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High-resolution, ultra-trace and major element chemical stratigraphy of a new Paleoproterozoic weathering profile

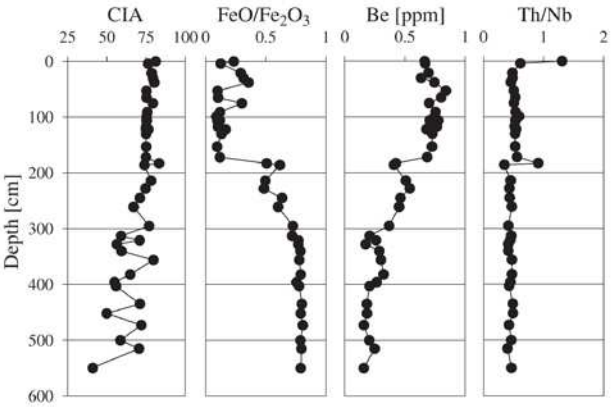
M.G. BABECHUK* AND B.S. KAMBER

Laurentian University, Sudbury, ON, Canada
(*correspondance: mbabechuk@gmail.com)

Paleosols contain information about ancient atmospheric and climate conditions, as well as the secular change in supply of nutrients to the ocean. A newly exposed, ~5 meters deep 1.85 Ga weathering profile is described. It developed on pillowed metabasalt (Flin Flon, Manitoba, Canada) and was sampled (~120 samples) and analyzed at much higher spatial resolution (>50 samples) than previous such profiles for ultra-trace, major element, and ferrous iron.

Consistent with previous studies on nearby paleosol exposures [1,2], the examined weathering profile is characterized by a spectacularly preserved, coherent upward Fe enrichment, accompanied by loss of Fe^{2+} and the development of a positive Ce anomaly, implying weathering in an oxic atmsophere. The new, high-precision trace element data collected reveal enrichment of several alkali (Cs, Rb, in addition to K, Na) and alkaline earth (Be, Sr, Ba) elements upward towards the paleosol contact with overlying sandstone. By contrast, the HFSE remained largely immobile in the profile which is evident through the highly consistent Zr/Hf, Th/Nb, and Nb/Ta ratios.

This presentation will discuss the distinction of original chemical features preserved in the profile, for example those inherited from the separate pillow basalt flows, versus those superimposed by weathering, water table fluctuation and possible extraneous sediment input.



[1] Holland *et al.* (1989) *Am. J. Sci.* **289**, 362-389. [2] Pan & Stauffer (2000) *Am. Mineral.* **85**, 898-911.

The volcanic-plutonic connection

O. BACHMANN[1], C. DEERING[1], J. DUFEK[2] AND C. HUBER[2]

[1]Departement of Earth and Space Sciences, University of Washington, Seattle, USA
[2]School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, USA

The broad similarities in age and compositonal range found in plutonic and volcanic exposures from a given magmatic province clearly indicate that these rocks types are closely related genetically. However, to which extent plutons (particularly the ones with intermediate to silicic compositions) are former magma reservoirs that have lost melt remains controversial. Recent work using both geochemical and physical modeling provides new avenues to explore these issues that are fundamental to our understanding of crustal evolution. First, mechanical constraints on rates of crystal-liquid separation indicate that most chemical differentiation is likely to occur within an melt extraction window located between 50 and 80 vol% crystals across the whole range of magma composition (from mafic to silicic). This extraction window will lead to compositional gaps in extracted liquids, as observed in numerous volcanic series around the world. In contrast, plutonic exposures will span a range of compositions that will vary continously as a function of how much melt was lost at a given location. Trace element modelling suggest that variable degrees of crystal accumulations are common in all plutonic sequences, including in intermediate to silicic compositions (tonalites - granodiorites). We also report erupted crystal cumulates, excavated from shallow magma chambers during large explosive eruptions. Such findings, alongside with thermal models of magma-crust interaction, suggest that crystal fractionation occurring by melt extraction in mush zones, and accompanied by a limited amount of crustal assimilation, is the dominant differentiation process in the Earth's crust. In this framework, volcanic rocks mostly represent liquids extracted from different reservoirs while plutons typically correspond to the left-overs crystal mushes that have been periodically stripped from a fraction of their interstitial melts.

Enhancing the accuracy of the environmental monitoring systems in mining areas

CALIN BACIU, DAN COSTIN*, CRISTIAN POP AND LAURA LAZAR

Babes-Bolyai University, Faculty of Environmental Science and Engineering, Fantanele 30, 400294 Cluj-Napoca, Romania (correspondence: dan_fl_costin@yahoo.com)

Mining operations generally have a significant impact on the environment. Traditional monitoring by periodically performing field measurements, sampling, and lab analyses is laborious, costly, and not always reproducible and reliable. Abundant series of monitoring data may be obtained by installing continuous measuring devices in selected points. In most of the mining areas, the number of such monitoring points is rather limited. The data series provided by such systems are usually interpreted as averages of the measured parameters for a certain area. Very often, this is not the case, either due to the limited representativity of the selected points, or because of the high dynamic of the environmental parameters. The environmental issues related to mining have become an ever increasing concern all over the world, with a direct impact on the prices of commodities, as opening a new mine is getting more and more difficult. A cost-effective and precise monitoring system is essential in the management of the environmental problems. Providing accurate monitoring data may also increase the confidence and acceptance of the communities and other stakeholders towards the mining activity. New methods and tools are needed for accomplishing this goal.

The EU-funded project ImpactMin (www.impactmin.eu) develops a combination of satellite remote sensing and aerial lightweight measurements for obtaining new methods of environmental monitoring in mining areas. Four test-sites were selected for calibrating and demonstrating the new toolset. Rosia Montana test-site (Romania) has a particular position in this context, as the cumulated impact of almost 2,000 years of gold mining can be observed. Currently the mine is inactive, the operations ceased in 2006 due to economic reasons. A new mining project is proposed on the same location, intending to implement a large scale open pit operation. The newly developed monitoring methods may represent an important contribution to the proper definition of the environmental baseline conditions, should the mining operations re-start.

Acknowledgements: The present work was financially supported by the FP7-ENV-2009-1 project 244166 – ImpactMin.

Distribution of rare elements in mineral-forming environments of rare-metal granites

E.V. BADANINA[1], A.Y. BORISOVA[2], R. THOMAS[3] AND L.F. SYRITSO[1]

[1]St.Petersburg State University, St.Petersburg, Russia (elena_badanina@mail.ru)

[2]University of Toulouse III – CNRS – IRD – OMP, France (borisova@lmtg.obs-mip.fr)

[3]German Research Centre for Geosciences GFZ Potsdam, Germany

The composition of melt and its evolution in space and time is traced at formation of ore-bearing Li-F granites and them sub-effusive analogs (ongonites, rhyolites, felsit-porphyries) from Orlovka, Etyka and Sherlovaja Gora in Transbaikalia (Russia) on the basis of melt inclusions study in quartz [1]. It is established that process of fractional crystallization is not the unique mechanism of concentration of LILE (Li, Rb, Cs) and HFSE (Nb, Ta, Zr, REE, W, Sn). A role of various mechanisms of concentration (fractionation, liquid immiscibility, metasomatism) estimate by calculation of distribution coefficients and saturation degree of melt for ore minerals. Contrast behavior of various rare elements is established at different stages of melt evolution [1]. High concentration of Li, B, Ta, Zn are found out in hydrosaline and fluid inclusions of Orlovka [2]. High concentration of some rare elements are found out in fluid inclusions (FI) in quartz from Sn-bearing rhyolites of Sherlovaya Gora by LA-ICP-MS. So, the Sn concentration varies from 1864 to 5879 ppm that explains formation of large tin deposit with finely dispersed cassiterite at a hydrothermal stage. High concentration of Zr in a fluid (to 1,5 wt %) from ultrapotassic felsite-porphyriy explains the formation here saturation zones of fine crystalline zircon in a topaz from famous a topaz-aquamarine greisen of Sherlovaya Gora and confirms probability of its crystallization at a hydrothermal stage. High uranium concentration in melt of rhyolites (up to 42 ppm U) exceed those in rhyolites of a Streltsovsky deposit. Sharp increase of U in FI up to 116 ppm unequivocally testifies to a potential role of rhyolites in genesis of uranium deposits of Transbaikalia that closes discussion about a source of uranium for them.

[1] Badanina *et al*. (2010) *Petrology*. **18**. 139-167. [2] Thomas *et al*. (2009) *Min Petrol*. **96**. 129-140.

Orbital scale alkenone based CO_2 records across the Pliocene intensification of Northern hemisphere glaciation

M.P.S. BADGER[1]*, G.C. BOWLER[1], C. DAVIS[2], A.C. HULL[1], M.D.A. POTTS[2], D.N. SCHMIDT[2] AND R.D. PANCOST[1]

[1]Organic Geochemistry Unit, School of Chemistry, University of Bristol, Cantock's Close, BS8 1TS, U.K. (*correspondance: marcus.badger@bristol.ac.uk, gb6139@bristol.ac.uk, ah7523@bristol.ac.uk, R.D.Pancost@bristol.ac.uk)

[2]Department of Earth Sciences, University of Bristol, Wills Memorial Building, Queen's Road, BS8 1RJ, U.K. (cd9861@bristol.ac.uk, mp0702@bristol.ac.uk, D.Schmidt@bristol.ac.uk)

The most informative analogues for future anthropgenic climate change are likely to be those with boundary conditions similar to today. The late Pliocene is the most recent time in earth history with elevated global temperatures and CO_2 estimated to be similar to that anticipated by the end of this century [1, 2, 3]. Furthermore, Pliocene continental positions and vegetation distributions are thought to be broadly similar to today. Consequently the IPCC fourth assessment report highlighted the Pliocene as an important time period for further study. Recently our understanding of Pliocene CO_2 and temperature has improved, with publication of multiple records from alkenone and boron isotope reconstructions for CO_2 [2, 3], and Mg/Ca, $U^{K'}_{37}$ and TEX_{86} reconstructions for sea surface temperature. However, none of the published CO_2 records have sufficient temporal resolution to resolve orbital scale variations in CO_2, or to determine the relationship between the apparent reduction in atmospheric CO_2 and the intensification of northern hemisphere glaciation. Here we present new high resolution records of CO_2 and temperature from ODP Site 999 over the critical interval from 3.3 to 2.6 Ma using alkenone palaeobarometry and the $U^{K'}_{37}$ and TEX_{86} palaeothermometers. By combining these with a full analysis of the biotic response to changing conditions and reconstructing haptophyte cell sizes [4], critical for the alkenone palaeobarometer, we present well constrained, coupled records of the response of the climate system to changing CO_2.

[1] Haywood *et al.,* (2000) *Geology* **28**, 1063-1066. [2] Seki *et al.*, (2010) *EPSL.* **292**, 201-211. [3] Pagani, *et al.,* (2009) *Nature Geoscience*. **3**, 27-30. [4] Henderiks & Pagani, (2007) *Paleoceanography*. **22**, 1-12.

A multidisciplinary study of core composition

JAMES BADRO

Institut de Physique du Globe de Paris, France. (badro@ipgp.fr)

Planetary cores form as a results of the major chemical differentiation even on a terrestrial planet; the melting of accretionary building blocks (dust, meteorites, planetesimals, protoplanets) leads to a separation of the metal from the silicate, ensued by a gravitationally-driven segregation of a dense metal-rich core at the centre of the planet, with the lighter buoyant silicates remaining on top. The process of core formation determines the composition of this deep reservoir, and leaves an imprint on the residual bulk silicate Earth.

Matching geophysical observables (seismically determined radial density and velocity profiles) and geochemical observables (siderophile trace-element concentration in the upper mantle, and through modelling in the bulk silicate Earth) with experimental and theoretical data provides a robust way to estimate both the present day composition of the core as well as the conditions under which it formed. Adding observational constraints, both from geophysics (gradients, anisotropy) and geochemistry (isotopic and trace-element fractionation) will help to continually improve the models and beyond that, define and refine the paradigm of core formation.

We will present the results obtained through (i) the study of phase equilibrium under extreme conditions in the laser-heated diamond anvil cell, (ii) the study of outer-core density and seismic velocity from first principles calculations, and (iii) the study of inner-core elasticity from experimental mineral physics. We will interpret these results in order to devise compositional models consistent with the observations, and to formulate scenarios for core formation.

Boundary depth of aragonite saturation during 10 years around Okinawa and East China Sea

D-Y. BAEK[1], H. FUJIMURA[1]*, T. OOMORI[1], T. HIGUCHI[2], B.E. CASARETO[2] AND Y. SUZUKI[2]

[1]Univ. of the Ryukyus, 1 Senbaru, Nishihara, Okinawa 903-0213, Japan
(*correspondance: fujimura@sci.u-ryukyu.ac.jp)
[2]Shizuoka Univ., 836 Ohya, Suruga-ku, Shizuoka-shi, Shizuoka 422-8529, Japan

Introduction

Since industrial evolution, anthropogenic activities have been releasing CO_2 by fossil fuels combustion. Ocean absorbs about 2.0 Gt of CO_2 every year and act as a sink for atmospheric CO_2 [1]. However CO_2 dissolved into seawater lower the ocean pH and CO_3^{2-} concentration. About 0.1 pH unit has already been decreased since industrial evolution. Lower pH have influences on marine organisms especially on growth of calcareous foraminifera and corals as one of the problem in "ocean acidification". Because lower CO_3^{2-} caused lower aragonite saturation of $CaCO_3$, saturated boundary in the ocean is predicted to be shallower in the future. In this study, we investigated carbonate system by taking vertical profiles around Okinawa and East China Sea to find the shift of the boundary depth over the past 10 years.

Materials and Methods

Seawater samples were taken from East China Sea and adjacent sea around Okinawa Island, Japan at scientific survey of T/S *Nagasaki-maru* in 2000 to 2010. Parameters related to carbonate system were measured on total alkalinity (ATT05, Kimoto), total inorganic carbon (CM5012, UIC), pH and salinity (PortaSal8410A, Guildline). Aragonite saturation of $CaCO_3$ (Ω) was estimated from a calculation of carbonate chemical equilibrium in seawater samples taken at each depth of vertical profile.

Results and Discussion

The boundary depth at which aragonite saturation shows below a saturation level (i.e. Ω=1) were 537±36 m from a surface (averaged value during 2000-2002). This boundary depth was shifted to 513 m during 10 years. Although this value was within the range of uncertainties, the shift indicated that the intrusion of the anthropogenic CO_2 caused lower CO_3^{2-} and hence shallower depth of the saturation boundary.

[1] Takahashi *et al*. (2002) *Deep-Sea Res. II* **49**, 1601-1622.

Study of geochemical reaction of rocks the under the supercritical CO_2-rock-groundwater system

KYOUNGBAE BAEK*, HYUNMIN KANG, JINYOUNG PARK AND MINHEE LEE

Department of Environmental Geosciences, Pukyong National University, Namgu, Busan, 608-737, Korea
(*darkbkb@naver.com)

Laboratory scale experiments to quantify the geochemical reaction in the supercritical CO_2-rock-groundwater system for CO_2 sequestration sites were performed in the high-pressurized cell. Seven types of rocks were cut into 1 cm x 1 cm x 0.3 cm size sections. Polished rock sections (granite, basalt, andesite, gneiss, limestone, sandstone and mudstone) and groundwater of 100 ml were reacted with supercritical CO_2 in the cell, maintaining the sequestration condition (100 bar and 50 °C). The gaseous CO_2 (99.99 % of purity) was injected into the cell and the high pressure condition was applied inside of the cell by using the periodic high pressure pump and the back pressure regulator. The temperature of the cell was maintained at 50 °C by using an oven. Each rock section was reacted with the supercritical CO_2 and groundwater for 10, 30 and 60days.

Before the experiment, the rock dried at 100 ℃ for a day and accurately weighed. After the reaction, the rock dried and reweighed to investigate the loss of minerals by dissolution. The alteration of pH was measured to compare before/after reaction. Rock surface was observed by using a reflecting microscope. Selected three minerals for each rock and three locations of each mineral on the rock surface were randomly selected for the image analysis of Scanning Probe Microscope (SPM). The average roughness value of those locations was measured to investigate the transmutation of rock surface compared to that before reaction. ICP-OES analysis was conducted to measure the major element concentrations dissolved in solution of the high pressure cell. SEM/EDS analysis was also performed to identify the precipitates in high pressure cell after the reaction.

Results of the experiment in the supercritical CO_2-rock-groundwater reaction showed that the concentration of cations in solution increased and the pH of solution decreased after the reaction. The average roughness value of the mineral surface in the rocks increased after 30 days. From the analysis of SEM/EDS, the interstitial spaces of rock surface could be infilled by secondary minerals, resulting in the change of void spaces (porosity) in the rock.

Controls on isotope and trace element systematics of slope facies Ediacaran carbonates, Yangtze Platform (South China)

W. BAERO*, H. BECKER AND U. WIECHERT

Institut für Geologische Wissenschaften, Freie Universität Berlin, Malteserstr. 74-100, 12249 Berlin, (*correspondence: wbaero@zedat.fu-berlin.de)

Trace element, Sr, C and O isotopic compositions of Ediacaran carbonates are used to assess the likely role of diagenetic processes and alteration by lokal fluid flow, relative to primary seawater derived signatures. The samples are from the slope facies Panmen section (Songtao, Guizhou) of the Yangtze Platform, South China. The section comprises the Ediacaran Doushantuo (DS) and Liuchapo Formations. At this section, carbonate bearing lithologies are restricted to the DS members I (cap carbonates in contact with Marinoan diamictites), III (dolostones and limestones) and IV (organic rich carbonate layers and carbonate concretions in black shales). Most of DS II appears to be missing from this section. Carbonates show variable negative $\delta^{18}O$ (-6 to -14) and $\delta^{13}C_{carb}$ (-2 to -10) values similar to DS I and III sediments at sections representing shallow water conditions. Acetic acid leachets of carbonates display decreasing $^{87}Sr/^{86}Sr$ upsection from high and variable values in DS I (0.722-0.717) to lower values in DS III (0.716-0.713). Ce/Ce* are near 1, with a few values significantly higher. The uppermost samples of DS IV show Ce/Ce* = 0.5 at $\delta^{13}C_{carb}$ of -1. Some of the extreme values in $\delta^{18}O$ are coupled with positive Ce (Ce/Ce* = 1.22) and Eu (Eu/Eu* = 1.33) anomalies, and particularly high $^{87}Sr/^{86}Sr$. Carbonate concretions in black shales of DS IV have extremely negative $\delta^{18}O$ but display normal $\delta^{13}C$, slightly neg. to no Ce/Ce* and strongly pos. Eu/Eu*. $^{87}Sr/^{86}Sr$ in the concretions are the lowest measured in the section (0.709), similar to values obtained for DS IV from shallow platform settings [1]. Most $^{87}Sr/^{86}Sr$ values of the section are substantially higher than seawater values during this time (0.708-0,709, [1]). High values of $^{87}Sr/^{86}Sr$, Ce/Ce* or negative $\delta^{18}O$ do not correlate with the amount of detrital material in the carbonates. Hence, we interprete high $^{87}Sr/^{86}Sr$ and Sr/Mn and the occasional presence of positive Ce anomalies to reflect recrystallization and interaction with reducing fluids that have interacted with silicate and organic material (and occasionally Fe-Mn oxides?) during the postdepositional evolution of the basin. The influence of these processes on $\delta^{13}C_{carb}$ is sometimes visible, but appears to be at the 1 ‰ level or less.

