dacites from Qorveh (W-Iran)

A. ESKANDARY[1]*, R. DE ROSA[2], S. AMINI[1]
AND H. MIRAJ[1]

[1]University of Kharazmi, Mofatteh Street, Tehran, Iran
(*correspondence:amir.eskandary157@gmail.com)
[2]University of Calabria, via P. Bucci I-87036 Arcavacata di
Rende (CS), Italy (rosanna.derosa@unical.it)

Polybaric crystallization in a volcano feeding system generally produces concave-up trends in diagrams of crystal size distribution (CSD) of the related emitted products, a feature testified both in natural and experimental studies [1,2]. In the present work, CSD technique has been applied to plagioclase crystals in plio-quaternary dacitic lavas of Qorveh volcano (Western Iran).

Crystal size distributions of more than 9000 plagioclases of the six collected samples were plotted in natural logarithmic scale (Ln) as the number of crystals per unit length and per unit volume $(n(L); mm^{-4})$ vs. crystal lengths $(L; mm)$. According to textural and CSD data, three distinct populations of crystals were identified: 1) phenocrysts $(L>0.6)$ with coarse sieve texture and complex zoning patterns; 2) micro-phenocrysts $(0.2<L<0.6)$ and 3) microlites $(L<0.2)$. Furthermore, CSDs show a fractal behavior, with fractal dimension ranging 2.44-2.75. In addition, based on the box counting method, also distribution patterns of plagioclase crystals present fractal dimensions.

Our study suggests a strong control on size and spatial distribution of plagioclase crystals by complex processes of crystallization related to decompression and degassing, different rates of ascent velocity and depth of crystals nucleation and growth.

[1] Armienti *et al*. (1994) *Contrib. Mineral. Petrol* **115**, 402–414. [2] Brugger, C, R. Hammer, J.E (2010) *EPSL* **300**, 246–254

Temporal evolution of subduction signatures in a continental back-arc

VENERA R. ESPANON [1,2]*, ANTHONY DOSSETO [1,2]
AND ALLAN R. CHIVAS[2]

[1]Wollongong Isotope Geochronology Laboratory,
[2]GeoQuEST, School of Earth and Environmental Sciences,
University of Wollongong, NSW (2522), Australia
*(vre981@uowmail.edu.au)

The Andino-Cuyana Basaltic Province (ACBP) constitutes part of the Quaternary continental back arc in southern Mendoza, Argentina. This basaltic province is divided into the Llancanelo Volcanic Field (LLVF) to the north and the Payunia Volcanic Field (PVF) to the south. The younger basalts are from the PVF and they range from <10 ka to approximately 50 ka [1], while the flows from LLVF are older Pleistocene basalts [1] lacking any Holocene volcanism. The ACBP presents a range of basaltic flows providing an appropriate setting to investigate changes in back-arc geochemistry during the late Quaternary.

In this setting, this study aims (i) to quantify the relative influence of the Andean arc and subducting slab in the back-arc, and thus (ii) to identify types and timescales of processes controlling back-arc volcanism in the ACBP. For this purpose, we present a suite of geochemical data (major and trace elemental analyses, REE, $^{87}Sr/^{86}Sr$, $^{226}Ra/^{230}Th$, $^{238}U/^{230}Th$) from the two volcanic fields and relate them to existing data from Andean arc basalts.

Our results show that basalts from the LLVF and the PVF have intraplate and arc related signatures with enrichment in LILE, HFSE and REE compared with basalts from the Andean arc. The older basalts from the LLVF and PVF have stronger arc signatures. In the PVF we observed a decrease in arc signatures from approximately 100 ka to 10 ka with a strong enrichment in LILE, HFSE and REE in the young basalts which could be related to metasomatised mantle or continental lithospheric mantle.

[1] Ramos & Folguera (2010), Journal of Volcanology and Geothermal Research **201**, 53-64.

Ascent of magmas associated with the Solchiaro eruption Procida Island (Italy) based on melt inclusions and glasses

ROSARIO ESPOSITO[1]*, MATTHEW STEELE-MACINNIS[2], CLAUDIA CANNATELLI[1], ANNAMARIA LIMA[1], BENEDETTO DE VIVO[1] AND ROBERT J. BODNAR[2]

[1]DISTAR, Università degli Studi di Napoli Federico II, Via Mezzocannone 8, Napoli, 80134, Italy (*Correspondence: rosario.esposito3@unina.it, claudia.cannatelli@unina.it, anlima@unina.it, bdevivo@unina.it)

[2]Department of Geosciences, Virginia Tech, 4044 Derring Hall, Blacksburg VA, 24061 USA (rjb@vt.edu, mjmaci@vt.edu)

The Solchiaro eruption on the island of Procida is one of the few trachybasaltic eruptions in the Phlegrean Volcanic District (PVD), Italy.

The goal of this study is to provide information on the magma dynamic associated with the Solchiaro eruption based on hourglass inclusions (HI), glass embayments (GE) and melt inclusions. HI are portions of melt ± vapour connected to the outside of phenocrysts through a narrow neck, and GE are portions of melt ± vapour delimited by an indentation in a phenocryst. We have characterized the major, minor and trace elements and volatile compositions of several HI and GE glasses. The HI and GE are associated with olivines of samples from the Solchiaro eruption, representing different stratigraphic heights.

The results show a good negative correlations between the maximum contents of dissolved H_2O, CO_2 and S of HI and GE and the eruptive time (stratigraphic heights). Reversely, minimum contents of Cl and F of HI and GE show positive correlation with the eruptive time.

The H_2O and CO_2 contents of some of the early-erupted HI are the same as those of early-erupted MI [1, 2] suggesting that residence times of early-erupted olivine were short enough to preserve the original dissolved volatile contents of HI. Alternatively, some HI were quenched to a glass from a great depth (up to 8 km) under equilibrium conditions. We develop a quantitative model to understand the duration of decompression for the Solchiaro eruption based on shape and size of both the HI and the contained bubble(s) as was previously done for the Bishop Tuff [3].

[1] Esposito *et al*.. (2011) *J. Petrol*. **52**, 2431-2460. [2] Mormone *et al*.. (2011) *Chem. Geol*. **287**, 66-80 [3] Anderson (1991) *Am. Mineral*. **76**, 530-547.

Attachment of aspartic acid at the brucite [Mg(OH)2]-water interface

C. F. ESTRADA[1,2]*, D.A. SVERJENSKY[1,2] AND R.M. HAZEN[2]

[1]Johns Hopkins University, Baltimore, MD 21218, USA (*correspondence: cestrada@jhu.edu, sver@jhu.edu)
[2]Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA (rhazen@ciw.edu)

The interaction of organic molecules at the mineral/water interface could play a key role in the emergence of more complex organic species in origins of life scenarios. In one such scenario, hydrothermal vents, particularly serpentinite-hosted hydrothermal vents, may possibly act as a suitable environment for this process to occur. We conducted a batch adsorption study between a stable mineral product of serpentinization, brucite $(Mg(OH)_2)$, and the amino acid aspartic acid at 25ºC. We studied the adsorption of 2-500 μM aspartate onto a pure synthetic brucite at a single pH value of ~10.4 and a solid to ligand concentration of 10 g•L^{-1} under conditions where the brucite was in thermodynamic equilibrium with the aqueous solution. The point of zero charge (pH_{ZPC}) of brucite is approximately 11.0 [1], thus resulting in weak electrostatic attraction between the weakly-positive brucite surface and the negative aspartate. We obtained an isotherm, in which the concentration of aspartate adsorbed onto brucite reached a maximum of about 0.1 μmol/m^2, after increasing linearly with the concentration of aspartate in solution ($[Asp]_{aq}$) from 2-100 μM and leveling off at 250-500 μM. We used an extended triple-layer surface complexation model (ETLM) to acquire a preliminary fit to the isotherm. The data and the ETLM suggest that the surface site density is restricted to a very low value. Model predictions also suggest that the extent of aspartate adsorption onto brucite will decrease with increasing background electrolyte concentration. In comparison with our previous batch adsorption study of aspartate onto rutile (TiO_2) [2], we conclude that aspartate adsorbs to a lesser extent onto brucite than rutile. This is the first study in which we have obtained an adsorption isotherm for a non-oxide, rock-forming mineral and an amino acid. We expect the adsorption data collected for this system at surface conditions to provide a necessary analog for future adsorption experiments at hydrothermal conditions with implications for the emergence of complex biomolecules on Early Earth environments.

[1] Pokrovsky & Schott (2004), *Geochim Cosmochim Act* **68**, 31-45. [2] Jonsson *et al*. (2010), *Geochim Cosmochim Act* **74**, 2356-2367.

Bacterial populations (first record) at two shallow submarine hydrothermal vents off west Mexico

A. ESTRADAS-ROMERO[1], S. DÁVILA-RAMOS[2], R.M. PROL-LEDESMA[1]*AND K. JUÁREZ-LÓPEZ[2]

[1]Instituto de Geofísica, Universidad Nacional Autónoma de México, Ciudad Universitaria, Delegación Coyoacán, 04510 México D.F., México (a_estradas@hotmail.com,*correspomdence: prol@unam.mx)
[2]Instituto de Biotecnología, Universidad Nacional Autónoma de México, Cuernavaca, Morelos. C. P. 62210, México (sdavilar@ibt.unam.mx, katy@ibt.unam.mx)

Thermophilic and metal oxidizing bacteria were identified in shallow hydrothermal vents on the western Mexican coast. The role of these bacteria in biomineralization processes observed in the vents is explained, and the effect of the vents on biodiversity of prokaryotes is discussed. Research was done at two shallow hydrothermal vent sites: Bahía Concepción in the Baja California Peninsula and Punta Mita, in the central Pacific coast. The study focuses on the biogeochemical processes related to the different species of bacteria present in the studied sites, which are involved in the anaerobic oxidation of methane (AOM), seawater sulfate reduction and metal oxidation. Vent water shows different composition in both sites; moreover, different pH and redox conditions control bacteria diversity. The composition of the discharged water ranged from nearly sea water to lower salinity fluids with a pH about 6, and the gas phase in the hydrothermal fluids was mainly CO_2 at the Baja California site, and N_2 and CH_4 at Punta Mita. The detected bacterial lineages represented typical deep vent species.