[1] Sawaki *et al*. (2010) – *Precambr. Res*. **176**, 46-64.

Fluid-rock interaction during eclogitisation: Evidence from HP metamorphic rocks from Sulawesi, Indonesia

R. BAESE* AND V. SCHENK

SFB 574: Volatiles and Fluids in Subduction Zones, Christian-Albrechts-University, 24118 Kiel, Germany (*correspondence: rb@min.uni-kiel.de)

Fluid-rock interactions within subduction zones are important for understanding recycling processes and magma generation at convergent margins that is triggered by fluid infiltration from the subducting slab. The aim of this study is to determine the composition of fluids liberated during eclogitisation reactions. The samples are high-pressure (HP) rocks from the Bantimala Complex in Sulawesi (Indonesia) that is part of the Cretaceous accretionary complex distributed all over Indonesia [1]. The eclogites are forming veins and vein networks within blueschists. The peak P-T-conditions are about 2.0-2.5 GPa and 450-550 °C. Trace element analyses of a relatively Cr-rich eclogite-blueschist pair reveal a pronounced depletion of fluid-mobile elements in the eclogite. Mass balance calculations show that the rock lost more than 80% of the REE during the fluid induced eclogitisation along the vein. The LILE (Cs, Ba, Rb, Sr), except K, are also depleted with up to 80%. In case of the HFSE (Pb, Zr, Hf, Ti, Nb) there is no depletion, and Zr, Hf and Ti are even enriched in the vein. Major element concentrations were not strongly affected by the dehydration process during eclogite formation. From these observations we deduce that the fluid produced during the blueschist-to-eclogite transformation in the veins should be enriched in the LILE and REE. The concentrations of the HFSE, Fe and Ni should be relativly low in the fluid, because these elements were incorporated in the vein minerals. These results are in agreement with those of a previous study by John *et al*. [2], who concluded that the mobilised elements during eclogitisation are those believed to be contained in slab fluids that trigger partial melting in the mantle wedge.

[1] Parkinson *et al*. (1998) *The Island Arc* **7**, 184-200. [2] John *et al*. (2008) *Lithos* **103**, 1-24.

Many-body effects in XPS and chemical bonding

P.S. BAGUS[1]*, C.J. NELIN[2], H.-J. FREUND[3] AND E.S. ILTON[4]

[1]Chemistry, University of North Texas, Denton, TX 76203-5017, USA (*correspondence: bagus@unt.edu)
[2]C. J. Nelin Consulting, Austin, Texas 78730, USA
[3]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany
[4]Pacific Northwest National Laboratory, 902 Battelle Blvd., P.O. Box 999, Richland, Washington 99352, USA

A major goal with x-ray photoelectron spectroscopy (XPS) is to derive both the character of chemical bonding and valence states from the spectra. Ionic compounds, especially oxides, often have complex and intense satellite features that arise from a combination of inter-atomic and intra-atomic many-body effects that can reflect both bonding and oxidation state. [1] While multiplet splittings arise dominantly from the open-shell structure within the ionized atom, [2] inter-atomic many-body effects may also make important contributions to the satellite structure. [1] Although these inter-atomic effects have been studied extensively, a quantitative and definitive connection between the relative energies and intensities of the satellites on the one hand and both the extent of covalent bonding and oxidation state on the other, has not been established. In the present work, we consider two oxides, UO_3 and CeO_2, where the metal cations are closed shell, which increases the importance of inter-atomic relative to intra-atomic many body effects. The CeO_2 satellites are intense while the UO_3 satellites are weak. We have established relations between the satellite energies and intensities with the extent of the covalent bonding. This theoretical information has been obtained using relativistic many-body molecular orbital wavefunctions. With these wavefunctions, the covalent character of the orbitals arises naturally. This work is an important step toward inferring material properties of interest to both geochemistry and more generally chemistry from the XPS satellite structure. This research was supported, in part, by the Geosciences Research Program, Office of Basic Energy Sciences, U. S. Department of Energy (DOE) and Geosciences Research Program, Office and, in part, by the German Science Foundation (DFG).

[1] Bagus *et al. (2010) Chem.* Phys. Lett. **487**, 237-240. [2] Bagus & Ilton, (2006) *Phys. Rev. B* **73**, 155110.

Whole rock and mineral composition constraints on the genesis of the giant Hongge Fe-Ti-V oxide deposit in the ELIP, SW China

Z.-J. BAI[1], H. ZHONG[1,*], C. LI[2], W.-G. ZHU[1] AND G.-W. XU[1]

[1]SKLODG, Institute of Geochemistry, CAS, Guiyang 550002, China (* correspondence: zhonghong@vip.gyig.ac.cn)
[2]Department of Geological Sciences, Indiana Univ., Indiana 47405, USA

The Hongge giant Fe-Ti-V oxide ore deposit, related to a plume activity (~260 Ma), is hosted in a layered intrusion located in the central part of the Emeishan Large Igneous Province (ELIP), SW China. Most of the economic Fe-Ti-V oxide ore layers occur within the middle clinopyroxenite zone of the intrusion. Opinions on the origin of the oxides vary from oxide-silicate liquid immiscibility to accumulation of titanomagnetite crystallizing from a basaltic magma.

Our new results favor the crystallization model. The occurrence of multiple Fe-Ti oxide layers within a single cyclic unit and the repetitive appearance of sulfide, olivine and Cr-rich magnetite in the base of each cyclic unit suggest that multiple pulses of magma was involved in the formation of the Hongge Fe-Ti-V oxide deposit. Magnetite and coexisting olivine in the Hongge deposit have much higher MgO contents than those in other oxide deposits associated with large layered intrusions in the world, underscoring the importance of relatively primitive parental magma and relatively early saturation of titanomagnetite in the magma in the formation of the giant Fe-Ti-V oxide deposits in the ELIP.

Phase equilibrium constraints suggest that the Hongge parental magma is similar to that of some most primitive Emeishan high-Ti basalts. Depletion of incompatible trace elements in the oxide ores and associated rocks in the intrusion as compared to the coeval high-Ti basalts suggest that not all the magma involved in development of the Hongge intrusion has been retained. We propose that this intrusion was a magma conduit and that some of the liquid was lost to the peripheral sills, shallower intrusions or lavas.

2D geochemical-thermomechanical modelling of Pb, Hf, Sr and Nd isotopes evolution in intra-ocean subduction zones

B. BAITSCH GHIRARDELLO[1] , K. NIKOLAEVA[2], O. JAGOUTZ[3] AND T.V GERYA[1]

[1]Geophysical Institute, ETHZ, Switzerland
[2]Facullty of Earth and Life Sciences, VU Amsterdam
[3]Dept. of Earth, Atmospheric, and Planetary Sciences, MIT, Cambridge, MA, USA

Isotopes behave differently in different processes involved in a subduction zone such as slab dehydration, mantle wedge hydration and partial melting. Therefore, they are indicative of when and where different processes are active. The aim of this study is to extend the 2D coupled petrological–thermomechanical numerical model (I2ELVIS) of intra–oceanic subduction processes to include a treatment of isotopic signatures. With this extension we hope to gain more insights into the recycling system within the mantle wedge and are able to visualize the interaction between slab components and the depleted mantle. This will allow us to draw conclusions form isotopic signatures in arc lavas about the involved chemical processes.

A chemical contamination of slab components with wedge peridotite leads to specified signatures in arc magmas. Two slab components play a key role in this contamination: first, the altered oceanic basalt crust, and second its thin layer of sediment (e.g. Poli & Schmidt, 2002). Based on these results and the well known enrichment of LILE, Pb, U, and Th as well as the decrease of HFSE, Nd and Hf in island arcs in respect to the N-MORB, we focus on a limited number of elements (Pb, Hf, Sr and Nd) for our numerical model.

Our first results show that combination of finite differences and marker in cell techniques allows successful coupling of thermomechanical evolution of subduction with mobilisation, transport and radioactive decay of isotopes. Preliminary modelling results reconcile well with observations. Particularly, our models predict a significant increase of Strontium and Lead and a slight increase of Hafnium and Neodymium in the newly formed magmatic arc crust relative to the depleted mantle (DMM), which is comparable with data from the literature. In addition, our model confirmed the evidence for slab derived fluid /melt in the newly formed crust.

Pyromorphite formation from natural and surfactant-modified montmorillonite adsorbed lead

T. BAJDA[1]*, A. FIGUŁA[1], M. MANECKI[1] AND T. MARCHLEWSKI[2]

[1]Dept. of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, Krakow, Poland (*bajda@geol.agh.edu.pl)
[2]Dept. of Geological Sciences, Miami University, Oxford, Ohio, USA

The objective of this study was to evaluate potential application of natural and surfactant-modified montmorillonite for sorption of Pb^{2+} and subsequent pyromorphite formation by the reaction of Pb-adsorbed smectite with aqueous PO_4 of various concentrations. Amine hexadecyltrimethylammonium bromide (HDTMA-Br) in the amounts of 2.0 Cation Exchange Capacity (CEC) of the clay was used to obtain surfactant-modified organo-smectite.

The reaction of Pb-adsorbed natural montmorillonite with aqueous solutions containing PO_4 and Cl ions results in the decrease in phosphate concentration associated with the formation of a new phase – pyromorphite $Pb_5(PO_4)_3Cl$. Precipitation of brom-pyromorphite $Pb_5(PO_4)_3Br$ is observed when surfactant is used for modification of montmorillonite.

Pyromorphite precipitates homogenously in the solution but crystals generally cover the surface of smectite (Fig. 1a). High concentration of K and Ca cations leads to a high desorption of Pb and formation of very fine crystals. On the other hand, low concentrations of cations results in the formation of larger crystals.

When PO_4 was sorbed on Pb–surfactant-modified smectite, formation of brom-pyromorphite $Pb_5(PO_4)_3Br$ was noted in the reaction products. Pyromorphite forms crystals on the surface of a surfactant-modified smectite (Fig. 1b). We gratefully acknowledge support of the MNiSW through grant N N525 461236.

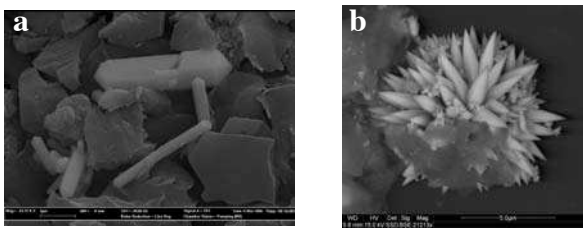


Figure 1: SEM microphotographs of (a) chlor-pyromorphite formed in the reaction of aqueous PO_4 and Pb-adsorbed montmorillonite, and (b) brom-pyromorphite formed in the reaction of aqueous PO_4 and Pb–surfactant-modified montmorillonite.

The influence of contaminant load on microbial ecology in a sandstone aquifer

K. BAKER[1,2], R. EDYVEAN[2], S. THORNTON[3], S. BANWART[2,3], J. SCHOLES[2] AND S. ROLFE[2]*

[1]School of Earth and Environment, University of Leeds, UK
[2]Cell-Mineral Research Centre, Kroto Research Institute, University of Sheffield, UK (*correspondence: s.rolfe@shef.ac.uk)
[3]Groundwater Protection and Restoration Group, University of Sheffield, UK

Due to widespread organic contamination derived from past industrial processes, microorganisms are becoming ever more important for the maintenance of potable groundwater supplies, as they have the ability to degrade organic contaminants *in situ*. Furthermore, the syntrophic relationships in mixed microbial communities found attached to geological surfaces results in an enhanced capability to degrade elevated levels of organic contaminants, making them integral to the natural bioremediation of contaminants [1]. Microbial biodegradation is also a sustainable alternative to costly and invasive engineering-based remediation techniques. However, contaminant toxicity can have a marked influence on microbial community structure and diversity [2], ultimately affecting the *in situ* biodegradation potential.

In this work, studies were conducted to investigate the effects of contaminant load on the indigenous microbial communities in a phenol-contaminated aquifer in the UK. Using denaturing gradient gel electrophoresis and pyrosequencing, groundwater (planktonic) microbial communities were profiled across the contaminant gradient, and compared to the attached communities formed on surrogate geological substrata incubated in the aquifer under the same hydrochemical conditions. Microbial community structure and function was found to be strongly influenced by contaminant load and groundwater hydrochemistry. Also, *in situ* microbial attachment studies reveal that the attached and planktonic communities differ markedly. These results are important for understanding the distribution and formation of microbial communities in contaminated environments and subsurface ecosystems, and lead to a better understanding of the function and limitations on *in situ* biodegradation processes in the Earth's Critical Zone.

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A new ore mineral assemblages from the Shilu iron-polymetallic deposit, Hainan Island, South China

N. BAKUN-CZUBAROW[1]*, S.Z. MIKULSKI[2], D. XU[3], D. KUSY[1] AND ZH. WANG[3]

[1]Institute of Geological Sciences, Polish Academy of Sciences, Warsaw, Poland (*correspondence: nbakun@twarda.pan.pl; dkusy@twarda.pan.pl);
[2]Polish Geological Institute – National Research Institute, Warsaw, Poland (stanislaw.mikulski@pgi.gov.pl)
[3]Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China (xuderu@gig.ac.cn)

The famous Shilu iron-polymetallic ore deposit located in western Hainan Island, South China, occurs within Meso-Neoproterozoic, low-grade metamorphosed volcanoclastic sediments and carbonates. The Shilu deposit is considered to be a structurally reworked as well as hydrothermally altered and enriched ore deposit of Banded Iron Formation type. The deposit is very important iron producer from magnetite and hematite ores [1]. In our work we focused on the polymetallic sulfide mineralization, that is younger than iron oxide ores [2] and, in places, overprinted them. For the research we have chosen from the Shilu deposit several samples of sulfide ores from the Beiyi mine and its close vicinity. We have performed detailed ore microscopic studies as well as electrone microprobe analyses using CAMECA SX 100 equipped with EDS and WDS systems. In the studied samples pyrrhotite, chalcopyrite and Co-bearing pyrite (up to 11 wt% Co) dominated among ore sulfides. These ore minerals occur in quartz or calc-silicate rocks, either as disseminated grains, sometimes in veinlets, or in aggregates, that may form massive ores. Pyrrhotite and chalcopyrite may contain numerous solid inclusions, overgrowths and intergrowths of subordinate sulfides (sphalerite, galena), sulfosalts (glaucodot, costibite, cobaltite, arsenopyrite, ullmannite), sulfospinels (siegenite) and cassiterite, that belong to the minerals crystallizing at medium to low temperatures. Among these minerals siegenite and Co-bravoite dominate. Tiny crystals (10-20 μm in size) of Sb-minerals (matildite, cosalite) are also present. Moreover, in association with barite, calcite and chlorite Ag-Hg amalgamate and cinnabar can occur. The results of our study point to the multistage medium- to low- temperature hydrothermal precipitation of ore sulfides that overprinted the Fe-oxide ores. We believe, our results will serve for better understanding of metallogenic processes in the Shilu iron-polymetallic deposit.

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Biogeochemistry and stable isotope investigation of acid mine drainage associated with abandoned Pb-Zn mine in Balya, Turkey

NURGUL BALCI[1]*, NEVIN KARAGULER[2], M. SEREF SONMEZ[3] AND EROL SARI[4]

[1]Department of Geological Engineering, ITU, Turkey (*correspondence:ncelik@itu.edu.tr)
[2]Department of Molecular Biology and Genetics, ITU, Turkey (karaguler@itu.edu.tr)
[3]Department of Metallurgy and Materials Engineering, ITU, Turkey (ssonmez@itu.edu.tr)
[4]Institute of Marine Science and Management, Istanbul University, Turkey (erolsari@istanbul.edu.tr)

The abandoned Pb-Zn mine in Balya Region contains mainly galena, sphalerite, pyrite, chalcopyrite, and arsenopyrite. The mine tailings and smelting waste rocks produce significant amount of acidity and heavy metals. We used laboratory and field approaches to elucidate oxidation mechanisms of galena, sphalerite and pyrite in the region. The biological and abiotic oxidation experiments with galena, sphalerite and pyrite under various conditions (pH (2-4), (4-25 ºC) conditions were carried for the laboratory studies. Sediment and water samples were collected from the mine sites. Areas of the mine flooded by water have acidic pH (3) and high concentrations of metals (Pb, Zn, Cu, Fe, Co, Cd and As). In acidic, Fe-rich waters, oxidation of Fe^{2+} after exposure to air is microbially catalyzed and follows zero-order kinetics (range of 0.92 to 1.5 mmol L^{-1} h^{-1}). Biological oxidation experiments with galena and sphalerite at 25 ºC showed high oxidation rate compared to chemical –control and suboptimal temperature (4, 10ºC) experiments. *A. thioxidans* was still active even under 4ºC although the oxidation rate of galena and sphalerite were significantly lower compared to 25ºC. Oxidation of pyrite with or without bacteria did not show significant reaction rate. The S isotopic composition of dissolved sulfate collected from the mine areas closely reflect sphalerite and galena values rather than pyrite. The $\varepsilon^{18}O_{SO4\text{-}H2O}$ values of 8.0 ± 0.2 ‰ and 7.8 ± 0.1 ‰ obtained from the field measurements is consistent with the values calculated from biological oxidation of galena and sphalerite experiments relative to pyrite experiments ($\varepsilon^{18}O_{SO4\text{-}H2O}$ values of 0.0 to 4.0 ‰) [1] . A clear distinction exits among the $\varepsilon^{18}O_{SO4\text{-}H2O}$ values produced during pyrite and sphalerite experiments may help to determine the source of acidity.