Physical and chemical characteristics of the geothermal manifestations play a major role in the biodiversity of bacteria in shallow hydrothermal vents. In the case of the submarine vents in Bahia Concepcion and Punta de Mita, the redox conditions determine the presence/absence of distinct species of bacteria: gamma, delta and epsilon bacteria as well as bacteriodetes in the oxidizing conditions of Bahia Concepcion; and thermotogae, aquificae and planctomycetes in Punta de Mita. On the other hand, there are some species that are ubiquitous in shallow vents, as the halophilic and chlorofleaxae bacteria.

Tracing antropogenic Hg emissions in an urban area in Northeastern France

N. ESTRADE[1], C. CLOQUET[1], D. AMOUROUX[2], E. TESSIER[2], O.F.X. DONARD[2] AND J. CARIGNAN[1]

[1]CRPG, UMR 7358, CNRS-Université de Lorraine, France
[2]IPREM/LCABIE, UMR 5254, CNRS-Université de Pau et des Pays de l'Adour, France
(*correspondence: nestrade@crpg.cnrs-nancy.fr)

Mercury (Hg) isotopes are giving new insights into the study of the Hg biogeochemical cycle through large mass dependent and mass independent fractionations (MDF and MIF). A few studies have evaluated the ability to trace atmospheric Hg using both direct atmospheric measurements [1] and indirect bio-accumulators such as lichens [2,3]. Species-specific isotopic compositions of atmospheric Hg display large ranges in both MDF and MIF, and their distinct signatures suggest the occurrence of isotopic fractionation during species conversion [4]. The isotopic compositions of atmospheric depositions potentially recorded in bio-accumulators can be altered through various fractionation processes [3], leading to ambiguous interpretation of Hg isotopic composition to track down atmospheric sources. As regards anthropogenic emissions, different species-specific compositions have been suggested [5] but direct field measurements have not yet been performed.

We report species-specific Hg isotope compositions inside and at the stack of a waste incinerator located in an urban area in northeastern France. Gaseous mercury concentrations and isotope compositions were measured simultaneously in the vicinity of the waste combustor. The main results from the exhaust indicate that oxidized Hg species are slightly enriched in heavier isotopes compared to Hg^0 species and initial Hg (waste). Diurnal variations recorded for Hg concentrations in the atmosphere are not compatible with the incinerator emissions. In contrast to incinerator emissions, isotopic compositions measured over several days of sampling display significant light isotope enrichment and indicate a little contribution of incinerator to surrounding atmosphere. Further interpretation and comparison with previously published urban topsoil and lichen compositions from the same urban area, provide us relevant informations to trace Hg anthropogenic emissions on such local scale.

[1] Sherman *et al*. (2010) *Env. Sc. Technol*., **46**, 382-390; [2] Estrade *et al*. (2010) *Env. Sc. Technol*., **44**, 6062-6067; [3] Blum *et al*. (2012) *Dev. Env. Sc*., **11**, 373-390; [4] Rolison *et al*. (2013) *Chem. Geol*., **336**, 37-49; [5] Sun *et al*. (2013) *Chem. Geol*., **336**, 103-111

Nickel isotope fractionation in the soil to hyper-accumulating plant system

N. ESTRADE[1]*, C. CLOQUET[1], T. DENG[2],
G. ECHEVARRIA[2], T. STERCKEMAN[2] AND J.L. MOREL[2]

[1] CRPG, UMR 7358, CNRS-Université de Lorraine, Nancy, France (*correspondence: nestrade@crpg.cnrs-nancy.fr)
[2] LSE, UMR 1120, INRA-Université de Lorraine, Nancy, France

Nickel stable isotopes are a promising non-traditional stable isotope system for understanding the Ni biogeochemical cycle, especially in contaminated or highly enriched environmental compartments such as ultramafic contexts. Ni hyperaccumulating plant species (e.g. *Alyssum murale*) growing in ultramafic soils can concentrate up to several weight percent in leaves and may be used in phytoremediation or phytomining. In addition to its insensitivity to redox-processes, nickel homeostasis in hyperaccumulating plants is poorly understood. In this work, we used Ni stable isotopes to document the isotopic fractionation range during accumulation processes from soil to Ni-hyperaccumulating plant species in a field investigation.

Sampling was carried out in Albania at four different sites and included the collection of several hyperaccumulating plant species as well as tolerant ones. Using two-step chemistry to isolate Ni and the double-spiking technique to correct for instrumental mass fractionation, we recorded Ni concentrations and Ni isotope compositions along the continuum of ultramafic rock, soil (different horizons), litter, roots, stems, leaves and flowers. In typical Ni-rich soil, root and litter concentrations ranged between 1-3 g kg^{-1} dry matter. Nickel accumulation increased to 3-6 g kg^{-1} in stems and reached up to 20 g kg^{-1} in leaves. In contrast, tolerant species present Ni concentrations in leaves within the 0.1 g kg^{-1} range.

Preliminary results in hyper-accumulator plant samples did not reveal large extent of isotope fractionation between roots and leaves (0.2‰). Further investigation is ongoing to confirm these results and evaluate the entire soils plants variations.