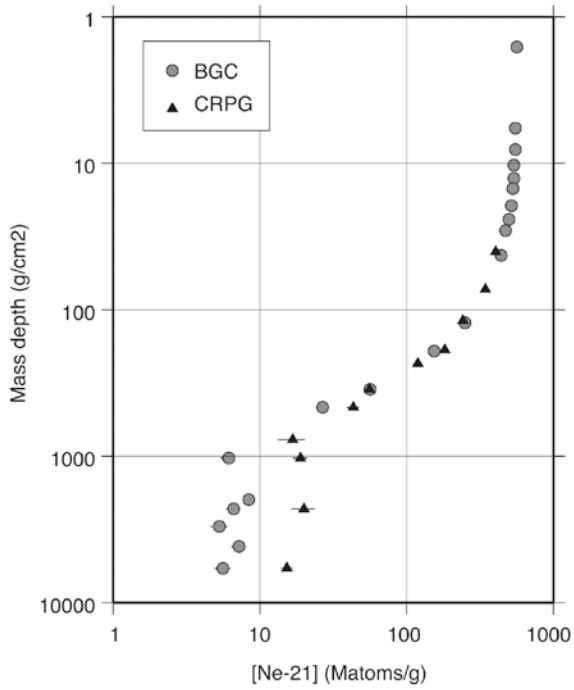
[1].Balci *et al*. (2007) *Geochimica Cosmochim. Acta* **71**, 3796-3811

Cosmogenic ^{21}Ne production systematics in quartz inferred from a 25-meter sandstone core

G. BALCO[1]*, D.L. SHUSTER[1], P-H. BLARD[2], L. ZIMMERMANN[2] AND J.O.H. STONE[3]

[1]Berkeley Geochronology Center, 2455 Ridge Rd., Berkeley CA 94550 USA (*correspondence: balcs@bgc.org)
[2]CRPG-CNRS-Université de Lorraine, 15 rue Notre Dame des Pauvres, 54501 Vandoeuvre-lès-Nancy, France
[3]Earth and Space Sciences, University of Washington, Seattle WA 98195-1310 USA

We measured ^{20}Ne, ^{21}Ne, and ^{22}Ne concentrations in quartz in a 25-meter sandstone core collected at Beacon Heights, Antarctic Dry Valleys, as part of the CRONUS-Earth project. ^{21}Ne concentrations computed as excess over atmospheric Ne are shown below. We intercalibrated measurements at BGC and CRPG by exchanging standards. A systematic difference between the two labs, most likely due to the effect of different sample preparation schemes on ^{21}Ne produced from alpha implantation at grain edges, is evident in deep samples. These data, with corresponding U and Th concentrations, permit resolution of the ^{21}Ne inventory into trapped, cosmogenic, and nucleogenic components, and thus estimates of ^{21}Ne production rates due to spallation and muon interactions.



A 3D snapshot from granitic system: Tourmaline nodules and their bearing on the granite evolution

D. BALEN* AND Z. PETRINEC

University of Zagreb, Faculty of Science, Croatia
(*correspondence: drbalen@geol.pmf.hr)

Peraluminous granites generated during the Late Cretaceous evolution of the LP-HT zone in the Adria-Europe plate boundary setting host tourmaline nodules. These tourmaline-bearing bodies from the Moslavačka Gora (MG), Croatia show great similarity with leucogranitic veins and can be described as compact spherical to ovoid aggregates (cm to dm in diameter) with a fine-grained (grain size 1-2 mm) core (slightly alkali-deficient dravite to schorl tourmaline (#Fe 0.40-0.66) + quartz + albite + K-feldspar ± muscovite) enveloped by a leucocratic halo (quartz + K-feldspar + oligoclase An_{11-21} ± muscovite). When observed in 2D sections solely, the isolated nature of tourmaline nodules can be easily mistaken with similar 2D cross-section of a leucogranitic vein. For that reason tourmaline nodules' spatial distribution inside the host, shape and internal structure of individual bodies have been reconstructed and visualized through destructive serial sectioning tomography with physical resolution of 3.5 mm (serial cutting) or 0.35 mm (serial lapping) between individual planes. Obtained 3D reconstructions of rock volumes containing tourmaline nodules showed that they are indeed isolated spherical bodies dispersed inside the granitic host and not vein formations. The two structural units of a nodule, core and halo, are clearly distinguishable in 3D and show sharp contacts to each other but also to the granitic host.

The morphology, peculiar texture, distribution and origin of tourmaline nodules inside granite can be most suitably explained through the emplacement mechanism and crystallization setting of the host granite at upper crustal level (at MG locality calculated approx. depth of 5-6 km, T=720 °C). During emplacement, decompression and arising immiscibility leads to melt unmixing and production of two different melt phases: "normal" granitic and B-rich one. Prominent depolymerization of B-rich melt, followed by density and viscosity decrease together with lowering of liquidus and solidus temperatures, leads to physical separation of a buoyant B- and fluid-rich phase in form of distinct B-rich bubbles or pockets, which coalesce in order to decrease surface tension. Such isolated volumes now contain necessary concentration of boron and other elements needed for tourmaline growth and become precursors for the future solidified tourmaline nodules.

Noble gases and halogens in the MORB-source mantle: Recycled?

C.J. BALLENTINE*[1], R. BURGESS[1], B. WESTON[1], D. CHAVRIT[1], H. SUMINO[2] AND D.A.H. TEAGLE[3],

[1]SEAES, The University of Manchester, Manchester, U.K. (*chris.ballentine@manchester.ac.uk)
[2]GCRC, University of Tokyo, Tokyo 113-0033, Japan
[3]NOC, University of Southampton, Southampton, U.K.

Powerful information from the extinct ^{129}I and ^{244}Pu systems is derived from the distribution of the daughter ^{129}Xe and ^{136}Xe between terrestrial reservoirs. Because of its simplicity, the conclusion that the Earth was open to Xe loss until ~80Ma after the Earth accreted, for example, is unequivocal. The $^{129}Xe/^{130}Xe$ ratio in the atmosphere, mantle and any primordial volatile rich mantle reservoir will then be determined by the ^{129}I (and ^{244}Pu)/Xe ratio in that reservoir and any subsequent interactions between reservoirs. The Earth's atmosphere, for example, has a lower $^{129}Xe/^{130}Xe$ than the convecting mantle. While there has been an exceptional concentration of the halogens at the Earth's surface compared to other incompatible elements (>90% BSE) [1], this is balanced by the atmosphere's high relative Xe concentration.

In the simplest (reference) model we can make the key assumption that the closure of the respective mantle reservoirs is the same as the atmosphere closure time of 80Ma. In the case where 80% of the convecting mantle Xe is recycled air [2], we calculate the iodine concentration, required to provide the convecting mantle ^{129}Xe excess caused by ^{129}I decay to be $[I]_{model}$ ~0.14ppb I. We then predict one of three cases when comparing $[I]_{observed}$ with $[I]_{model}$: 1) They will be in close agreement, in which case we can consider the convecting mantle to be closed with respect to the I/Xe system; 2) $[I]_{observed}$ will be lower than $[I]_{model}$, which then requires either an earlier closure age of the reservoir or significant net loss of I from the system after ^{129}I has ceased to be active; or 3) $[I]_{observed}$ will be greater than $[I]_{model}$ due to a net excess of dead iodine being added to the system. Current convecting mantle I concentration estimates, based on MORB, range from <0.7 ppb to orders of magnitude higher [3] and point towards the latter, consistent with recent observation of noble gas and halogen subduction to at least 100km depth [4]. Iodine determination of the MORB (and OIB) source remains a critical objective for future work.

[1] Burgess *et al.*, (2002) *EPSL* **197**, 193-203. [2] Holland & Ballentine (2006) *Nature* **441**, 186-191. [3] Aiuppa *et al.*, (2009) *Chemical Geology* **263,** 1-18. [4] Sumino *et al.* (2010) *EPSL* **294**, 163-172

Late volatile addition to Earth

C. BALLHAUS[1]*, V. LAURENZ[1], R. FONSECA[1], C. MÜNKER[2], F. ALBARÈDE[3], A. ROHRBACH[4], M.W. SCHMIDT[4], K.P JOCHUM[5], B. STOLL[5], U. WEIS[5] AND H. HELMY[6]

[1]Steinmann Institut, Universität Bonn, Germany (*correspondence: ballhaus@uni-bonn.de)
[2]Universität zu Köln, Germany
[3]Ecole Normale Supérieure de Lyon, France
[4]ETH Zürich, Switzerland
[5]Max Planck Institut für Chemie, Mainz, Germany
[6]Minia University, 61519 Minia, Egypt

It is known for some time that relative to CI chondrite, Earth's mantle is depleted in elements more volatile than Mg and Si. Early workers attributed this to volatile loss from Earth's mantle during accretion. In recent years, however, consensus has been emerging that the opposite may be true: that the inventories of the Earth's mantle in moderately and highly volatile elements and compounds, including Earth's hydrosphere and atmosphere, may be late additions, to a silicate earth initially far more refractory than the present-day upper mantle.

We report metal-silicate experiments at 1 to 5 GPa over a temperature range from 1773 to 2573K to quantify how selected refractory and volatile elements may have partitioned between silicate and Fe metal melt. We study the partitioning of two refractory elements (i.e. W and Cr) and four elements (i.e. Pb, Cd, Sn, Se) from the volatile inventory of the Earth's mantle. Except for Se, all elements regardless of volatility become more siderophile with increasing temperature, reflecting the effect of thermal reduction. By correlating measured metal/silicate partition coefficients with the relative abundances of these elements in the mantle, the physical state of the mantle can reconstructed when the respective element abundances were established; W and Cr at magma ocean conditions around 2550K, and Pb, Cd, Sn, and Se to a mantle that must have been largely crystalline at the time of volatile addition, with core melt segregation inactive.

The experiments provide independent support for a latter-day volatile addition. Had Pb, Cd, Sn, and Se been present at magma ocean conditions, they would have been seriously depleted in abundance relative to the abundances in lithophile volatiles with similar condensation temperatures, far more than observed; Pb by up to two orders of magnitude relative to its present-day mantle concentration. Our Ds confirm that a large proportion of the volatile element inventory of Earth's mantle, including its water content, was part of a late volatile component, most likely material from the asteroid belt and added to a relatively cool mantle, at a time when core formation was completed. There is little basis to assume that the apparent Pb deficit in the silicate Earth is to be sought in the core. Rather, the $^{238}U/^{204}Pb$ ratio (μ) of Earth's mantle reflects late addition of Pb, to a highly refractory proto-mantle seriously depleted in volatiles. A late (post-core) addition of Pb via a CI-type impactor, to a refractory mantle highly depleted in lead, may also be key to solving the first lead paradox.

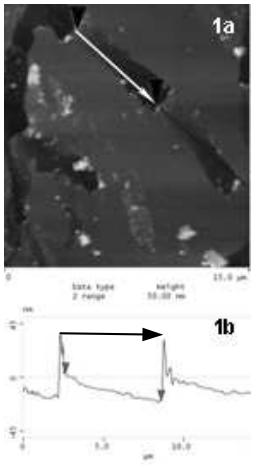
Surface characterization of biotite from a mesh bag field study

Z. BALOGH-BRUNSTAD[1,*,2], L. SACCONE[3], M.M. SMITS[4], C. BERNER[5], H. WALLANDER[5], T. J. MCMASTER[3] AND S.L.S. STIPP[2]

[1]Hartwick College, Oneonta, NY, 13820 USA (*correspondence: balogh_brunz@hartwick.edu)
[2]NanoGeoScience, Nano-Science Center, Dept. of Chemistry,University of Copenhagen, Denmark
[3]H.H. Wills Physics Laboratory, University of Bristol, UK
[4]Environmental Biology, Hasselt University, Belgium
[5]Microbial Ecology, Lund University, Sweden

Direct fungal-mineral contact has been proposed to play an important role in soil mineral dissolution. Indeed, nanoscale observations in controlled laboratory settings have demonstrated both physical and chemical interactions with biotite at the scale of the individual fungal hyphae [1, 2]. We incubated biotite flakes in the soil, to test if similar fungal-mineral interactions could be observed in the field. The biotite was incubated in spruce forest soils for two years at three sites with serpentinite, leucogranite and amphibolite bedrocks and contrasting tree nutrient status. Mineral surfaces were examined with scanning electron microscopy and atomic force microscopy. Ectomycorrhizal biomass was determined by Ergosterol analyses.

Microscopy revealed patchy biofilms on the biotite surfaces (19 to 44%) with the highest values found at the low Mg site (leucogranite). Direct hyphal attachment was only 3 to 5% with the lowest values found at the low Mg site, which was supported by the the lowest Ergosterol concentrations at this site. We saw shallow channels, similar to hyphae in size and branching pattern on most of the flakes (Figure 1a). The channels widened with time, probably from dissolution, and at each "pulse," the channel deepened in the direction of growth (Figure 1b). We propose that this morphology reflects the pulsive growth of the hyphal tip, inducing shear stress to the top T-O-T biotite layers.



These observations support the laboratory results that fungal hyphae exercise both chemical dissolution and physical force at the hyphal-mineral interface.

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[2] Bonneville *et al.* (2009) *Geology* **37**, 615-618.

Cloud condensation nuclei concentrations and actual supersaturations in real clouds

U. BALTENSPERGER, Z. JURÁNYI, E. HAMMER, M. GYSEL, N. BUKOWIECKI AND E. WEINGARTNER

Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

The number of cloud condensation nuclei (CCN) at a given supersaturation has an important influence on cloud properties and is therefore crucial for a better quantification of the indirect aerosol effect on climate. Only in recent years, CCN data have become available from different sites in a systematic manner. We have measured the CCN number concentration continuously at the high alpine site Jungfraujoch (3580 m asl) continuoulsy for several years, in the framework of the Global Atmosphere Watch (GAW) programme of the World Meteorological Organization [1], and perfomed a closure with other aerosol variables measured simultaneously at the same site [2]. We show that the critical dry diameter, above which the aerosols activate as CCN, does not show a distinct seasonal cycle, nor substantial variability, indicating that aerosol hygroscopicity stays fairly stable throughout the year. Therefore, the CCN number concentration at this site can be reliably predicted from the time-resolved particle number size distributions with approximate knowledge of the time averaged chemical composition.

Since the Jungfraujoch is within clouds about 40% of the time this site provides the possibility to compare the measured CCN number concentrations with the activation that occurs in the real clouds. For this purpose, two different inlets were used: A total inlet, heated to 25°C was used to evaporate cloud droplets and ice crystals and to sample both their residual (previously activated and/or nucleated) particles and the interstitial (non-activated) particles. A second, interstitial inlet was equipped with a cyclone to remove cloud particles and sample only the non-activated aerosol particles (smaller than 2 μm). A comparison of the size distributions behind these two inlets allows to retrieve the activation diameter in the real cloud [3]. Together with the measured CCN spectra this provides the maximum supersaturation the cloud experienced in the vicinity of the Jungfraujoch.

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An animal model (sheep) for Fe, Cu and Zn isotopes cycling in the body

VINCENT BALTER[1]* AND ANTOINE ZAZZO[2]

[1]UMR 5276 Laboratoire de Géologie de Lyon, Ecole Normale Suéprieure de Lyon, BP7000, 69342 Lyon Cedex 07, FRANCE (*Vincent.Balter@ens-lyon.fr)

[2]UMR 7209 Archéozoologie, Archéobotanique, Muséum National d'Histoire Naturelle, 55 Rue Buffon, F-75231, Paris cedex 05, FRANCE (zazzo@mnhn.fr)

Iron, copper and zinc are three essential metals for life. The concentration of these metals is regulated by the metabolism to reach body requirements, but almost nothing is known about the variations of the stable isotopes in the body. This could bring new insights on the metabolism of the metals, but the mapping of the isotopic variability in normal conditions is necessary prior to any applications for the study of metal metabolic disorders. Here, we report Fe and Cu isotope compositions (δ^{56}Fe and δ^{65}Cu) and concentrations in various organs of sheep raised experimentally with constant diet (δ^{56}Fe and δ^{65}Cu ≈ 0‰). Iron isotope compositions range from about -4‰ to -1‰ (muscle and liver/kidney, respectively), and copper isotope compositions range from -1.5‰ to +1.5‰ (liver and kidney, respectively), therefore covering almost the geological variability. The variability of the Fe and Cu isotope compositions is higher than for Zn (-0.6‰ to +0.6‰, [1]), suggesting that biologically-induced metals isotope fractionations depend more on redox conditions than on ligand coordination. Contrary to humans [2], the Fe and Cu isotope compositions are similar in serum and red blood cells. The isotopic cycling of the metals in the body is discussed using mixing equations and box modeling.

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Particulate trace metals and dust particles in the subtropical Atlantic

W. BALZER*, W. BARKMANN AND H. DIERSSEN

University of Bremen, FB 2, 28334 Bremen, Germany (*correspondence: balzer@mch.uni-bremen.de)

During the expedition Meteor M81/1 in the subtropical Atlantic Ocean (GEOTRACES Cruise A11; February/March 2010) particulate trace metals were sampled (by using *in situ*-pumps) to study (i) the fate of dust particles in the water column, (ii) its impact on the vertical distribution of particulate trace metals and (iii) to investigate the interaction between trace elements in solution and in the particulate phase.

The cruise track from the Canary Islands to the Brasil basin followed an approximate gradient from high to low dust input. While mineral dust and aerosol deposition is the most important source of trace elements in the open subtropical Atlantic, the surface distribution of particulate trace metals is also affected by the biotic productivity and the rate of organic matter sedimentation which tends to remove the mineral particles from the surface ocean and also decreases along the cruise track.

There is evidence to suggest that the small dust particles do not sink by themselves but that they are removed from the mixed layer by forming aggregates with sticky organic particles. These aggregates might be large enough to leave the surface ocean rapidly, sink, disaggregate, re-aggregate, etc., thus producing an observable vertical distribution of e.g. particulate Al (taken as a proxy for dust particles).

For this assemblage of processes acting on the distribution of suspended dust particles (including aggregation between organic and mineral particles, disaggregation and joint sinking) a model has been developed. The simulated concentration profiles of refractory trace metals (of suspended dust particles) are strongly related to the rate of atmospheric dust deposition and show a similar pattern as in the observed vertical concentration profiles.

Below the surface mixed layer, the different particulate trace metals exhibit extreme differences in the vertical distribution depending on the major form of their particulate transport: the concentration of the more refractory metals in inorganic entities (e.g. Al, Fe, Mn) tend to be constant or even increase with depth, while the nutrient-type elements (e.g. Cd, Ni) being associated with organic particles exhibit dramatic decreases of the concentration with depth in the deep sea. The results for the different elements are compared with those from a similar cruise in 1997 to evaluate interannual variability.

Petrogenesis of monotonous dacitic Taapaca Volcanic Complex, N. Chile

M. BANASZAK* AND G. WÖRNER

University of Göttingen, Geoscience Centre Göttingen, Goldschmidtstr. 1, 37077 Göttingen, Germany (*correspondence: mbanasz@gwdg.de)

Taapaca Volcanic Complex (TVC) located in the Andean Central Volcanic Zone (18°S) generated monotonous high porphyric dacites (61-65.5 wt.% SiO_2) during its main eruptive history ~1 Ma [1]. Taapaca dacites show textural and mineralogical characteristics similar to the Fish Canyon Tuff [2], including sanidine megacrysts, lack of pyroxene and presence of mafic inclusions.

The occurrence of sanidine megacrysts up to 12 cm in length in intermediate volcanic rocks is a unique feature. All Taapaca sanidine show similar growth patterns, pronounced Ba-zoning, and invariable incompatible trace element contents as well as Sr- and O- isotopic compositions. Chemical characteristics of the sanidine, enclosed plagioclase, and magnesiohornblende compositions suggest crystallization in a closed-system at 700-770°C and 1.0-3.4 kbar. Microphyric basalt andesitic inclusions (52-54 wt.% SiO_2) in Taapaca dacite show a uniform mineral assemblage of plagioclase, magnesiohastingsite and Fe-Ti oxide with varying proportions of incorporated felsic components. The mafic inclusions represent compositionally two kinds of parental magma reported from neigbouring Parinacota Volcano [3], differing significantly in Sr and Ba contents, FeO^*/TiO_2 and REE patterns. Estimated P-T conditions from magnesiohastingsite composition reveal 900-1020°C and 2-8 kbar. Taapaca dacites reveal both P-T ranges obtained from two coexisting amphibole and plagioclase populations.

The composition of the dacites and compositionally diverse hybrid mafic inclusions form an array of distinct mixing lines, which converge to one rhyodacitic composition. The composition of the dacites indicates mixing between an evolved sanidine-bearing end-member composition of ~68 wt.% SiO_2 and a range of basaltic andesites in the constant ratio of 3:1. Neither basaltic andesite nor rhyodacite erupt as end-member compositions at Taapaca Volcano. Following reactivation, the uniform dacitic composition of TVC sugessts steady-state magma throughput, and a uniform volume-ratio between remobilized resident rhyodacite crystal mush and variable mafic input.

[1] Clavero *et al*. (2004) *J. Geol. Soc., London* **161**, 603-618.
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[3] Hora *et al*. (2009) *EPSL* **285**, 75-86.

Spectroscopic study of influence of silica on the stability of actinide(IV) colloids at near-neutral pH

D. BANERJEE[1,2]*, S. WEISS[1], H. ZAENKER[1], A.C. SCHEINOST[1,2] AND C. HENNIG[1,2]

[1]Institute of Radiochemistry, Helmholtz-Zentrum Dresden-Rossendorf, 01314 Dresden, Germany
[2]The Rossendorf Beamline at ESRF, B.P. 220, 38043 Grenoble, France (*correspondence: banerjee@esrf.fr)

The migration of tetravalent actinides in natural waters occurs predominantly as sorption complexes at the surface of colloidal particles like clay, but also by the formation of actinide oxyhydroxide colloids ($MO_n(OH)_{4-2n}\cdot mH_2O$ where M = Th or U [1]). Colloid-facilitated migration of plutonium has also been documented in subsurface groundwater conditions [2]. In a recent study it was observed that the stability of U(IV) and Th(IV) oxyhydroxide colloids is dramatically enhanced by the presence of silica [3]. In this study we investigate the influence of silica on the formation and stability of U and Th colloids at near-neutral pH conditions, which might have important environmental implications due to the uniquitous nature of silica in aquifers and surface waters.

U and Th colloids with varying U/Si and Th/Si ratios were synthesized and characterized using a range of spectroscopic and microscopic techniques. TEM and XRD measurements indicated that the structure of thorium/silica colloids is highly amorphous, which is clearly different from the ordered actinide(IV) oxyhydroxide colloids which are stable at pH < 3 but agglomerate and precipitate at near neutral pH within minutes. Comparison of O 1s X-ray photoelectron spectra (XPS) of actinide(IV)-silica and actinide(IV)-oxyhydroxide colloids revealed that two types of oxygen bonds (oxo and hydroxo) occur in presence of silica, which may explain the high degree of structural disorder. Moreover, the presence of O-Si bonds at near-neutral pH values suggest that silica is able to stabilize such colloids through modification of the structure by replacing the An-O(H)-An bonds of the oxyhydroxide structure with An-O(H)-Si bonds and consequently influencing the surface charge. These observations are consistent with X-ray absorption spectroscopy (XAS) data which demonstrate higher An-Si interaction and lower An-An interaction with increasing silica content in these colloids.

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Sorption and redox behavior of neptunium on Opalinus clay and Callovo–Oxfordian argillite

N. L. BANIK*, C.M. MARQUARDT, D. SCHILD, J. ROTHE AND T. SCHÄFER

Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE),D-76344 Eggenstein-Leopoldshafen, Karlsruhe, Germany (*correspondence: nidhu.banik@kit.edu, christian.marquardt@kit.edu, dieter.schild@kit.edu, joerg.rothe@kit.edu, thorsten.schaefer@kit.edu)

Clay stone is considered as a potential host rock for a high level deep nuclear waste repository. The Opalinus clay (OPA) and the Callovo-Oxfordian argillites (COx) are being investigated as candidate host rock formation at the underground research laboratory in Mont-Terri (Switzerland) and at Bure (France), respectively. The migration behavior of Np is strongly influenced by the oxidizing and reducing conditions of the geological environment. The understanding of Np sorption and diffusion mechanisms in argillaceous rocks is necessary for the safety assessments of a nuclear waste repository.

The objective of the present work is to use Kd values determined by batch experiments for transport modeling, and to gain understanding in underlying coupled redox and sorption phenomena. The batch sorption experiments of Np(V) on OPA (pH 7.6) and COx (pH 7.2) are performed at four different solid to liquid ratios, S/L (10, 20, 50, 200), in artificial pore water under argon atmosphere (<1 ppm O_2) with 1% CO_2 conditions, at Np concentrations between 3.0×10^{-4} and 1.0×10^{-8} M and with contact times up to 1 year. Np redox speciation in clay suspension is followed at low Np concentration by TTA extraction and capillary electrophoresis coupled to ICP-MS and at high Np concentration by UV-Vis, XAFS, and XPS spectroscopy.

Np(V) sorption increases with increasing sorbent amounts (S/L ratio) and with increasing contact time. More than 80 % of Np sorbed on the clay rocks within 4 months. The preliminary Kd values are calculated to 1.03 mL/g for OPA and 0.85 mL/g for COx (S/L ratio: 20) after 4 months contact time. In concentration series at 10^{-4} M, Np was identified on the clay in the form of Np(V) by XAFS and XPS spectroscopy after 1 week contact time, whereas in solution Np(V) is detected by TTA extraction and UV-Vis spectroscopy. At $<10^{7}$ M, Np(V) is found in solution by TTA extraction after 1 week contact time, while after 4 months Np(IV)/Np(V) mixtures are analyzed. The obtained results will be presented.

Sulfate mineral solubilities in Na-Ca-Cl brines

JONATHAN BANKS AND SIMONA REGENSPURG SIMONA

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

Geothermal brines produced from deep sedimentary basins show a strong tendency to produce mineral precipitants (scales) during operation of a power plant. Measured SO_4^{2-} concentrations (up to 3 mM) in the fluid at the Groß Schönebeck (GrSk) *in situ* geothermal laboratory, Germany suggest that sulfate-bearing minerals may be significant scale forming phases. Of particular concern are the behavior of (1) Ba^{2+} and Sr^{2+} in the high salinity (up to 5 M Cl^-) Na-Ca-Cl fluid, and (2) the overall equilibrium concentration of SO_4^{2-} that subsequently controls the mass of $CaSO_4 \cdot xH_2O$ precipitation. In order to predict the estimated amount and nature of these scales, we have both modeled and experimentally determined mineral solubilities in synthetic GrSk brines under proposed plant operating conditions (15 bar, 70°C – 150°C).

Modelling was performed using the PHREEQc Quintessa database, with anhydrite ($CaSO_4$), barite ($BaSO_4$), and celestite ($SrSO_4$) as the equilibrium phases. Experiments were performed using a "flooding method," in which a deliberately oversaturated concentration of SO_4^{2-} was injected into a Na-Ba-Ca-Sr- Cl brine filled pressure vessel. While there is general agreement between the PHREEQc and experimental results, some significant differences do exist. PHREEQc over-estimates the amount of barite precipitation by up to three orders of magnitude and underestimates the amount of celestine precipitation by up to one order of magnitude. In total, both PHREEQc and experimental results predict between 10^1 and 10^4 grams of total sulfate mineral precipitation per m^3 of produced fluid, depending on the conditions and total available SO_4^{2-} .

Microbial cycling of sulfur in the aphotic zone a meromictic lake

B. DYLAN BANNON[1], SHUHEI ONO[2], STEFANIE P. TEMPLER[3] AND TANJA BOSAK[4]

[1]EAPS MIT, Cambridge MA 02139, (bannon@mit.edu)
[2]EAPS MIT, Cambridge MA 02139, (sono@mit.edu)
[3]Emmy Group, Ostermundingen, Switzerland, (stefanie.templer@emmi.ch)
[4]EAPS MIT, Cambridge MA 02139, (tbosak@mit.edu)

Fayetteville Green Lake (FYG) is a meromictic euxinic lake characterized by large differences in the composition of sulfur isotopes of sulfides and sulfates ($\delta^{34}_{sulfate\text{-}sulfide}$ of 56-57.5‰) [1]. Similar $\delta^{34}_{sulfate\text{-}sulfide}$ values are commonly thought to involve microbial sulfate reduction (MSR) coupled with microbial disproportionation of sulfur (MSD). Because our recent study suggests that MSR limited by the availability and quality of organic compounds can produce similar $\delta^{34}_{sulfate\text{-}sulfide}$ in the absence of MSD, here we study molecular, metabolic and physiological diversity of microbes from the sulfidic water column and the bottom sediments of FYG.

Enrichment cultures confirm the presence of S-disproportionating microbes in the sediments and the water column. Preliminary most probable number counts (MPNs) suggest that these organisms may be as abundant in sediments as sulfate reducing microbes. The MPNs also indicate a marked increase with depth of organisms that are able to couple sulfate reduction to the oxidation of acetate. Isolated microbes from the lake bottom sediments include at least two phylogenetically distinct organisms that can disproportionate S.

Preliminary studies suggest that microbes in the bottom sediments of FGL can metabolize recalcitrant organic substrates, reduce sulfate and disproportionate S. Further physiological, metabolic and isotopic analyses of enrichment cultures and isolates, as well as molecular comparisons of the diversity of dissimilatory sulfate reductase genes (*dsrAB*) and 16s rDNA genes in the water column and the sediments are in progress.

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The landscape change of salt and alkaline land in semi-arid district before and after flooding

CHUNHONG BAO[1,2] LINSHU XU[2] YUNJUN WU[3] AND SHUWEN ZHANG[4]

[1] Hunan Agricultural University, Changsha 410128, China (Email:baoch159@163.com)
[2]College of Urban and Environmental Sciences, Northeast Normal University, Changchun 130024, China
[3]The Land and Resources Deportment of Hunan Province, Changsha 410007, China
[4]China Graduate School of Chinese Academy of Sciences, Beijing 100049, China

This paper adopted relief map and TM, SAR image, impaling the image disposal technology of Remote Sensing and the space analysis technology of Geography Information System, and combining landscape ecology theory to analyze the effect of flooding before and after 1998 on soil salinization. The analysis includes several aspects such as quantiy, spatial distribution and landscape distribution of salt and alkaline land in Zhenlai county. The results show that the sun-acreage of saline-alkali land in Zhenlai Counly in creased by 13929.5hm2 after the flood. The connectivity and integrity of saline-alkali land increased as well. Furthermore, the center of Gravity of saline-alkali offset from west to east 1.57km. The offset of the flooded area is 1.53km, and that of the non-flooded area is 3.68km. The offset distance, flooding has the effect to slow up the offset of the saline-alkali land. By contrasting the change ratio of unit area of saline-alkali land between flooding zone and no-flooding zone , it is found that the change ratio of all kind of saline-alkali land in flooding zone is higher than that in no-flooding zone at large. For example, the ratio of heavy grade of saline-alkali land in flooding zone is 5 times of that in no-flooding zone. The ratio of moderate grade saline-alkali land in flooding zone is 4.5 times of that in no-flooding zone. The ratio of gentleness grade saline-alkali land in flooding zone is 1.1 times of that in no-flooding zone. It is conculuded that the flooding has the effect to promote the extension of saline-alkali land in half arid district after the flooding. Though studying the integrity and average area of the saline-alkali patch of the landscape distribution, the landscape distribution of the saline-alkali land in the flooded area is obviously different from the non-flooded area. At the same time, the degree of salinization is higher in the flooded area than that in the non-flooded area after the flooding. The flooding push forward the speed and speed of the saliniztion in the half arid district where the terrain is low-lying and level of groundwater is higher.

Paleoproterozoic crustal growth in West Africa: Archean or modern tectonics?

L. BARATOUX[1], J. GANNE[1], M.W. JESSELL[1], S. NABA[2], AND V. METELKA[134]

[1]IRD, GET, 14 Ave E. Belin, 31400 Toulouse, France (*correspondence: lenka.baratoux@get.obs-mip.fr)
[2]Dépt. de Géologie, Univ. de Ouagadougou, Burkina Faso
[3]Institute of Geology and Paleontology, Charles University, Albertov 6, Praha 2, 12843, Czech Republic
[4]Czech Geological Survey, Klárov 3, 11821, Praha 1, CR

The Paleoproterozoic granite-greenstone terrains of the West African Craton represent the key area to study the transition from the Archean so-called “vertical” tectonics towards the modern “plate” tectonics. Our study was focused on structural evolution, geochemistry and metamorphism of the eastern and western Burkina Faso and eastern Senegal.

Geochemical data suggest that the greenstone (GS) belts, composed of tholeiitic basalts/gabbros and voluminous calc-alkaline intermediate sequences, originated in the volcanic arc setting at ~2.2 Ga. Presence of subduction zones is furthemore supported by the cold metamorphic gradient in some of the metasediments found in the eastern Burkina Faso. Compared to the Archean terrains, the proportion of komatiites and ultramafic rocks is extremely low, which suggests only limited mantle plume activity.

The calc-alkaline tonalite-trondjemite-granodiorite magmas, associated with the subduction zones, as well as younger granitoids were syntectonically emplaced into the greenstone belts during a long period from 2.18 to 2.10 Ga. No structures indicative of “sagduction” of greenstones into granitoids were found in the study area. Structural analysis of three GS belts in western Burkina Faso shows that the regional scale geometry is controlled by the rheologically strong mafic and intermediate volcanic rocks, which form up to 400 km long synforms. The granitoids are syntectonically emplaced into the presumptive antiforms between the belts.

Some of the granitoid intrusions induced a thermal overprint of the pre-existing cold metamorphic gradient in the tectonically burried greenstone belts. This is recorded as isobaric heating of Barrovian-like assemblages of garnet, straurolite and kyanite bearing micaschists. Decompressional cooling documented by the growth of sillimanite and cordierite is consistent with tectonic exhumation from the depth of at least 18 km to the depths of 4-6 km.

To conclude, our data point to the existence of subduction and collisional zone settings, which operated in a modified way compared to the present-day analogues.

Past fire reconstructions in ice core through the determination of specific molecular markers

CARLO BARBANTE[1,2]

[1]University of Venice, Department of Environmental Science, Calle Larga S. Marta, 2137, I-30123 Venice, Italy
[2]IDPA-CNR, Calle Larga S. Marta, 2137, I-30123 Venice, Italy

The reconstruction of the chemical composition of aerosol during the past is important for understanding the organic component contribution of biomass burning emissions to the atmosphere and complements existing data on the signatures of direct organic emissions from biomass sources. Compounds from biomass burning include monosaccharide anhydrides (MAs), and the most important tracer compound among them is levoglucosan. This is a specific molecular tracer utilized for the assessment of particulate matter composition from biomass burning in the atmosphere because it cannot be generated by non-combustive processes or by non-wood combustion. Molecular markers such as levoglucosan are important tools in tracking the transport of particles produced by biomass burning.

In order to the current concentrations of levoglucosan in the atmosphere in prespective, it is important to quantify the fluxes of this compound during the past by examining environmental archives such as snow and ice cores. Polar ice core studies have extensively documented large changes in the content of aerosol constituents such as ionic species, dust, trace elements, and organic compounds during the late Quaternary period.

The study of past fire activity using ice core records opens regions of the world where no paleofire data previously exited. Polar and low-latitude, high-altitude ice cores provide data for regions which are not represented in the global charcoal database. The available temporal resolution matches that of the ice core, with the longest temporal resolution being that of the EPICA Dome C ice core that extends back approximately eight glacial cycles. The spatial resolution of chemical markers in ice cores depends on the location of the core itself. Low-latitude ice cores primarily reflect regional climate parameters, while polar ice cores reflect a global signal. Here, we present levoglucosan flux measured across the past 600,000 years in the EPICA Dome C ice core (75°06'S, 123°21'E, 3233 masl) ice core, during the past 4000 years in the Kilimanjaro (3°04.6'S; 37°21.2'E, 5893 masl) ice core, and the applicability for determining levoglucosan in the NEEM, Greenland (77°27' N; 51°3'W, 2454 masl) ice core.

Short term environmental reconstruction from rich CO_2-spring deposits (Massif Central, France)

F. BARBECOT[1]*, B. GHALEB[2], E. GIBERT[1] AND A. NORET[1]

[1]Université Paris-Sud, Laboratoire IDES, UMR8148, Orsay, F-91405, France
(*correspondance: florent.barbecot@u-psud.fr)
[2] GEOTOP, Université du Québec À Montréal, BP 8888, suc. Centre ville, Montréal, QC, H2V 3W8, Canada

Our work focuses on the understanding of the hydrogeochemical processes related to carbo-gaseous springs relation with recent environmental changes (0-20 yr), including evolution of recharge areas and fluxes for surrounding aquifers. A 80-cm sequence has been cored from carbonated travertines in order to document recent environmental fluctuations (0-20 yr) and the related geochemical parameters that control isotopic signatures of modern carbonate deposits [1]. The core was drilled on a flat zone approximately located 200-m under the emerging spring in the Limagne Plain (French Massif Central). Sediments consist of indurated carbonate, ideal for the reconstruction of hydrological fluctuations at very high resolution as they are fine, laminated deposits. Samples were taken every 1 to 2 cm according to the induration degree of the core.