Dusts from metal smelters in Africa: Mineralogy, leaching and contaminant bioaccessibility

V. ETTLER[1]*, M. VITKOVA[1,2], M. MIHALJEVIC[1] AND B. KRIBEK[3]

[1] Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University in Prague, Albertov 6, 128 43 Prague 2, Czech Republic (*correspondence: ettler@natur.cuni.cz, mihal@natur.cuni.cz)
[2] Department of Environmental Geosciences, Faculty of Environmental Sciences, Czech University of Life Sciences Prague, Kamycka 129, 165 21 Prague 6 – Suchdol, Czech Republic
[3] Czech Geological Survey, Geologicka 6, 152 00 Prague 5, Czech Republic

Dry climate and strong winds are believed to be responsible for dispersal of contaminated dust particles in areas affected by mining, mineral processing and smelting [1]. We evaluated the solid speciation, leachability and potential bioaccessibility of metals (Co, Cu, Pb, Zn) and As in fly ashes and slag dusts originating from the metal mining and smelting areas of Zambia (the Copperbelt Province) and Namibia (the Tsumeb area). Dusts were highly enriched in inorganic contaminants (up to 273 g Cu/kg, 8.9 g Co/kg, 39 g Pb/kg, 21 g Zn/kg and 437 g As/kg). Based on XRD, SEM, EPMA and HRTEM investigations, major contaminant-bearing phases were cuprospinel ($CuFe_2O_4$), chalcanthite ($CuSO_4.5H_2O$), delafossite ($CuFeO_2$), arsenolite (As_2O_3) and minor galena (PbS), anglesite ($PbSO_4$), sphalerite (ZnS) and elemental Cu [2, 3]. The pH-static leaching tests indicated that contaminants were released from the fly ash mostly at low pH [2, 3], corresponding to conditions found in laterite soils from this area. We also adopted *in vitro* methods based on simulated gastric fluid (SGF) and simulated lung fluid (SLF). The maximum bioaccessibilities in SLF were relatively low (Co 16%, Cu 2%, Zn 1.2%, As 2.9%), whereas values higher than 20% were obtained for SGF (Co 80%, Cu 50%, Zn 77%, As 83%). The obtained data indicate that a severe health risk related to smelter dust ingestion/inhalation should be taken into account in these areas. This study was supported by the Czech Science Foundation (projects no. 13-17501S and P210/12/1413) and IGCP project no. 594.

[1] Ettler *et al..* (2012) *J. Geochem. Explor.* **113**, 68-75. [2] Vítková *et al..* (2011) *Appl. Geochem.* **26**, S263-S266. [3] Vítková *et al..* (2013) *Appl. Geochem.* **29**, 117-125.

Aerosol impact on the stratiform cloud and light precipitation in mid-Korean peninsula

SEUNG-HEE EUN AND BYUNG-GON KIM*

[1]Department of Atmospheric Environmental Sceinces, Gangneung-Wonju National University, Jibyun, Gangneung, Korea (bgk@gwnu.ac.kr)

Many observational and numerical studies have indicated that land cover and aerosol effect modify cloud property, precipitation, and further weather pattern over and downwind of urban region. Because these effects have occurred in the urban region together, it is important to understand each effect over and downwind of urban region. Eun *et al*. (2011) showed increasing trend of precipitation amount and frequency downwind of Seoul Metropolitan Area (SMA) from 1972 to 2007, for particularly light precipitation (less than 1 mm per day) and westerly condition only. It implies the possible influences of land cover change and aerosol on the precipitation in the downwind region of SMA. Based on observed results, we selected golden case (10 February 2009) to investigate the impact of aerosol on light precipitation using the Weather Research & Forecasting (WRFV3.2) model. The sensitivity run sets up 1,000 $\#/cm^3$ for the initial number concentration of cloud condensation nuclei (CCN) at SMA, but the background uses 100 $\#/cm^3$.

The results show that mean horizontal wind from surface to 850 hPa have easterly wind and approximately 5~6 m/s. Cloud thickness is about 500 m, and locates within 2 km. Also the results of cloud properties indicates that the enhanced CCN at SMA is associated with smaller effective radius (re; μm) and more cloud droplet number concentration (Nc; $\#/cm^3$) over and downwind of urban region than control run. Especially after 3-hour, change of re and Nc was distributed much more widely downwind of urban region. On the other hand, precipitation amount appears to widely increase in the downstream region of SMA. In the near future, further sensitivity tests need to be conducted for combined effect of land cover and aerosol effect on the light precipitation.

Reconciling seawater Mg/Ca reconstruction with foraminifera geochemistry

DAVID EVANS[1]*, WOLFGANG MÜLLER[1], JONATHAN EREZ[2], SHAI ORON[3] AND WILLEM RENEMA[4]

[1]Dept. of Earth Sciences, Royal Holloway Univ. of London, UK
[2]Earth Science Inst., The Hebrew Univ. of Jerusalem, Israel
[3]Interuniversity Institute for Marine Sciences, Eilat, Israel
[4]Naturalis Biodiversity Center, Leiden, The Netherlands
*(correspondence: david.evans.2007@rhul.ac.uk)

Virtually all Paleogene seawater Mg/Ca (Mg/Ca_{sw}) proxy data suggests values 2-4 times lower than the present day. Despite this, the majority of studies utilising foraminifera Mg/Ca (Mg/Ca_{test}) as a palaeothermometer during this period have argued for ratios around twice as high as the proxy evidence suggests. This is because the use of lower Mg/Ca_{sw} values resulted in unrealistically high palaeotemperature estimates. It has now been shown that this inconsistency is the result of an incorrectly assumed linear relationship between Mg/Ca_{sw} and Mg/Ca_{test}, as detailed in Evans & Müller [2012].