The chronology of these finely laminated deposits has been determined through $^{210}Pb/^{226}Ra$ radiometric method [2,3]. Deposits accumulation rate is of 5.5 cm/yr excepted for events at 30 cm and 60 cm depth that display gaps of carbonates accumulation. Those events correlate precisely with two historical main heat waves, 2003 and 1998 [4], that confirms the indirect records of both the recharge decrease and the drying-up of the springs.

While solid carbonates precipitating along the surface flowpath originate from water with a nearly constant ^{18}O composition, highlighting the inertia of the system that gives rise to the springs, the ^{13}C signatures of those carbonates have likely registered past meteorological conditions [4]. Moreover, this environmental record offers a significant correlation between ^{13}C signal and the East Atlantic Pattern of the North Atlantic Oscillation. Higher mean temperatures can be identified by an enriched ^{13}C content, because of prominent fractionating geochemical processes involved, such as degassing and carbonate precipitation.

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REE behaviour in acid mine drainage conditions in the Ríos Tinto and Odiel (Iberian Pyrite Belt, SW Spain)

L. BARBERO[1], M. OLÍAS[2], A. HIERRO[3], M. CASAS-RUIZ[4] AND J.P. BOLÍVAR[3]

[1]Dpto. CC de la Tierra, Universidad de Cádiz, Spain. (luis.barbero@uca.es)
[2]Dpto Geodinámica y Paleontología, Universidad de Huelva, Spain
[3]Dpto Física Aplicada, Universidad de Huelva, Spain
[4]Dpto Física Aplicada, Universidad de Cádiz, Spain

The Ríos Tinto and Odiel constitues one of the most extreme cases of acid mine drainage in the word and they are considered as the origin of one of the most important heavy metal discharge to the world's oceans.

In the Odiel river, the uppermost waters are clean and show geochemical parameters (pH, C, TDS, ORP, etc) typical of non-contaminated waters. The Río Tinto river shows acidic conditions from the headwaters down to the discharge into the sea. Total disolved REE contents in both rivers increases suddenly at pH values below 2.5 reaching values as high as 16000 μg/L, being lower than 1000 mg/L at pH higher than 2.5. Most enriched NASC-normalized REE patterns in Río Tinto show a negative Eu anomaly, this being progressively reduced as waters are diluted downstream and element precipitation or coprecipitation occurs. In the Río Odiel this slight negative Eu anomaly is mantained downstream which suggest that this feature is a proxy of the succesive AMD inputs. This Eu negative anomaly indicate that REE pattern are inherited from the massive sulfide or the waste rock. Another characteristic of the REE patterns of the Rios Tinto and Odiel is a MREE enrichment typical of waters related to AMD. Hypothesis to explain this include: acid leaching/dissolution of MREE-bearing amorphous iron oxyhydroxides [1]; fractionation by surface/solution reactions between MREE-enriched minerals and acid waters [2]; stabilization and coagulation by colloidal material [3]; combined action of different mechanisms [4]. To these, the possibility of disolving minerals with contrasting REE fractionation patterns should be considered.

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Geochemical profiles to study the last deglaciation and its impact on rivers

EDOUARD BARD

CEREGE, College de France, Aix-Marseille University, CNRS, IRD, Technopole de l'Arbois BP 80, 13545 Aix-en-Provence Cedex 04, France (*correspondence: bard@cerege.fr)

The last deglaciation is fascinating for climatologists as it allows to study first-order climate changes that accompanied the retreat of the large Laurentide and Fennoscandian ice-sheets [1, 3]. Between 21000 and 6000 years before present, the climate system experienced a complete reorganization of all its compartments, e.g. atmosphere, oceans, lakes and rivers together with their associated ecosystems and biogeochemical cycles.

Linking records of the last deglaciation on land and in oceans requires accurate dating and comparison of different geological archives. A complementary way is to measure geochemical tracers of terrestrial and marine origins in the very same sediments raised in coastal environments.

Paleoclimate records at a particular location witness the successive phases of the last deglaciation. These various events, pauses and accelerations, have been known for many years (famous events such as Heinrich #1, Bolling, MWP1A, Allerod, Younger Dryas…), but it is only recently that geochemistry has provided analytical techniques allowing to produce high-resolution time series of various proxies based on elemental ratios (e.g. [2, 8]), organic compounds (e.g. [4, 5]) or stable and radiogenic isotopes measured in different sediment fractions: detrital, biogenic, authigenic phases or even interstitial waters (e.g. [6]).

To illustrate this growing research field, I will review what we know about deglacial sea level based on tropical corals and then go on to consider the associated changes in a few selected records from coastal zones, past river mouths or marginal seas (e.g. [4-9]). The aim is to illustrate the complex linkage between sea level rise, paleoclimatic changes and the reactivation of rivers during the last deglaciation.

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Redox reaction of pyrite with Se

FABRIZIO BARDELLI[1]*, MINGLIANG KANG[1,2], ANTOINE GEHIN[1] AND LAURENT CHARLET[1]

[1]ISTerre, Maison de Geosciences, 38041 Grenoble, France (*correspondence: fabrizio.bardelli@gmail.com)
[2]Chinese Academy of Sciences, Guangzhou, 510640, China

The radioactive isotope ^{79}Se with a half-life of 2.95×10^5 years, is presently considered as the key mobile fission product for the disposal of spent fuel and high-level radioactive waste [1]. Its solubility largely depends on redox conditions: Se(IV) and Se(VI) prevail as very mobile aqueous oxyanions, while the oxidation states 0, -I, and -II are solids with low solubility [2]. Due to the weak adsorption of Se(IV) and Se(VI) on natural minerals, and in particular on granite or claystone minerals, chemical reduction is considered to be the most effective way to immobilize ^{79}Se.

On the other hand, pyrite (FeS_2) is the most frequent sulfide mineral and is also present in geological barriers of nuclear waste repositories [3]. Its strong reducing capacity and its stability under anoxic condition make it a good candidate for the immobilization of redox-sensitive radionuclides, like ^{79}Se. Many works have focused on the identification of the reduced form of selenium when reacted with pyrite, but reported conflicting results [4,5,6]. Therefore we report a systematic where we investigate the effects of the reaction of Se(IV) and Se(VI) with pyrite in several different experimental conditions.

Experiments where conducted at ph 5.05, 5.65, 6.1, 7.0, and 8.5, reaction times of 7, 24, 36, and 48 days, and, at pH 7.0 and 8.5, with and without the addition of extra Fe^{2+} (10^{-4} mol/l). ICP-OES measurements where used to monitor the iron and Se concentrations and showed a decreasing trend of Se and increasing iron as a function of time. XAFS spectroscopy was used to unravel the selenium speciation. At pH 5.05 and 5.65 Se(0) was found to be the main reaction product, while at pH > 5.65, in addition to Se(0), XANES suggested the formation of iron selenides (Se -I or –II), in an amount which increased with the reaction time. The presence of iron selenides is further supported by Mössbauer spectroscopy clearly showing two different environments for Fe^{2+} in pyrite reacted with Se.

The results carried out in this study suggest that pyrite can significantly attenuate the mobility of ^{79}Se through chemical reduction.

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Analysis of methanogen communities

LARRY BARESI

California State University, Northridge, CA 91330 USA (correspondence: larry.baresi@csun.edu)

Methanogens are an exciting group of microorganisms that live under conditions that are of interest to many engineers. They have been found to be active in coals, shales, and other carbon rich environments acting as both the final hydrogen and carbon sink producing methane as the final product. Physiological, molecular biology, biochemical, genetic, and ecological studies of these organisms can play a key role in optimizing their use. I will discuss the role of both past and present techniques such as DGGE/TGGE, 16s sequencing, bioinformatics, and metagenomics in expanding our understanding of this group and their associated organisms. I will also discuss how these new advances in our knowledge base can be used for the development of more effective biodegradation processes.

Speciation and dynamics of biologically reduced U(IV) in the Old Rifle, CO, aquifer

J.R. BARGAR[1]*, J.E. STUBBS[2], E.I. SUVOROVA[3], K.H. WILLIAMS[4], K.M. CAMPBELL[5], J.S. LEZAMA-PACHECO[1], J.M. CERRATO[6], M.A. STYLO[3], D.S. ALESSI[3], S.M. WEBB[1], R. BERNIER-LATMANI[3], D.E. GIAMMAR[6], J.A. DAVIS[4], P. FOX[4] AND P.E. LONG[7]

[1]Stanford Synchrotron Radiaion Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA, 94025, USA (*correspondence: bargar@slac.stanford.edu)
[2]University of Chicago, Chicago, IL 60637, USA
[3]Ecole Polytechnique Fédérale de Lausanne, Lausanne, CH-1015, Switzerland
[4]K.H. Williams, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, USA
[5]US Geological Survey, Boulder, CO, 80303, USA
[6]Washington University, St. Louis, MO 63130, USA
[7]Pacific Northwest National Laboratory, Richland, WA 99352, USA

The chemical and physical forms of U(IV), as well as the biogeochemical processes by which they form and transform, profoundly influence the behavior of uranium in reduced sediments. Obtaining this information for sediments biostimulated *in situ*, *i.e.*, in the field, has been one of the most important and difficult scientific challenges in the field of uranium bioremediation. We have used in-well columns to obtain direct access to sediment U(IV) species, evolving microbial communities, and trace and major ion groundwater constituents in the Old Rifle, CO (USA) aquifer. Sediments were examined using x-ray and electron microscopy (XRM and SEM/TEM), x-ray absorption spectroscopy (XAS), and chemical digestions. EXAFS analysis showed that U(IV) occurred predominantly or exclusively as monomeric U(IV) complexes under both metal- and sulfate-reducing conditions, and was associated with biomass or Fe sulfides. Intriguingly, U(IV) was bonded to oxygen atoms, even when associated with iron sulfides. A fraction of these monomeric complexes transformed into uraninite in the aquifer over a subsequent 12 month period. This work establishes the importance of monomeric U(IV) complexes in subsurface sediments at the Old Rifle site and provides a conceptual framework in which previously observed U(IV) reduction products can be related. These experiments also establish that U(IV) species are dynamic in aquifers and can undergo non-oxidative transformation reactions. These new results have imortant implications for uranium reactive transport models and remediation technologies.

Influence of citric acid, EDTA and fulvic acid on U(VI) sorption onto kaolinite

M. BARGER* AND C.M. KORETSKY

Department of Geosciences, Western Michigan University, Kalamazoo, MI 49008, USA (*correspondence: michelle.l.barger@wmich.edu)

Batch sorption experiments were used to investigate U(VI) sorption on kaolinite (2 g/L KGa-1b) as a function of pH (3-10), ionic strength (0.001 - 0.1 M $NaNO_3$), pCO_2 (0-5%), U(VI) (10^{-6} - 10^{-4} M U) and organic acid (10^{-4} and10^{-2} M citric acid, 10^{-4} - 10^{-2} M EDTA, and 10 - 20 mg/L fulvic acid). Ligand sorption on kaolinite was also assessed in the absence of U(VI).

In the absence of ligands, U(VI) sorption on kaolinite increases from pH 3 to ~7, plateaus at nearly 100% between pH ~7 - 8.5, and decreases at pH > 8.5. Ionic strength has little effect on U(VI) sorption. Thus, at circumneutral pH, kaolinite could have a strong influence on U(VI) mobility in natural systems. Compared to atmospheric conditions, U(VI) sorption under 0 pCO_2 is slightly enhanced from pH 3 – 7, and unchanged from pH of 7-10, likely due to strong aqueous U(VI)-OH^- complexes. However, with increased pCO_2, up to 5%, U(VI) sorption diminishes significantly between pH 5-10, due to formation of U(VI)-carbonate aqueous complexes.

Addition of 10^{-4} or 10^{-2} M citric acid results in decreased U(VI) sorption at all pH values, with up to 50 or 90% reduction in U(VI) sorbed, respectively. Similarly, addition of 10^{-4} -10^{-2} M EDTA yields a decrease in sorption of up to ~70% compared to organic-free experiments. TOC analyses of citric acid and EDTA sorption on kaolinite in the presence or absence of U(VI) demonstrate that less than 10% of either ligand is sorbed to the solid surface. Thus, ternary complex formation at the kaolinite surface is unlikely to occur. Instead, U(VI) binds preferentially to organic acids as aqueous complexes. Addition of 10 or 20 mg/L fulvic acid causes an increase in sorption from pH 3 to ~5 respectively, and a decrease from pH ~5 to 10. Up to 40% of 10 mg/L fulvic acid or 20% of 20 mg/L fulvic acid sorbs on kaolinite at low pH, with the amount adsorbed linearly decreasing to ~10% at pH 10. Fulvic acid complexation at the kaolinite surface results in enhanced U(VI) sorption at low pH, likely due to the formation of ligand bridges. However, at high pH, U(VI) sorption is suppressed, presumably due to formation of strong aqueous U(VI)-fulvic acid complexes.

These data suggest that U(VI) sorption on kaolinite could be significant at circumneutral pH, but that organic acids may significantly retard or enhance U(VI) mobility. The data are currently being used to develop surface complexation model parameters describing U(VI) sorption to kaolinite.

Mantle lithologies from minor elements in olivine: Cape Verde

A.K. BARKER[1], P.M. HOLM[2] AND V.R. TROLL[1]

[1]CEMPEG, Dept. of Earth Sciences, Uppsala University, (Abigail.Barker@geo.uu.se)
[2]Dept. of Geography & Geology, University of Copenhagen.

The Cape Verde Archipelago is known to display source heterogeneity on a 100-200 km scale, with different isotopic domains sampled in the northern islands (mixed HIMU and DMM), compared with the southern islands (mixed EM1 and HIMU). Detailed temporal studies of lavas from Santo Antão and Santiago, representing the northern and southern islands respectively, have shown that the EM1 and DMM components have uniform composition with time, whereas the HIMU component shows a synchronous decrease in $^{208}Pb/^{204}Pb$ with time throughout the Cape Verde Archipelago.

We present minor element data for primitive olivines (Fo>75%), to unravel the mantle lithologies associated with the isotopic heterogeneity in the Cape Verde archipelago.

Lavas from Santiago with low $^{206}Pb/^{204}Pb$ (18.8) and positive Δ8/4, are associated with EM1. They have olivines with Ca = 990-2040 ppm, Mn/FeO = 90-150 and Ni*FeO/MgO = 480-750. Lavas from Santiago with high $^{206}Pb/^{204}Pb$ (19.4), associated with HIMU, have Ca = 2100-2600 ppm, Mn/FeO = 106-120 and Ni*FeO/MgO = 500-640 in olivines from the old volcanics. The Ca and Mn/FeO decrease and Ni*FeO/MgO increases with time from the old volcanics to the intermediate and young volcanics.

Lavas from Santo Antão with $^{206}Pb/^{204}Pb$ of 19.2 sample local DMM and have olivines with Ca = 1900-2750 ppm, Mn/FeO = 95-110 and Ni*FeO/MgO = 305-580. Lavas from Santo Antão with $^{206}Pb/^{204}Pb$ of 19.9, representing the HIMU component, have Ca = 2100-2650 ppm, Mn/FeO = 106-116 and Ni*FeO/MgO = 540-660 in the old volcanics and lower Ca, Mn/FeO and higher Ni*FeO/MgO in the young volcanics.

The DMM of Santo Antão is peridotitic in nature, whereas the EM1 and HIMU components are sourced from mixed peridotite-pyroxenite mantle lithologies. The uniformity of the DMM and EM1 components with time shown by the isotope heteorgeneity is also reflected in the mantle lithologies, i.e. dominantly peridotitic DMM and constant proportions of peridotite and pyroxenite in the EM1 source. However, the changes in $^{208}Pb/^{204}Pb$ of the HIMU component th time observed throughout the Cape Verde archipelago are also reflected by increasing proportions of pyroxenite in the source shown by minor elements in olivine. We will present modelling results of the proportions of peridotite and pyroxenite in the EM1 and HIMU sources with time.

Phosphate dissolution/precipitation controls on isotopic compositions of continental assimilants

J.E. BARKMAN[1]*, J.G. BRYCE[1], E.B. WATSON[2], J. BLICHERT-TOFT[3], E.F. BAXTER[4] AND S.A. BOWRING[5]

[1]UNH Earth Sciences, Durham NH, USA (*correspondence: julie.barkman@unh.edu)
[2]RPI Earth & Environmental Sciences, Troy, NY, USA
[3]Ecole Normale Supérieure de Lyon, Lyon, France
[4]Boston University Earth Sciences, Boston, MA, USA
[5]EAPS, MIT, Cambridge, MA, USA

Partial melting and assimilation of lower and often ancient crustal rocks contribute to the chemical and petrologic evolution of continental magmas. In the past three decades, geochemical models have used isotopes and elemental abundances to improve the parameterization of thermal and mass transfer within the crust. Recent advances in microanalytical techniques have enabled the documentation of subtle isotopic and trace element variations at high spatial and temporal resolutions, allowing testing of assimilation models. Still, interpreting the geological implications of these chemical variations remains challenging, primarily due to the lack of experiments that can be used to parameterize the isotopic signatures of crustal anatexis products in existing assimilation models. Though experiments and theoretical treatments have improved the potential to assess Sr and Nd isotopic signatures of partial crustal melts, parameterization of Pb and Hf continue to be problematic. This has remained an issue because the isotopic signatures of Pb and Hf, two elements with many promising microanalytical applications, are strongly controlled by accessory phases.

To address these issues, we carried out isotopic measurements on partial melts generated experimentally at 900°C, 1 GPa by partially melting a 1.7 Ga two-mica granite. Resulting melts were rhyodacitic in composition (SiO_2 ~ 71 wt%), with elemental and isotopic measurements suggesting that with <10% melting, the Pb and Hf isotopic systems are in disequilibrium with their whole rock. Uranogenic ($^{206}Pb/^{204}Pb$ ~ 23) and thorogenic ($^{208}Pb/^{204}Pb$ ~ 47) Pb signatures and extraordinarily radiogenic Hf (ε_{Hf} ~ +250) suggest the melt isotopic systematics are strongly influenced by contributions from phosphates. This extremely radiogenic Hf, coupled with sluggish Hf diffusion and predictions from solubility models, provides support for the notion that ongoing dissolution and reprecipitation reactions of phosphates may play an important role in effectively redistributing radiogenic signatures of accessory phases through the melt.