In order to empirically show that this theory is applicable to foraminifera, we have produced the first combined Mg/Ca-temperature and Mg/Ca_{sw}-Mg/Ca_{test} calibrations for the same species, derived from both cultured and field-sampled *Operculina ammonoides*, a shallow-dwelling large benthic foraminifera. We apply these calibrations to Eocene samples from Java and the southern UK; *O. ammonoides* is the closest living relative of the abundant Paleogene *Nummulites*. We utilise laser-ablation ICPMS as a highly spatially resolved analytical technique capable of identifying newly precipitated calcite in cultured material (via a [Ba] spike), and less well-preserved areas of fossil calcite through the simultaneous analysis of proxy and diagenesis-identifying trace elements.

The consistency between our field and culture Mg/Ca-temperature calibration suggests secondary controls on Mg incorporation are less problematic for large benthic foraminifera in comparison to planktic species. Our Mg/Ca_{test}-Mg/Ca_{sw} calibration confirms the power relationship described by studies based on other foraminifera.

By placing reasonable constraints on palaeotemperature, our calibrations enable us to demonstrate for the first time that foraminifera-derived data imply Mg/Ca_{sw} in excellent agreement with other proxy evidence.

[1] Evans & Müller, 2012, *Paleoceanography*, **27**, PA4205.

Sources of sulfur and sulfur preservation in subducted rocks: An *in situ* sulfur isotope study

K.A. EVANS*[1] A.G. TOMKINS[2] AND J. CLIFF[3]

[1]Applied Geology, Curtin University, GPO Box U1987, Perth, WA 6845, Australia. (*correspondence: k.evans@curtin.edu.au)
[2]School of Geosciences, Monash University, Melbourne, VIC3800, Australia
[3]Centre for Microscopy Characterisation and Analysis, University of Western Australia, WA6009, Australia

A number of lines of evidence suggest that the sub-arc mantle is 1-2 log units more oxidised than mantle elsewhere, though this conclusion is controversial, and the processes that may contribute to sub-arc mantle oxidation are poorly understood. Sulfur has been proposed as a vector for transfer of redox budget from subducting slab to sub-arc mantle. Sulfate may be present in altered ocean crust in significant quantities, and the transfer of 8 electrons as S(+6) in sulfate is transformed to S(-2) in sulfides means that the addition of sulfate to sub-arc mantle could significantly alter mantle redox budget and oxygen fugacity on geologically reasonable timescales. However, little is known of the relative stability or solubility of sulfur-bearing phases under subduction conditions so this possibility is hard to evaluate.

Sulfur isotopes provide one way to investigate sources of sulfur, and the processes that affect sulfur content during subduction. $\delta^{34}S$ of seawater-derived sulfate is around 20‰ while $\delta^{34}S$ of magma-derived sulfides is around 0‰. Calculated fractionation of sulfur isotopes at subduction temperatures for all but the most extreme open system conditions suggest that this difference between sources should be recognisable even after significant devolatilisation. *in situ* sulfur isotope measurements of pyrite associated with high pressure mineral parageneses in high pressure mafic rocks from the Eastern Alps and from New Caledonia were performed. The New Caledonia samples contain pyrite with $\delta^{34}S$ in excess of 5‰, while samples from Pfulwe pass in the Eastern Alps contain pyrite with $\delta^{34}S$ up to 15‰. These elevated $\delta^{34}S$ values suggest that sulfur ultimately derived from seawater is preserved in these rocks to depths greater than 60km.

In situ RESOchron helium dating: Progress, pitfalls and prospects

[1]NOREEN EVANS[1], BRENT MCINNES[1], BRAD MCDONALD[2], PIETER VERMEESCH[3,] MIKE SHELLEY[4] AND ESTEPHANY MARILLO SIALER

[1]AuScope GeoHistory Facilty, John de Laeter Centre for Isotope Research, Curtin University, Australia, (noreen.evans@curtin.edu.au);
[2]Department of Earth Sciences, University College London, UK;
[3]Laurin Technic Pty Ltd., Canberra, ACT;
[4]School of Earth Sciences, University of Melbourne, Australia

Recent advances in *in situ* double dating[1-3] prompted us to develop the *RESOchron*, a purpose-built laser ablation U-Th-Pb-He system (see McInnes *et al.*, this meeting). Polished zircon grains, mounted in indium, were loaded into an UHV cell where helium was extracted via 193 nm laser ablation for 30 seconds using a 33-75 μm beam at 7Hz. U and Th were subsequently analysed in an adjacent pit using traditional ELAICP-MS methods. Pit volumes were measured on a Zeiss LSM700 confocal laser microscope and (U-Th)/He ages calculated using published methods[1,3]. The mean zircon helium age from the *in-situ* ablation experiment fell within 10% of helium ages obtained using traditional single crystal methods for an 11.4 ± 0.5 Ma subvolcanic stock from the Reko Diq mine, Pakistan.
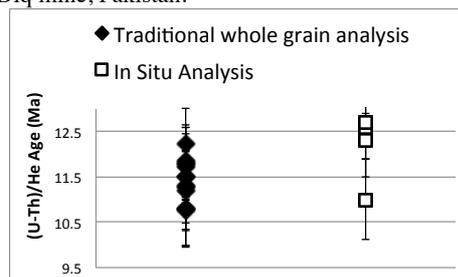
Improvements in analytical precision require refinement of sample preparation for UHV conditions. Indium, despite being inert under high vacuum conditions, is non-ideal for zircon mounting because its high surface reflectance makes navigating around the mount and focusing the laser difficult. Due to its extreme softness, grains cannot be polished *in situ* and even slight contact can damage the surface and cause grains to shift position. Zonation of U and Th also impacts the accuracy of results, as does the accuracy of pit volume measurements as suggested previously [1-3]. Other mounting media are being explored (eg. FEP teflon) and optimization of laser protocols is underway.

[1] Boyce J.W. *et al.*, 2006, *GCA* **70**, 3031–3039; [2] Boyce J.W. *et al.*, 2009 *G-cubed* 10. doi:10.1029/2009GC002497; van Soest M.C. *et al.*, 2012, AGU Fall Meeting Abstracts, pp. B2161+. [3] Vermeesch, P. *et al.*, 2012, *GCA* **79**, 140-147.

Subseafloor microbial community in the Benguela upwelling area characterized by lipid biomarkers and intracellular DNA

T.W. EVANS[1]*, L. WÖRMER[1], M.-A. LEVER[2], R. ZHU[1], L. LAGOSTINA[2], B. B. JØRGENSEN[2] AND K.-U. HINRICHS[1]

[1]MARUM, University of Bremen, 28359 Bremen, Germany (*correspondence: tevans@marum.de)

[2]Center for Geomicrobiology, University of Aarhus, 8000 Aarhus C, Denmark

The subsurface biosphere in marine sediments is one of the least understood ecosystems on our planet. Currently, it is even subject to debate which domain of microbial life, Bacteria or Archaea, is dominant. So far, studies based on intact polar membrane lipids (IPLs) have indicated dominance of lipids associated with Archaea [1], while most DNA-based studies have suggested a higher proportion of Bacteria [2]. These contradictory results are thought to result from analytical and/or systematic biases of both techniques. In the case of IPLs, the associated organic matrix may hinder proper HPLC-MS detection due to ion suppression. In addition, both IPLs and DNA analysis may be affected by a potential pool of fossil compounds [3, 4]. To overcome these problems and achieve a more realistic view of the microbial subseafloor biosphere, novel methods were applied to samples of a transect across the Namibian Continental Margin.

We employed a new protocol for separating intracellular DNA (iDNA) from the remaining extracellular DNA-pool. For IPLs, a new method was developed and applied, based on solid phase extraction (SPE) of lipids with a phosphatic head group, resulting in strongly improved detection.

The analysis of iDNA and IPLs showed a distinct change of the microbial community. iDNA- and IPL-data were in good agreement. SPE clean-up of IPLs resulted in the detection of phospholipids that could be attributed to sulfate reducing bacteria. Previously it was not possible to detect any phospholipids in subsurface samples of upwelling areas [5]. Both iDNA and IPL analysis showed a dominance of Archaea in organic-rich sediments below the upwelling cell, while further offshore the sediments were dominated by Bacteria. Further interpretation of these trends and the downcore profile of iDNA and IPL distribution is ongoing.

[1] Lipp *et al.* (2008), *Nature* **454**, 991-994. [2] Inagaki *et al.* (2006), *PNAS* **103**, 2815-2820. [3] Xie *et al.* (2013), *PNAS* **110**, 6010-6014. [4] Dell'Anno and Danovaro (2005), *Science* **309**, 2179 [5] Lipp and Hinrichs (2009), *GCA* **73**, 6816-6833.

Revealing the 'blind spot': A simple physical model for the temporal evolution of silicate mineral weathering

JAIVIME A. EVARISTO* AND JANE K. WILLENBRING

Department of Earth and Environmental Science, University of Pennsylvania, Philadelphia, PA 19104, USA (*correspondence: evaristo@sas.upenn.edu)

Closing the gap in the orders-of-magnitude difference between field and laboratory weathering rates has been considered essential to effectively modeling silicate mineral reactivity from centennial and millenial to geologic timescales[1]. However, what if finding the rates in the mid-range (i.e. $10^{1.5}$-$10^{3.5}$ yr) between far-from-equilibrium conditions in laboratory experiments and near-equilibrium conditions in the field is just as useful as what we now know about the two time-dependent rate extremes? We test this hypothesis by comparing the effects of two models ("gap" or blind spot and "filled") of weathering rate constants k to a mineral dissolution model driven only by the physics of reaction-diffusion dynamics. The explicit neglect of intrinsic factors, like chemical composition and mineralogical structure, in this simple model is an attempt not only to put an emphasis on the frequency and, in effect, duration of time with which a mineral surface interacts with pore fluids; but also to test if the reported agreement in phenomenological effective rates $K(t)$ between numerical and analytical solutions in comparable decay systems [2] also hold true for silicate weathering rates. Preliminary findings from our model simulations indicate that (1) there is no marked difference in effective silicate weathering rates $K(t)$ (yr^{-1}) between the two models of rate constants (4.86×10^{-2} t^{-1} and 4.88×10^{-2} t^{-1} for "filled" and "gap" distributions, respectively), suggesting that the apparent "blind spot" within the centennial to millennial range may not preclude our ability to predict mineral dissolution at these timescales; (2) the subsequent weathering beyond $t \sim k^{-1}$ exhibits a fall in rates of up to $\sim$3 orders of magnitude since the effective cessation of logarithmic decay, possibly reflecting the onset of a progressively refractory stage due to finite-size effects; and (3) a simple reaction-diffusion model may be able to predict the temporal evolution of silicate weathering as an integral of both field- and lab-derived rate constants, putatively identified by a lognormal distribution and therefore the kinetic heterogeneity associated with mineral dissolution.