The first multiple sulfur isotope evidence for a 2.9 Ga Mesoarchean sulfate reservoir

M.E. BARLEY[1]*, S.D. GOLDING[2], G.J. HEGGIE[1] AND M.L. FIORENTINI[1]

[1]School of Earth and Environment, The University of Western Australia, Crawley, Western Australia, 6009, Australia (correspondence: mark.barley@uwa.edu.au)
[2]School of Earth Sciences, The University of Queensland, Brisbane, Queensland. Australia

The relationship between the evolution of Earth's atmosphere and hydrosphere during the Archean are important and mass-independent fractionation (MIF) of multipe sulfur isotopes caused by ultrviolet photolysis of atmospheric SO_2 is a key contribution to this when the atmosphere was oxygen poor and ocean was sulfur poor. In particular understanding why there are significant variations in the degrees of mass independent fractionation during the Archean and why it was lowest in the Mesoarchean (from 3.3 to 2.8 Ga) is important. This had been suggested to be a result of an early rise of oxygen. However, more recent studies show there is no clear evidence that oxygen rose then and the strongest Mesoarchean $\Delta^{33}S$ MIF values ranged from -0.13 to 1.31 between 2.96 Ga and 2.9 Ga [1] that coincide with volcanic events during this period that erupted volcanic gasses to the atmosphere for development of MIF and the most abundant Mesoarchean sulfur. Because prior to 2.7 Ga there is a limited rock record and most samples analysed from the Mesoarchean are from continental margin sedimentary ocean basins, the lack of significant negative $\Delta^{33}S$ values has provided no evidence for oceanic sulfate during this period. However, the ~2.9 Ga Lake Johnston Greenstone belt in the Yigarn Craton is a marine rift with submarine volcanic rocks (basalts, felsic volcanics and komatiites) shales and banded iron formations (BIFs) with a significant amount of low temperature volcanogenic massive sulfides (VMS) and the Maggie Hays komatiite-hosted Ni sulfide deposit. The $\Delta^{33}S$ values we recently obtained from this belt range from -1.7 to 0.1 providing the first strong negative $\Delta^{33}S$ data from the Mesoarchean consistent with inorganic sulfate reduction similar to that observed in the Neoarchean VMS, komatiite-hosted Ni sulfides and BIFs. This provides evidence for a Mesoarchean sulfate reservoir linked to a subaerial volcanic plume and oceanic volcanic island eruptions.

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An isotopic perspective on mass bias and matrix effects in MC-ICP-MS

JANE BARLING AND DOMINIQUE WEIS

PCIGR, EOS, University of British Columbia, Vancouver, BC V6T 1Z4, Canada (jbarling@eos.ubc.ca)

Precise and accurate correction for instrumental mass bias is required to achieve the level of precision and accuracy needed for isotope ratio measurements by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). However, instrumental mass bias and the causes of its variation are not well constrained. With the excellent internal precision of isotope ratio measurements by MC-ICP-MS, we can investigate mass bias variation at an isotopic as opposed to elemental level in order to shed light on the processes underlying mass bias variation in the plasma. For this study we measured the spatial variation of Pb and Tl isotope ratios in dry plasma and their response to the presence of matrix.

Mass dependent radial variation of Pb isotope ratios indicates that lighter isotopes show greater dispersion from the axis of the plasma than heavier isotopes, in agreement with elemental observations by ICP-MS [1]. Axial variations in Pb and Tl isotope ratios show that isotopic signal maxima (I_{max}) are distributed in a mass dependent manner (Pb I_{max} separation: 3.47±2.07μm/amu), with I_{max} for heavier isotopes closer to the load coil than I_{max} for lighter ones; the reverse of the elemental mass dependence observed in ICP-MS [2]. This difference in mass dependent behaviour may be due to processes in the interface related to, for example, the high acceration potentials (4-10kV) used in MC-ICP-MS.

Addition of a low first ionization potential (1.IP) element to the plasma promotes ionization of Pb and Tl closer to the load coil, whereas a high 1.IP element results in ionization further from the load coil. Elements with low second ionization potential and those forming refractory oxides may also promote ionization further from the load coil. In addition to shifting the position of Pb and Tl I_{max}, the presence of matrix also reduces run-to-run variations in the mass dependent separation of isotope I_{max} (Pb I_{max} separation: 3.50 ± 0.54μm/amu). This reduced variability in mass dependent isotope separation under matrix-loaded conditions may provide an explanation for improved accuracy and external reproducibilty of dry plasma Pb isotope ratio measurements in the presence of a common matrix [3].

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1500 yr cyclicity during mid- Holocene in the Eastern Mediterranean

M. BAR-MATTHEWS* AND A. AYALON

Geological Survey of Israel, Jerusalem, Israel (*correspondence:matthews@gsi.gov.il, ayalon@gsi.gov.il)

High-resolution (~3 to 20 years) speleothems records from the Eastern Mediterranean (EM) during mid-Holocene (7.0 to 4.0 ka) reveals 4 important patterens: a) ~1500 years cyclicity; b) correlation between half a cycle and archeological time framework; c) "dogtooth" pattren representing fast ~50-100 years increase in rainfall followed by gradual drying over a longer period of ~100-500 years. The structure of these changes resembles the structure the D-O events d) rapid climate changes (RCC) lasting 20-50 years [Fig. 1]. It is not clear what controls the 1500 years cycle (Bond cycles) and the so called "D-O events" that are clearly recognized during mid-Holocene speleothems in mid latitudes, the EM.

Intrestingly each half cycle is associated with cultural-technological tranzitions, suggesting that these tranzitions follow long term climate trends (~400-800 years) rather than a response to RCC. Two of the tranzitions occur at the peak of the wettest period: the tranzitions from Mid- to Late Chalcolithic and from the Early Bronze II to III at 6.55-6.45ka and 4.8-4.7ka respectively, when annual precipitation increased by up to ~30% relative to present. The end of the Chalcolithic period and the transition from Early Bronze IV to the end of the Mid Bronze age occurred after of a long drying trend at 5.7-5.6ka and at 4.2-4.05ka respectively when precipitation dropped by ~30% relative to present.

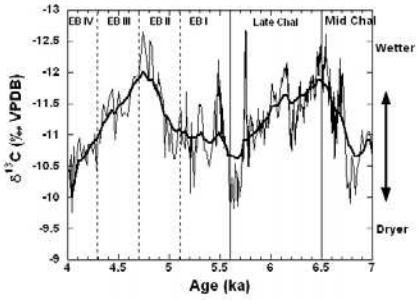

Figure 1: carbon isotopic composition showing the 1500 y cyclicity, D-O type events, RCC and the archeological time framework.

Li isotope compositions of Hawaiian post-shield lavas

ELSPETH M. BARNES, DOMINIQUE WEIS AND DIANE HANANO

Pacific Centre for Isotopic and Geochemical Research, University of British Columbia, Vancouver, BC V6T 1Z4 Canada (dweis@eos.ubc.ca)

Hawaiian post-shield lavas show more depleted geochemical signatures than their shield equivalents and the difference is attributed to material in the plume source, where the very enriched trace element concentrations in post-shield lavas clearly indicate that the source material is not MORB. We investigated Li isotope compositions in a series of well-characterized post-shield samples [1] to explain the origin of these geochemical characteristics and assess the potential contribution of recycled oceanic crust in post-shield lava.

Hualalai volcano δ^7Li values range between 1.91±1.00 (2SD) and 3.53±0.53‰, Mauna Kea samples show the smallest range, 3.39±0.89 to 4.93±1.92‰, contrasting with δ^7Li from the oldest sampled volcano, Kohala, which shows the broadest range, 1.97±0.35 to 4.04±0.44‰. For comparison, a 1993 tholeiitic sample from Kilauea volcano has δ^7Li of 3.72±1.29‰, while a Koolau Makapuu sample shows a relatively heavy δ^7Li value at about 4.5‰. In contrast to other isotopic ratios (e.g., ^{208}Pb/^{204}Pb), Kilauea and Koolau do not appear to represent compositional end-members of Hawaiian compositions in the Li isotope system.

Li isotope signatures of the studied post-shield lavas tend to be 'light' relative to shield lavas (δ^7Li 3.45 to 5.7‰; Mauna Loa and Mauna Kea)[2] and correlate positively with Nd, Hf and Pb isotope signatures, and negatively with Sr isotopes, possibly defining the history of the source material.

Our results indicate that the youngest post-shield lava sampled (Hualalai) has some of the 'lightest' δ^7Li values. Hualalai Volcano also has some of the lowest radiogenic Pb ratios that may derive from ancient recycled oceanic lithosphere and sediments that have geochemically evolved in the presence of low U/Pb during subduction dehydration processes in the upper mantle. We suggest that these dehydration processes may have driven ^{7}Li off in the fluid from the residual slab resulting in an isotopically 'light' Li signature in the plume source material [3].

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Chlorine chemistry of altered oceanic crust

J.D. BARNES*

Department of Geological Sciences, Jackson School of Geosciences, University of Texas at Austin, Austin, TX, 78712, USA (jdbarnes@jsg.utexas.edu)

Chlorine strongly partitions into aqueous fluids, thereby making Cl and its stable isotopes (^{37}Cl and ^{35}Cl) powerful tracers of fluid-rock interaction, including interaction between oceanic lithosphere and hydrothermal fluids. Although altered oceanic crust (AOC) is considered to be a major Cl reservoir estimated to subduct ~2.5-3 x 10^{12} g of Cl worldwide each year [1, 2], work on the Cl chemistry of AOC is surprising limited. Here I present new Cl concentration and isotopic data for AOC from seven DSDP/ODP/IODP drill sites (801C, 735B, 894F/G, 504B, 1256D, 417A/D/418A, 332A/B), greatly expanding the previous data set.

Chlorine concentration and $\delta^{37}Cl$ values of AOC are heterogeneous among and within individual drill sites. Cl concentrations range from <0.01 to 0.09 wt% (n = 26) and $\delta^{37}Cl$ values range from -0.8 to +1.5‰ (error < ± 0.2‰) vs. SMOC (Standard Mean Ocean Chloride) (n = 20). These data greatly expand the range of previously reported AOC $\delta^{37}Cl$ values (-1.6 to -0.9‰; n = 3; Hole 504B; [3]). Neither Cl concentration nor isotopic composition is correlated with tectonic setting or crustal age. The Cl concentration decreases with depth in ODP Hole 735B from the SW Indian Ridge from 0.09 wt% at the top of the hole to <0.01 wt% at depth. A similar pattern is seen for $\delta^{37}Cl$ values ranging from -0.6 to +1.5‰ with the most positive values located near the top of the hole. The high Cl concentrations and $\delta^{37}Cl$ values are correlated with increased hydrothermal alteration (increased amphibole abundance) near the top of the hole. However, this trend is not consistent among all the holes implying that Cl chemistry is influenced by a variety of factors. Detailed future petrography and additional geochemical work will further test the correlation between Cl concentration and isotopic composition and mineralogy, as well as, examine the role of water-rock ratios, deformation, and temperature of hydrothermal alteration. These data can ultimately be used to reevaluate mass balance calculations improving our understanding of subduction recycling.

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Is the platinum in the Bushveld complex derived from the lithospheric mantle ?

SARAH-JANE BARNES[1], WOLFGAND D. MAIER[2] AND EDWARD A. CURL[3]

[1]Universite du Quebec a Chicoutimi, G7H 2B1, Canada (sjbarnes@uqac.ca)
[2]University of Oulu, Finland, (wolfgang.maier@oulu.fi)
[3]Monash University, Australia, (edcurl@yahoo.com)

The Bushveld Complex of South Africa contains ~ 80 % of the world's Pt and almost half of its Pd resources in the form of three large ore deposits, the Merensky Reef, the UG-2 reef and the Platreef. Two questions arise a) were the magmas that formed the Bushveld Complex pariticularily Pt- and Pd-rich? and b) what is the origin of these magmas? In order to consider these questions we have estimated the compositon of the Bushveld magmas based on 40 new whole rock analyses of quench textured rocks from the margins of the intrusion.

Broadly speaking, there are two types of magmas present, a Mg-rich basaltic andesite and a tholeiitc basalt. Both of these magmas are enriched in large ion lithophile elemnts, light rare earth elements and in Pb. Both magmas have negative Ta, Nb, P and Ti anonmalies. The PGE contents of both magmas are similar to primary basalts and they do not appear to be enriched in PGE, except for Pt. The Pt/Pd ratio and Pt/Ti ratios are 1.5 to 2 times that of most basalts.

It is possible to model the lithophile element composition of the two magma types by up to ~ 50 % crustal contamination of komatiitic basalt or picrite. This conclusion is supported by Sr, Nd and oxgen isotopic work. However, the Pt contents of the model magmas and the Pt/Pd and Pt/Ti ratios are much lower than those observed. An alternative is to suggest that the Bushveld magmas formed by parital melting of the metasomatised lithosphere. But, modeling using Kaapvaal mantle xenoliths compositions and MELTS shows that this magma would be too Al_2O_3 rich and SiO_2 poor.

Two possible solutions to this are: a) the melts formed by zone refining melting of the lithosphere (to attain usually high Pt concentrations) followed by contamination with crustal melts; OR b) the current estimate of primitive upper mantle with a Pt/Pd of 1 is incorrect and it should be closer to 2, in which case mixing of a plume derived magma with continental crust melts approximates the composition of the Bushveld magmas

Microprospecting for platinum group minerals by X-ray fluorescence mapping using the Maia detector

STEPHEN J. BARNES[1], BELINDA GODEL[1] AND CHRISTOPHER G. RYAN[2]

[1]CSIRO Earth Science and Resource Engineerin Perth Western Australia (steve.barnes@csiro.au)
[2]CSIRO Earth Science and Resource Engineering Clayton Victoria

X-ray fluorescence microprobe mapping (XFM) has been used to locate micron-sized grains of platinum group element minerals in mantle nodules, komatiites and nickel sulfide ores using the Maia massively paralleled detector on the XFM beamline at the Australian Synchrotron [1]. The technique enables whole thin sections to be mapped at a pixel resolution of 2 microns, producing images up to 80 Mpixels in a few hours.

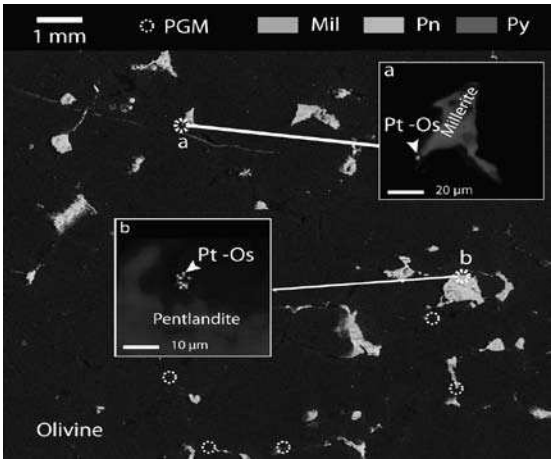

Figure 1. XFM image of sulfide-bearing dunite, Betheno, WA. Mil = millerite, Pn pentlandite, Py pyrite.

The example presented in Fig 1. shows one quarter of a standard thin section of a disseminated sulfide bearing fresh komatiitic dunite [2] containing 16 ppb Pt. XFM mapping revealed presence of 7 distinct PGM grains, only one of which had been located in a previous SEM search. This follows from the capability of the XFM method to detect buried grains within the 100 micron thickness of the section. PGMs are commonly found close to, but not in direct contact with, base metal sulfide globules.

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Chalcophile elements in magmas and magmatic sulfide deposits: Can we see the mantle signals?

STEPHEN J. BARNES[1], MARCO L. FIORENTINI[2] AND WOLFGANG D. MAIER[3]

[1]CSIRO Perth Western Australia (steve.barnes@csiro.au)
[2]University of Western Australia Perth
[3]University of Oulu, Finland

Magmatic sulfide deposits are associated with a very wide variety of magma compositions from komatiites to andesites, spanning ranges of more than an order of magnitude in Ni content and three orders of magnitude in platinum group elements. Similar ranges are seen in sulfide ore tenors.

Late Archaean komatiites[1,2] show a strong consistency in PGE and Ni contents implying lack of S saturation except in the immediate environment of ore formation, and a broad homogeneity of deep mantle plume sources after 3 Ga.

Three trends are evident in post-Archaean basalts: source sulfide control, resulting in Pt and Pd depletion at high Mg#; cotectic sulfide fractionation, resulting in steady decrease in Pt and Pd with decreasing Mg#; and catastrophic depletion due to bulk crustal S assimilation [1]. Mantle signals are overprinted and difficult to discern in the latter two trends.

Basalts show very wide variability, and fall under a near-universal envelope of maximum Pt and Pd contents when normalised to moderately incompatible elements such as Ti. This maximum is lower than that for komatiites, implying either that all post-Archaean mantle sources are Pt-Pd depleted compared with Archaean plume sources, or that there is a universal global control owing to retention of sulfide in source mantle. However, source sulfide should produce a larger depletion, as seen in the Pt and Pd signal in primitive MORB and OIB. Within post-Archaean mafic magmas, only the Bushveld Complex sills stand out as being unusually PGE enriched, and even then the signal is only evident as a twofold enrichment in Pt [3]. Otherwise the Bushveld magmas appear to fall on extensions of the komatiite trends.

Iridium, Ru and Os are decoupled from Pt and Pd in basalts and komatiites, and show evidence for control by solubilities of Ir-rich phases [4]. This greatly limits the ability to read mantle abundances from magma compositions, and may have implications for Os iotope signals.

[1] Fiorentini *et al* (2010) *Journal of Petrology*, **52**, 83-112. [2] Fiorentini *et al* (2010) *Economic Geology*, **105**, 795-823. [3] Sarah Barnes *et al*. (2010) *Economic Geology* **105**, 1491-1512. [4] Barnes and Fiorentini (2008) *Chemical Geology* **257**, 44-58.