[1] White and Brantley (2003), Chem. Geol. 202, 479.
[2] Rothman and Forney (2007), Science 316, 1325.

The uplift history of the western Andes, north Chile, constrained by cosmogenic ^{3}He in alluvial boulders.

LAURA EVENSTAR[1], FINLAY M. STUART[2]
AND ADRIAN J. HARTLEY[2]

[1]Dept. of Geology and Petroleum Geology, University of Aberdeen, Aberdeen, AB24 3UE, UK
[2]Isotope Geoscience Unit, Scottish Universities Environmental Research Center, East Kilbride, Glasgow, G75 0QF, UK
*Now at School of Earth Science, University of Bristol, Wills Memorial Building, Queens Road, Bristol, BS8 1RJ

Accurate timing of uplift of the Andes is essential for understanding continental tectonics processes. Current models vary from gradual uplift of the Andes from the Late Eocene due to crustal shortening/thickening [1] to rapid uplift in the Late Miocene due to large-scale mantle delamination [2]. Existing paleoelevation proxies are afflicted by either large uncertainties or reliance on assumptions about past climate-elevation histories [1]. The production rate of *in situ* cosmogenic isotopes is strongly dependent on elevation and thus has potential to constrain surface uplift histories.

The arid climate in the Atacama Desert, Northern Chile has prevailed since at least 25 Ma [3] leading to low erosion rates and high cosmogenic nuclide concentrations within alluvial boulders overlying the Pacific Planation Surface (PPS). The PPS in the Aroma Quebrada formed at < 13.9 Ma. Alluvial boulders which lie on the PPS, have high concentrations of cosmogenic ^{3}He that suggest deposition soon after surface formation [4]. The concentration of cosmogenic ^{3}He in the boulders are compared to those calculated for Early Miocene and Late Miocene uplift histories. The high concentration of cosmogenic ^{3}He in five boulders cannot be generated by Late Miocene uplift of the Andes (irrespective of scaling factor-production rate). The data require early uplift of the paleosurface prior to 8 Ma. This rules out rapid uplift of the Andes due to mantle delamination in the Late Miocene instead supporting progressive shortening and thickening of continental crust initiating in the Early Miocene or earlier.

[1] Barnes and Ehler (2009) *Earth-Science reviews* **97**, 105-132. [2] Garzione *et al.* (2008b) *Science* **320**, 1304-1307. [3] Dunai *et al.* (2005) *Geology* **33**, 321-324. [4] Evenstar *et al.* (2009) *Geology* **37**, 27-30.

Nuclear materials under extreme conditions

RODNEY C. EWING*

University of Michigan, Ann Arbor, MI 48109 USA
(*correspondence: rodewing@umich.edu)

During the past forty years, the materials science of nuclear waste forms has focused mainly on the stability and long-term behavior of nuclear waste glasses and the UO_2 in used nuclear fuel. However, during this time, substantial quantities of Pu, now more than 2,000 metric tonnes, have been produced. Some 200 mettric tonnes of Pu have been separated along with much lesser amounts of "minor" actinides (Np, Am and Cm). The *nuclear solution* is to prepare a mixed-oxide (MOX) fuel of Pu and U or an inert matrix fuel (IMF) to fission transuranium elements in a reactor. The *geologic solution* is to develop very durable materials for disposal in a geologic repository or a very deep borehole. However, radiation damage in the reactor or self-radiation damage due to the alpha-decay of actinides is a concern, as radiation-induced transformations of the atomic structure decrease the chemical durability.

A variety of materials, with mineral analogues, including oxides, silicates and phosphates, have been investigated because they have a high capacity to incorporate actinides, are chemically durable, and in some cases, are resistant to radiation damage. There has been substantial interest in isometric pyrochlore, $A_2B_2O_7$ (A = rare earths, actinides; B = Ti, Zr, Sn, Hf), for the immobilization of transuranium elements. Four radiation-induced transformations may occur: i) periodic-aperiodic, ii) order-disorder, iii) crystalline-to-crystalline, and iv) chemical decomposition. Certain pyrochlore compositions (B = Zr, Hf) remain crystalline to very high doses of alpha-recoil damage, which is mainly caused by ballistic interactions with the alpha-recoil nucleus.

Most recently, the radiation response of pyrochlore has been investigated using relativistic heavy ions for which high energy deposition occurs by electronic excitation. Energetic ions deposit exceptional amounts of kinetic energy (GeV) within an exceedingly short time (less that a femtosecond) into nano-scale volumes. Energy deposition is up to tens of eV/atom, foming damage tracks, very similar to fission tracks in zircon and apatite. These irradiations have been done at high pressures (>50 Gpa) and temperatures (up to 500 °C) within a diamond avil cell (DAC). The combined use of advanced *in situ* (synchrotron X-ray diffraction and Raman spectroscopy) and *ex situ* (transmission electron microscopy) characterization techniques has shown that normal phase relations are changed by the radiation and that most materials can be amorphized.