Volcanic, solar activity, and atmospheric circulation influences on cosmogenic 10Be fallout at Vostok and Concordia (Antarctica) over the last 60 years

M. BARONI[1], E. BARD[1], J.-R. PETIT[2], O. MAGAND[2] AND D. BOURLES[1]

[1]CEREGE, Aix-Marseille University, CNRS, IRD & College de France, Technopole de l'Arbois BP 80, 13545 Aix-en-Provence Cedex 04, France (baroni@cerege.fr)

[2]Laboratoire de Glaciologie et de Géophysique de l'Environnement (CNRS-UJF 5183), 38402 Saint-Martin-d'Hères, France

The cosmogenic nuclide beryllium 10 (10Be), recovered from ice cores, is often used to study solar activity on long timescales. However, the 10Be signal is also influenced by factors other than the Sun. In order to identify and quantify various contributions to the 10Be signal, two Antarctic snow records from the Vostok and Concordia sites spanning the last 60 years were studied at a sub-annual resolution. Three factors that contribute to the 10Be signal were identified. First, in both records, a significant period of approximately 11 years, that can be associated with the modulation of 10Be production by solar activity, was detected. Then, peaks in 10Be concentrations during the time of the stratospheric volcanic eruptions of the Agung (in 1963) and the Pinatubo (in 1991), respectively, were observed. The data indicate that stratospheric volcanic eruptions can impact 10Be transport and deposition. Also, an interannual variability of ~4yrs was determined in both 10Be records. As with species of marine origin, this 4yrs variability is interpreted as a tropospheric signal that could be associated with atmospheric circulation inherited from the coupled Southern Ocean ocean-atmosphere system. The results presented, here, from sites within the high Antarctic plateau open perspectives for ice cores dating over the last few centuries, as well as for the reconstruction of past solar activity in relation to climate.

Characterization of Anaerobic Methane Oxidation in Lake Kinneret (Israel)

ITAY BAR-OR[1], ORIT SIVAN[1], ADLER MICHAL[1], ARIEL KUSHMARO[2], ANN PEARSON[3], WERNER ECKERT[4]

[1]Department of Geological and Environmental Sciences, Ben-Gurion University of the Negev, Beer Sheva, Israel. (barorit@bgu.ac.il, oritsi@bgu.ac.il, sela@bgu.ac.il)

[2]Department of Biotechnology Engineering, Ben-Gurion University of the Negev, Israel, arielkus@bgu.ac.il.

[3]Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138, USA, (pearson@eps.harvard.edu).

[4]Israel Oceanographic and Limnological Research, The Yigal Allon Laboratory, Tiberias , Israel, (Werner@ocean.org.il)

In this study we show biogeochemical evidence for anaerobic oxidation of methane (AOM) in deep lake sediments and demonstrate that this AOM is likely driven by iron reduction. This is by producing porewater chemical and isotope profiles from Lake Kinneret (Sea of Galilee, Israel), together with incubation experiments, lipid analysis and molecular microbiology methods, including PCR, cloning and sequencing of archaea and bacteria.

Porewater profiles of methane and the stable carbon isotopes of the total lipid and methane indicate a sink for methane below the depths at which nitrate and sulfate are completely exhausted and the zone of methanogenesis. At that depths Fe(II) showed an increase, and iron isotopes decrease, suggesting that Fe(III) is the probable terminal electron acceptor. Based on these results incubation experiments of sediment cores and slurries were conducted to verify and quantify the rate of this process and its key parameters. This is by using amorphic ferric oxide and labelled methane. The results strengthened the iron dependent AOM hypothesis, and the obtained AOM rates were about 10% of the production rates. Analyses of the community structure and diversity of bacteria and archaea along the sediment gradients showed indeed the appearance of involved bacterial methanogens and methanotrophs in the deep sediment.

Gaseous mercury in soils over deeply buried sulfide deposits

F.C.D. BARROS[1,2], J. ENZWEILER[2]*, O.A.B. LICHT[3], Z. CASTILHOS[4] AND P.C. ARAUJO[4]

[1]University of Campinas/Votorantim Metais – Brazil, (fernanda.barros@vmetais.com.br)
[2]University of Campinas, P.O. Box 6152, CEP13083-970, Brazil, (*correspondence:jacinta@ige.unicamp.br)
[3] MINEROPAR - Serviço Geológico do Paraná - Brazil, (otavio@mineropar.pr.gov.br)
[4]Centro de Tecnologia Mineral (CETEM) - Brazil, (zcastilhos@cetem.gov.br; paraujo@cetem.gov.br)

The measurement of gaseous mercury in soils over a deep (~90 m) zinc sulfide mineralization was used to evaluate its potential as a mineral exploration technique. The Zn-Pb Santa Maria deposit (Camaquã Basin, RS, Brazil) contains sphalerite and galena as main ore minerals and up to 7 μg/g Hg. Holes at depths of 30 cm and 50 cm were made at preselected sample locations on three soil transects, two of them over the ore body. The Hg in soil pore gas was measured during 30 s, after inserting the hose of a portable Hg analyser in the hole and air purging. The concentrations of Hg in soil pore gas samples were typically low (< 5 ng/L) but significantly higher values were measured in the deeper holes, i.e., up to 18 ng/L. The higher Hg concentrations marked the position of the ore body. Total Hg in soil samples attained 40 ng/g, which also coincides with the mineralization, while median value was 21 ng/g.

Application of DSC and NMR to study the soil organic matter in the Atacama desert

N. BARROS, S. FEIJOO, J.A. RODRIGUEZ-AÑON, J. PROUPIN, M. VILLANUEVA AND J. SALGADO

Dept. Applied Physics. University of Santiago de Compostela. Spain. (nieves.barros@usc.es)

The study of the organic matter in desert soils makes necessary the development of sensitive methods to detect low percentages of SOM.Differential scanning calorimetry (DSC), together with ^{13}C CPMAS and 2D liquid H NMR was applied to study the SOM composition and structure of different mineral soils collected in the Atacama desert. DSC was very sensitive to study the SOM of those samples in base on their thermal properties. SOM combustion was detected in the DSC curves at C percentages up to 0.5 %. Most of them showed two well defined combustion peaks at temperatures atributed to carbohydrates and aromatic compounds.The heat of combustion obtained by the direct integral of those curves were directly correlated with the C and OM percentages of the soils as found in soils rich in organic matter content. The normalization of the heat of combustion to the OM content of the samples indicated different OM composition in the soils from Atacama. ^{13}C CPMAS NMR spectra indicated the existence of carbohydrates and aromatic compounds too.The aromatic compounds could be assigned to phenols derived from lignin. 2D liquid H NMR showed predominance of the aliphatic compounds when these soils are treated with chloroform.Most of the aliphatic C detected is attributed to Acetyl C and Methyl C in lipids or/and suberin. Nevertheless, the aliphatic fraction of the organic matter was not detected by the DSC and ^{13}C CPMAS NMR. Application of the three methods gives accurate information about the OM composition in these soils. It seems the carbohydrates and aromatic compounds are the main constituents in these mineral soils. Aliphatic C takes part of the general OM composition too but at lower percentages and it is necessary the specific extraction to be detected.

Stalagmite reconstruction of Moroccan climate from geographically spaced records

J.J. BARROTT[1]*, C.C. DAY[1], R.N.E. BARTON[2], A. BOUZOUGGAR[3] AND G.M. HENDERSON[1]

[1]Department of Earth Sciences, University of Oxford, UK, (*correspondence: julia.barrott@earth.ox.ac.uk)
[2]Institute of Archaeology, University of Oxford, UK (nick.barton@arch.ox.ac.uk)
[3]Institut National des Sciences de l'Archaéologie et du Patrimoine (abouzouggar@yahoo.fr)

Located at the boundary between Mediterranean and Saharan climates and within the southern limit of the North Atlantic storm tracks, Morocco is strategically placed for studying glacial to sub-millennial timescale shifting of climate boundaries. There is a specific lack, however, of high-resolution terrestrial records with high-precision, absolute chronology. Consequently, climate variation arising from interplay between climate systems is poorly understood and IPCC (2007) predictions of rainfall are presently uncertain. Precisely-dated, high-resolution, records of palaeoclimate linked with Morocco's extensive, rich archaeological records will also provide valuable insight into the potential effects of rapid climate change on pre-historic communities.

This study provides high-resolution and precisely dated U/Th records from speleothems discretely sampled from six caves in three sites (Ghar Cahal on the NW Mediterranean coast [5°3 W, 35°5 N]; 3 caves near Ouarzazate close to [7°3 W, 30°2 N]; and 2 caves in the SE close to Errachidia [4°2 W, 32°0 N]). Continuous growth and more negative $\delta^{18}O$ values in northern Morocco concurrent with abundant speleothem growth in the currently arid area south of the Atlas mountains suggests overall wetter conditions during the mid-Holocene and allow assessment of the pattern of rainfall and air-masses. We investigate the temporal and spatial relationships between these sites and compare them with existing records from the Holocene Climatic Optimum period, and with archaeological records in the region.

Comparison of oil sands process waters and natural water using Fourier transform ion cyclotron resonance mass spectrometry

MARK P. BARROW[1]*, JOHN V. HEADLEY[2], KERRY M. PERU[2], BRIAN FAHLMAN[2], RICHARD A. FRANK[3] AND L. MARK HEWITT[3]

[1]Department of Chemistry, University of Warwick, Coventry, CV4 7AL, United Kingdom (*correspondance: M.P.Barrow@warwick.ac.uk)
[2]Water Science and Technology Division, Environment Canada, Saskatoon, Canada
[3]Water Science and Technology Division, Environment Canada, Burlington, Canada

As the demand for petroleum has continued to rise, it has become necessary to increasingly turn to previously non-viable sources of oil, such as the oil sands in the Athabasca region of Canada. Using an alkaline hot water extraction process, the bitumen can be extracted from the oil sands prior to being upgraded to synthetic oil. Approximately three barrels of fresh water are required during the process to produce one barrel of synthetic oil. The exploitation of the Athabasca oil sands is therefore placing a burden upon the aquatic ecosystem in particular.

Fourier transform ion cyclotron resonance (FTICR) mass spectrometry has played a key role in the advent of the field of "petroleomics." The inherent ultra-high resolving power and mass accuracy is unrivalled within mass spectrometry, making the technique highly-suitable for the analysis of complex mixtures.

A 12 T Bruker solariX FTICR has been used to characterize a range of samples from the Athabasca region of Canada. The samples originate from natural water sources, such as rivers and lakes, and industrial sources, such as tailings ponds. High field FTICR mass spectrometry affords the ability to characterize the thousands of components present within the samples, which create characteristic signatures. Subsequent usage of principal component analysis (PCA) has demonstrated that these profiles can be used to determine the origins of samples, including distinguishing between industrial sources. There is potential for FTICR mass spectrometry to delineate between naturally-occurring profiles and anthropogenic sources.

Stable isotope (C-N) and noble gas (Ne-Ar) evidence for recycled plume components at the CIR

P.H. BARRY*[1], D.R. HILTON[1], E. FÜRI[1], B. J. MURTON[2], C. HEMOND[3] AND J. DYMENT[4]

[1]Geosciences Research Division, Scripps Institution of Oceanography, UCSD, La Jolla, California 92093, USA (*correspondence: pbarry@ucsd.edu)
[2] University of Southampton, Southampton Oceanography Centre, European Way, Southampton SO14 3ZH, UK
[3] UMR 6538 Domaines oceaniques IUEM Place Nicolas Copernic, Plouzane, 29280, France
[4] UMR-CNRS 7097, Institut de Physique du Globe de Paris, 4 Place Jussieu, 75005 Paris, France

We present new CO_2 ($\delta^{13}C$), N_2 ($\delta^{15}N$) and Ne-Ar isotope results on basaltic glasses of the Central Indian Ridge (CIR) (~17 – 21°S). Our aim is to assess whether the Réunion plume component evident along the CIR [1] also reveals a recycled contribution in the stable isotope and noble gas systematics. Positive $\delta^{15}N$ are attributed to post-Archean subduction whereas low $\delta^{15}N$ are associated with Archean recycling [2].

Nitrogen isotopes ($\delta^{15}N$) range from +3 to -3‰ (n=10) and overlap with positive $\delta^{15}N$ anomalies previously observed in Réunion xenoliths [3]. C-isotopes (n=17) range from -4 to -20‰ vs. PDB with the majority of samples falling in the MORB range. Equilibrium degassing models suggest that C-source characteristics may extend to -2.5‰. $^{20}Ne/^{22}Ne$ values range from 9.8 to 11.3 and when extrapolated to solar (Ne-B) values, $^{21}Ne/^{22}Ne$ ratios are ~0.049. $^{40}Ar/^{36}Ar$ ratios range from 298 up to 8413 with the highest $^{20}Ne/^{22}Ne$ value occurring in the highest $^{40}Ar/^{36}Ar$ sample. Notably, positive $\delta^{15}N$ samples display Ne and Ar only slightly higher than air-values, whereas negative $\delta^{15}N$ samples display distinct primordial Ne. $\delta^{15}N$ shows no correlation with $^{4}He/^{40}Ar^*$ [1] indicating $\delta^{15}N$ values are independent of degassing effects.

Taken together, the N-Ne-Ar results suggest multiple recycled components in CIR basalts, including Archean (low $\delta^{15}N$) and post-Archean (high $\delta^{15}N$) components, both of which are potentially integrated into the Réunion plume. Conversely, CO_2 results retain close to canonical MORB-like signatures, suggesting that either the source CO_2 is masked by external processes (e.g. - degassing and/or crustal contamination) or that CO_2 in the (upper and lower) mantle is homogenized to the extent that we cannot differentiate between the various reservoirs.

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The influence of F, P and B content on pegmatitic melt viscosity

A. BARTELS[1], J. KNIPPING[1], H. BEHRENS[1], F. HOLTZ[1] AND B.C. SCHMIDT[2]

[1]Institute for Mineralogy, Leibniz University of Hannover, Germany, (a.bartels@mineralogie.uni-hannover.de)
[2]Experimentelle und Angewandte Mineralogie, GZG, Georg-August Universität Göttingen, Germany

The key property governing dynamics in strongly depolymerized partially melted systems is the melt viscosity. To test the individual influences of elements like F, P and B on melt viscosity of pegmatitic water-bearing systems a starting glass was prepared from a mixture of SiO_2, Al_2O_3, Na_2CO_3, and K_2CO_3. This starting composition (67.73wt% SiO_2, 20.20wt% Al_2O_3, 7.80wt% Na_2O and 4.27wt% K_2O) was then doped with different amounts of F (up to 4.8 wt%), P_2O_5 (up to 4 wt%) and B_2O_3 (up to 0.93wt%).

The viscosity of hydrous melts (1 to 6 wt% H_2O) was determined in internally heated gas pressure vessels using the falling sphere method (low viscosity range) in the temperature range 1173 - 1573 K at 200 MPa and 300 MPa. In the low temperature range the viscosity was determined between 580 and 880 K at ambient pressure using the micropenetration technique.

The results demonstrate that the viscosity decreases with the addition of F at all investigated temperatures. This viscosity decrease is more pronounced at low temperature and at low water content. The viscosity of pegmatitic melts containing ~ 6 wt% H_2O and 4.8 wt% F is 225 Pa·s at 1273 K. This value is about 1 log unit higher than that of complex pegmatitic melts containing F, B, P and Li [1]. Thus, although we confirm that F is clearly a fluxing agent, additional elements and their mutual interaction play a crucial role in the viscosity of natural pegmatite melts.

Our results indicate that phosphorus may not play a major role in viscous flow. In comparison to F the effect of P_2O_5 on melt viscosity is much lower (0.5 log units compared to 1.5 log units at 1373 K, 2.5 wt% H_2O), and in water-rich samples (~6 wt% H_2O) no significant effect of P_2O_5 has been detected. Additional experiments with variation of B_2O_3 content are in progress to determine wether this component will significantly influence melt viscosities in highly fluxed water rich systems.

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The cause of high Nb/Ta in K-rich lavas from the Sunda arc system

A.R. BARTH[1,2], M. KIRCHENBAUR[1,2], S. KÖNIG[1,2], S. SCHUTH[3], A. LUGUET[2], A. IDRUS[4] AND C. MÜNKER[1]

[1]Institut für Geologie und Mineralogie, Universität zu Köln, Germany (anne.barth@uni-koeln.de)
[2]Steinmann-Institut, Rheinische-Friedrich-Wilhelms-Universität Bonn, Germany
[3]Institut für Mineralogie, Universität Hannover, Germany
[4]Department of Geological Engineering, Gadjah Mada University, Yogyakarta, Indonesia

The overall depletion of many terrestrial silicate reservoirs in Nb has been explained in some studies by the existence of superchondritic Nb/Ta reservoirs in either the core or mantle (e. g. [1–2]). As one example, K-rich lavas from the Sunda arc, Indonesia, have been invoked to tap such a high Nb/Ta reservoir, a hybridised mantle [3]. In order to elucidate the petrogenetic processes active beneath the Sunda arc and the causes for the apparently high Nb/Ta in some of these lavas, we determined major and trace element concentrations, Sr-Nd-Hf-Pb isotope compositions, and HFSE concentrations via isotope dilution by MC-ICP-MS on a representative set of 18 mafic samples, covering along and across arc sections from Krakatau to Lombok.

Similar Pb isotope compositions of all lavas, and mixing arrays of the Sunda arc lavas in εNd vs. $^{87}Sr/^{86}Sr$ space (εNd +1.3 to +5.6, $^{87}Sr/^{86}Sr$ 0.7040–0.7059) with local ocean floor sediments are in agreement with previous studies on the Sunda arc, suggesting a significant overprint of the mantle sources by fluids derived from subducted sediments. In contrast, the particularly K-rich back-arc lavas (e. g., Muriah volcano) do not lie on this mixing array (εNd -1.3 to +2.2, $Sr/^{86}Sr$ 0.7042–0.7046), and are the only ones exhibiting superchondritic Nb/Ta (18–25), attributed to slab melt overprint. However, other Sunda arc rocks yield sub-chondritic Nb/Ta (13–18).

In accord with previous studies [3–5], the incompatible trace element inventory of Indonesian high-K lavas can therefore be attributed to partial melts derived from rutile-bearing mafic oceanic crust with a thick cover of sediment. The more fluid-dominated trace element enrichment in the sources of the other Sunda arc lavas is also related to subducted sediments, resulting in distinct trace element and isotope compositions.