The effect of nuclear radiation on the structure of zircon

RODNEY C. EWING*

University of Michigan, Ann Arbor, MI 48109 USA
(correspondence: rodewing@umich.edu)

In 1955, Heinrich Holland and David Gottfried published a remarkable paper in *Acta Crystallographica* on radiation damage accumulation in a suite of natural zircons from Sri Lanka [1]. The purpose of their study was to investigate the possibility of using radiation damage accumulation as a method of age determination. This was one of the first quantitative studies of damage accumulation and annealing in a complex ceramic and provided a solid basis for extrapolating radiation damage effects in actinide-bearing nuclear waste forms over geologic periods [2,3]. The paper is not only remarkable for the data, measurements of unit cell parameters and optical properties, as a function of increasing dose, but also because the interpretation of the data was in the context of a damage ingrowth model that quantifies the accumulation of amorphous domains, the accummulation of isolated defects, the formation of new crystalline structures and the change in crystallite size. The authors also recognized the possibility of alpha-particles enhancing the effects of damage accumulation and annealing caused by the alpha-recoil atom.

Subsequent studies of radiation effects have utilized Pu-doping experiments [4] and ion beam irradiations (MeV to GeV energies) [5,6]. Most recently, high-energy irradiations have been completed at high pressures using a diamond anvil cell [7]. These studies have provided a fundamental understanding of the radiation damage processes that has supported the use of zircon as an optic wave guide [8], the development of nuclear waste forms for excess weapons plutonium [9] and fission track dating and thermochronology [10, 11]. For all of these applications, the early work by Holland and Gottfried remains the fundamental foundation.

[1] Holland & Gottfried (1955) *Acta. Cryst.* **8**, 291-300. [2] Murakami *et al..* (1991) *Amer. Mineral.* **76**, 1510-1532. [3] Weber *et al..* (1994) *J Mater. Res.* **9**, 688-698. [4] Exarhos (1984) *Nucl. Instr. Method Phys. Res.* **B1**, 538-541. [5] Wang & Ewing (1992) *Nucl. Inst. Method Phys. Res.* **B59**, 395-400. [6] Bursill and Braunshausen (1990) *Phil Mag.* **A62**, 395-420. [7] Glasmacher *et al..* (2006) *Phys. Rev. Lett.* **96** 195701-195705. [8] Babsail *et al..* (1991) *Nucl. Instr. Method Phys Res.* **B59**, 1219-1222. [9] Ewing *et al..* (1995) *J. Mater. Res.* **10**, 243-246. [10] Lang *et al..* (2008) *EPSL* **274**, 355-358. [11] Li *et al..* (2011) *EPSL* **302**, 227-235; Li *et al..* (2012) *EPSL* **321**, 121-127.

Formation and geochemistry of rutile from garnet gabbros of the Jijal Complex, Kohistan island arc

T.A. EWING* AND O. MÜNTENER

Institut de Sciences de la Terre, UNIL, CH-1015 Lausanne, Switzerland (*correspondence: tanya.ewing@unil.ch; othmar.muntener@unil.ch)

The Kohistan paleo-island arc preserves a ~50 km-thick section of Jurassic–Cretaceous arc crust renowned as one of the best exposures of an exhumed island arc. The lowermost Jijal Complex comprises an ultramafic and a mafic section. The latter is dominated by garnet gabbros, the origin of which is controversial. Formation of garnet in these rocks has been ascribed to dehydration melting of hornblende-bearing precursors [e.g. 1], prograde metamorphic reactions [e.g. 2] or fractional crystallisation at high pressures followed by isobaric cooling [3, 4].

Rutile (TiO_2) is an accessory phase in garnet-hornblende pyroxenites, garnet gabbros, paragonite gabbros and epidote-bearing pegmatites. In some samples garnet cores preserve ulvöspinel inclusions while garnet rims host rutile, suggesting formation of rutile at the expense of ulvöspinel. In paragonite gabbros rutile is associated with epidote–quartz intergrowths and may have formed as a result of the breakdown of clinopyroxene and garnet to form epidote and amphibole. Both reactions are consistent with isobaric cooling.

Garnet gabbros, paragonite gabbros and epidote-bearing pegmatites give Zr-in-rutile temperatures of 650–700°C. A few analysed rutiles are in contact with quartz and have indistinguishable Zr from other rutiles. These lithologies are largely zircon-free and Zr-in-rutile thus gives minimum temperatures. The Zr-in-rutile temperatures are lower than ~800–1000°C Fe–Mg temperatures for the same lithologies, and it is unlikely that this difference can be explained entirely by the lack of equilibrium with zircon. Zr content within individual grains displays little variation, arguing against diffusive re-equilibration, but it remains to rule out complete recrystallisation. Rutile from the Jijal Complex samples has Zr/Hf distinct from that of rutile from lower continental crustal metapelites, pointing to different controls on these geochemical tracers in rutile from different settings.

[1] Garrido *et al.* (2006) *J. Petrology* **47**, 1873–1914. [2] Yamamoto & Yoshino (1998) *Lithos* **43**, 219–234. [3] Ringuette *et al.* (1999) *Geology* **27**, 139–142. [4] Jagoutz *et al.* (2011) *EPSL* **303**, 25–36.