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Karst versus sandstone and anthropogenic influences on small rivers of the Franconian Alb

J.A.C. BARTH*, M. MADER, R. VAN GELDERN, I. SCHREITER, P. ZIMMERMANN, T. TÜRK AND P. SCHULTE

GeoZentrum Nordbayern, Friedrich-Alexander Universität Erlangen-Nürnberg, 91094 Erlangen, Germany (*correspondence: barth@geol.uni-erlangen.de)

The small rivers Wiesent, Schwabach, Pegnitz and Regnitz drain the area of the Franconian Alb in Southern Germany, a typical karst terrain. Therefore the chemistry of the rivers should trace limestone weathering as the principal influence on river water composition. However, also urban influences by the city agglomeration of Nuremberg and signals of siliciclastic rock weathering may become more important in their lowland regions. Such changes of influence may best be studied in small rivers (< 52 $m^3 s^{-1}$ for the Regnitz and < 12 $m^3 s^{-1}$ for its tributaries) with major element and stable isotope analyses of dissolved organic and inorganic carbon. For instance, CO_2 partial pressures in the Wiesent River headwaters were up to 50 times higher than those in the atmosphere (> 21000 ppmV) and exceeded values found in African tropical rivers. For the Wiesent, such high pCO_2 values originate from soils and groundwater as they primarily occur in the groundwater-dominated source region. These waters are also characterized by carbon isotope signals of the dissolved inorganic carbon ($\delta^{13}C_{DIC}$) that are more negative than –14 per mil versus the VPDB standard. This deviates from typical values found in limestone weathering areas and indicates influences of CO_2 from recycled C3 plant material. These first data from the Wiesent indicate that weathering is not limited by CO_2. However, high pCO_2 values reduced rapidly towards values around 2500 ppmV over the course of the river due to degassing. In addition, lower reachers of the Wiesent showed dilutions in ion contents that may be related to increasing influences of sandstone weathering. First results of the other rivers studied showed mainly $\delta^{13}C_{DIC}$ signals of limestone weathering with values ranging around –12 permille and confirmed that carbonate weathering is the major control in these rivers. Influences of within-river turnover of dissolved organic carbon (DOC) may be revealed by simultaneous concentration and carbon isotope analyses.

Melting in the deep crust: Message from melt inclusions in peritectic garnet from migmatites

O. BARTOLI[1]*, B. CESARE[2], S. POLI[3], R.J. BODNAR[4], M.L. FREZZOTTI[5], A. ACOSTA-VIGIL[6] AND S. MELI[1]

[1]Dipartimento di Scienze della Terra, Univ. Parma, Italy (*correspondence: omar.bartoli@libero.it)
[2]Dipartimento di Geoscienze, Univ. Padova, Italy
[3]Laboratory of experimental petrology, Univ. Milano, Italy
[4]Fluids research laboratory, Virginia Tech, VA, USA
[5]Dipartimento di Scienze della Terra, Univ. Siena, Italy
[6]Instituto Andaluz de Ciencias de la Tierra, CSIC, Univ. Granada, Spain

S-type granites and leucosomes in migmatites provide information on the composition of crustal anatectic melts. However, their reliability as witnesses of primary anatectic melts has been questioned by several lines of evidence. Previously, the composition of the melt produced during crustal anatexis has been assumed from glass obtained in equilibrium melting experiments of crustal rocks. However, Cesare *et al*. [1, 2] have shown that peritectic minerals in migmatites can trap droplets of melt, that were formed by incongruent melting reactions during crustal anatexis.

We performed for the first time an experimental and analytical study of melt inclusions (MI) within peritectic garnets, using the metasedimentary migmatites from Ronda (S Spain). These garnets contain primary 2-10 μm MI that range from totally glassy to fully crystallized (*nanogranite*, [1]). Raman spectroscopy has documented the presence of liquid H_2O-filled micro-pores in nanogranites. Piston cylinder remelting experiments led to the rehomogenization of crystalline MI at conditions (700 °C, 500 MPa) close to those inferred for anatexis. Remelted MI have a peraluminous, granitic composition with high (up to 7.5 wt %) H_2O content; they overlap the composition of glassy MI, but differ from the composition of leucosomes in the host rock. Some CO_2 bubbles are present after remelting experiments, suggesting fluid present, $a_{H2O} < 1$ conditions, in agreement with graphite occurrence in the protolith. Our study identifies the natural anatectic melt composition and fluid regime at the onset of crustal melting, otherwise unknown. Hence, MI in migmatites represent a unique tool for the *in situ* characterization of anatexis in its early stages, and provide the only means of determining the volatile fluid content of anatectic melts.

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Lime lumps in gothic joint mortars from Kruszwica (Central Poland): An insight into the lime production

W. BARTZ[1]* AND M. RUDY[2]

[1]University of Wroclaw, Cybulskiego 30, 50-205 Wroclaw, Poland (correspondence:wojciech.bartz@ing.uni.wroc.pl)
[2] Nicholaus Copernicus University, Sienkiewicza 30/32, 87-100 Torun, Poland

In this study we present the complete characterization of joint mortars from the 'Mouse Tower'. The tower is a remnant of a gothic castle, erected in mid-14th century by King Casimir the Great.

All mortars comprise a calcitic binder (micrite) and a fine- to medium-grained inert aggregate, dominated by a detrital quartz. Smaller or larger binder-related particles, so called 'lime lumps' could be found in the micritic matrix. The inner part of these lime lumps is typically composed mainly of calcite crystal and aggregates of minerals rich in CaO and/or SiO_2, identified by means of SEM-EDX as wollastonite, silica (identified as cristobalite by means of XRD), belite (C_2S), minerals with a composition close to the melilite group (gehlenite-åkermanite) and less common rankinite. The core of lime lump is rimmed by a thin zone composed of micrite and unidentified amorphous silicates.

As suggested by different authors, the presence of lime lumps is attributed to low water/quick lime ratios for slaking, rapid slaking, slaking with excess of water, or technologies based on the nonseasoning of lime. However, in our particular case the lime lumps should be considered as overburnt lumps, formed due to local increase of the temperature above mean in the kiln.

The chemical analysis revealed that the percentages of acid soluble SiO_2, which indicates the existence of hydraulicity, reach very low values. The cementation index (C.I. <0.13) classifies the joint mortars as non-hydraulic. The volume of hydraulic phases (i.e. belite) is very small, they are enclosed in the almost impermable structure, thus their presence had no impact on the hydraulic properties of whole mortar.

On the basis of our studies, we conclude the joint mortar was poorly homogenized, non-hydraulic lime, derived presumably from the calcination of impure limestone rich in clay and silt, possibly the lacustrine chalk. Deposits of this material, very common in post-glacial lakes of northern Poland, occur in the Gopło Lake, situated in the nearest vicinity of the tower.

U-Pb zircon ages of the Alto Paranaíba and Juína kimberlitic provinces, Brazil

M. BASEI[1]*, D. SVISERO[1], W. IWANUCH[2] AND K. SATO[1]

[1]Instituto de Geociencias, USP-Brasil
(*correspondence : baseimas@usp.br)
[2]Faculdade de Geologia, UERJ, RJ, Brasil

This work presents a set of zircon U/Pb ages of kimberlitic and akin rocks of the Alto Paranaíba (Minas Gerais – Goiás) and Juína (Mato Grosso – Rondonia) provinces. The Alto Paranaíba province is composed of hundreds of Cretaceous bodies intrusive in the southwestern border of the São Francisco Craton. The Juína Province is in the NW portion of the Mato Grosso State.

Ten zircon concentrates from APP corresponding to the Mata da Corda Group conglomerate and 74 zircon concentrates from intrusive bodies of kimberlitic affiliation of the Coromandel region were studied. Sixteen fractions corresponding to nine intrusive bodies yield $^{206}Pb/^{238}U$ ages around 87.36 ± 0.75 Ma Two younger bodies yielded ages around 80 Ma. Ten analyses corresponding to three kimberlitic bodies of the Juína Province present older $^{206}Pb/^{238}U$ ages of 93.69 ± 0.43 Ma. Whole-rock isotopic studies (Sr, Nd and Pb) suggest that the Alto Paranaíba Province kimberlitic-type rocks show signatures distinct from those that characterize the South-African bodies. The whole-rock Sm-Nd age of 850 Ma is similar to the zircon U-Pb ages of most of the juvenile granites that characterize the initial phases of the Goiás magmatic arc. It is possible that this value indicates the time of an important mantle melting associated with the Neoproterozoic subduction process that led to the generation of the arc. This frozen lithospheric mantle coupled to the base of the São Francisco Craton would be the source of the Cretaceous kimberlites of the Alto Paranaíba Province.

Seepage of subsurface brines into a major lake system using Ra and stable isotopes of oxygen and hydrogen: A case study from Lake Huron

M. BASKARAN[1]*, T. NOVELL[1], S. RUBERG[2], B.A. BIDDANDA[3], T. JOHENGEN[4], N. HAWLEY[2] AND V. KLUMP[5]

[1]Department of Geology, Wayne State University, Detroit, USA (*correspondence: Baskaran@wayne.edu).
[2]GLERL, NOAA, Ann Arbor, USA
[3]Grand-Valley State Univ., Muskegon,USA
[4]CILER, University of Michigan, Ann Arbor, USA
[5]University of Wisconsin, Madison, USA

Exchanges of water between major reservoirs such as groundwater and lake water that are common can alter the biogeochemical cycling of chemical species and thereby affect relevant ecosystems. Recently discovered sinkhole vents in Lake Huron were found to discharge highly anoxic, reducing, high-sulfate and -chloride waters with strinkingly different chemical signatures.

We collected and analyzed a suite of water samples from three sinkhole vents and adjoining waters from Lake Huron for $\delta^{18}O$, δD, $^{223,224,226,228}Ra$ and a suite geochemical ancilliary parameters. Our results show: i) Ra concentrations in the vent waters are 1 to 2 orders of magntidue higher than that of the lake water; ii) A plot of δD vs $\delta^{18}O$ show considerable deviation from the Global Meteoric Water Line indicating mixing of different water masses that have undergone different evaporation cyles; and iii) The variations in the $^{223}Ra/^{226}Ra$ and $^{224}Ra/^{228}Ra$ activity ratios in the vent waters is related to the time-scales involved in the vertical movement of the vent waters. We also have modeled the variations in the Ra activity ratios in the vent waters to obtain time scales of transport from the source waters to the place where the vent water is discharged.

Comparing carbon isotopic signatures between meteorites and terrestrial mantle samples: Need for reassessment of carbon composition of Earth's mantle

S.BASU[1]*, S. MIKHAIL[1,2], A.P. JONES[1] AND A.B. VERCHOVSKY[2]

[1]Department of Earth Sciences, University College London (*correspondence: sudeshnabg@yahoo.com, s.mikhail@ucl.ac.uk, adrian.jones@ucl.ac.uk)
[2]PSSRI Open University, Milton Keynes (A.Verchovsky@open.ac.uk)

Carbon isotopic composition of Earth's mantle is supposed to be -5‰ based on mean values obtained from bulk measurements of oceanic basalts, carbonatites, diamonds and other terrestrial samples [1]. This value is the most significant assumption made in order to understand how carbon is cycled between the surface and interior of the Earth. But there are specific localities that exhibit different mean values, bimodality and outliers [2].

However, the value of -5‰ may not be representative of the entire mantle. Carbon compositions in the terrestrial mantle samples show considerable variations like E-chondrites, the fundamental building blocks of Earth [3]. The carbon composition of Earth does not coincide with the Martian mantle value of -20 ‰ although both the planets should have started with similar initial compositions [4]. Carbon can form various stable compounds in the mantle governed by different oxygen fugacity, and fractionation in isotopic composition is likely to occur under high pressure-temperature conditions [5]. It becomes important to reassess the mantle compositions of Earth, particularly since Si-rich carbide-bearing diamonds from great mantle depths (> 1100 km) is now available [6]. Following preliminary combustion investigations for carbon and nitrogen, measurements of carbon isotopic compositions of these Jagersfontein diamonds and inclusions at high resolution by NanoSIMS are underway.

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Measurements of ocean derived aerosol off the coast of California

T.S. BATES[1]*, P.K. QUINN[1], A. FROSSARD[2], L.M. RUSSELL[2], J. HAKALA[3], D.J. KIEBER[4] AND W.C. KEENE[5]

[1]NOAA PMEL, 7600 Sand Point Way NE, Seattle, WA 98115, USA (*correspondence: tim.bates@noaa.gov, patricia.k.quinn@noaa.gov)
[2]University of California, San Diego, CA, USA (afrossar@ucsd.edu, lmrussell@ucsd.edu)
[3]University of Helsinki, Helsinki, Finland (jani.hakala@helsinki.fi)
[4]State University of New York, Syracuse, NY, USA (djkieber@esf.edu)
[5]University of Virginia, Charlottesvile, VA, USA (wck@virginia.edu)

The oceans are a major source of aerosol number and mass to the atmosphere. Over the remote oceans, coarse-mode sea-salt particles dominate aerosol light scattering. Recent measurements suggest that direct emissions of ocean-derived particles also control the aerosol number concentration and thus the aerosol cloud condensation nuclei concentration. Measurements of atmospheric aerosols over the ocean include particles directly emitted from the ocean and particles produced by gas phase reactions in the atmosphere, making it difficult to distinguish between the two sources. Here we report recent measurements of particles directly emitted from the ocean using a newly developed *in situ* particle generator/sampler (SeaSweep). Bubbles were generated 1 m below the ocean surface alongside the research vessel *Atlantis* off the coast of California and swept into a hood/vacuum hose to feed a suite of instruments on board the ship measuring aerosol physical, chemical, optical, and cloud nucleating properties.

The number size distribution of the directly emitted (nascent) particles had a dominant mode at 55-60nm (dry diameter) and a secondary mode at 200-300nm. The aerosol was not volatile at 230°C. This temperature rules out ammonium sulfate and nitrate as significant components of the nascent aerosol but does not distinguish between particulate organic matter and sea salt. The organic component of the nascent aerosol volatilized at a temperature between 230 and 600°C. The nascent aerosol was not enriched in Ca, K, or Mg above that found in surface seawater. The submicrometer organic aerosol was primary composed of carbohydrates based on FTIR analysis. The nascent organic aerosol concentration did not increase in regions of higher surface seawater chlorophyll.

Geophysical and geochemical data used to infer origin and evolution of natural CO_2 in Italy

A. BATTANI, E. BROSSE AND C. LOISELET

IFPEN, Paris, France

CO_2-degassing is well documented throughout the whole Italian peninsula and previous studies based on geochemistry of gases have already shown the existence of different CO_2 sources, (Minissale *et al*., 1997) ranging from deep mantle-derived CO_2 related to volcanism, to more "crustal" sources", that are less documented. Italian Peninsula is characterized by a high R/Ra gradient increasing from the North to the South. Geochemical ratios (R/Ra and $CO_2/^3He$) fit quite closely to a mixing curve between a mantle-derived end member (in the south) and a crustal end member in the North.

The high R/Ra ratio recorded in Southern Italy is easily related to Calabria slab mantle wedge processes.
Concerning the central Italian volcanism, the R/Ra ratio reaches 4, indicating a strong influence of mantle-derived helium, with an important continental/ crustal contribution.

Geochemical (elemental and isotopic ratios) and seismological (P-wave tomography and SKS splitting) data support the existence of a large window in the Adrian plate underneath the southern Apennines. The influence of the slab mantle wedge is not observed here. However, window appears at the northern lateral Calabria slab edges allowing mantle inflow induced by the Calabria retrograde motion (Gasparini *et al*.,2002; Faccenna *et al*., 2005; 2007).

In the North-Central part of Apennines, the reported helium isotopic ratios point to a general prevalence of crustal influence (typical crustal values estimated around 0,02 and 0,05 Ra). A significant component of mantle-derived helium is only found in the geothermal areas of Larderello (Northern Italy) where a large thermal anomaly is present at depth. (Cloetingh *et al*., 2010). By combining geophysical and geological observations we propose to explain this local anomalous ratio by a local asthenospheric upwelling, probably associated with lithospheric delamination, or slab break off processes.

Using this approach, we provide a new insight on the origin of CO_2, and we propose a strong relationship between diagenesis and/or metamorphic processes associated with subduction dynamics, rather than thermal decomposition of carbonates.

Mussel shells as archives of geogenic and anthropogenic dissolved REE

M. BAU[1], G. MERSCHEL[1,2], S. KULAKSIZ[1], K. SCHMIDT[1], M. BRENNER[3], S. BALAN[1,4] AND A. KOSCHINSKY[1]

[1]Earth & Space Sciences, Jacobs University, Campus Ring 1, 28759 Bremen, Germany; (m.bau@jacobs-university.de)
[2]Environment and Resource Management, Free University, 1081 HV Amsterdam, Netherlands
[3]IMARE - Institute for Marine Resources GmbH, Klußmannstr. 1, 27570 Bremerhaven, Germany
[4]Environmental Science, Policy, and Management, UC Berkeley, 137 Mulford Hall, Berkeley, CA 94720, USA

Mussel shells may be used to evaluate trace element bioavailability, as the carbonate shell precipitates from the mussel's internal extrapallial fluid and not from external ambient water. We determined the REE distribution in shells of marine hydrothermal *Bathymodiolus* and littoral *Mytilus edulis* and of freshwater *Corbicula fluminea* mussels, and in the respective ambient river or seawater. Marine *Bathymodiolus* and *Mytilus edulis* shells reflect the presence and absence, resp, of positive Eu anomalies in their ambient waters, suggesting that positive Eu anomalies in mussel shells might be used to detect hidden or fossil high-temperature hydrothermal vent sites, thus helping exploration of VMS deposits [1]. Water from the Weser and Rhine rivers both display anthropogenic positive Gd anomalies that result from input of Gd used in MRI contrast agents, and the lower reaches of the Rhine River also show large an-thropogenic positive La anomalies [2]. While this La anomaly also occurs in *Corbicula* shells from the Rhine River, neither shells from the Rhine nor from the Weser River show a Gd anomaly. This demonstrates that in contrast to anthropogenic La, the Gd complexes used as MRI contrast agents are not bioavailable, which is further evidence of their conservative behaviour.

[1] Bau, M., Balan, S., Schmidt, K., Koschinsky, A. (2010) *Earth Planet. Sci. Lett*., 299, 310–316. [2] Kulaksiz, S. & Bau, M. (2011) *Environment International*, in press

Analysis of δD and $\delta^{18}O$ in clay minerals for reconstructing paleoenvironmental parameters

K. BAUER[1,2]*, T.W. VENNEMANN [1] AND A. MULCH[2]

[1]Institut de Minéralogie et Géochimie, Université de Lausanne, Switzerland (*correspondence: kbauer@unil.ch)
[2]Institut für Geowissenschaften, Johann Wolfgang Goethe-Universität Frankfurt am Main, Germany

Clay minerals in Molasse sediments are potential proxies for the stable isotope composition of Neogene paleowaters in the circum-Alpine region. To use this proxy requires the formation of clay minerals in weathering zones in equilibrium with ambient surface waters and no post-formational diagenetic nor low-grade metamorphic exchange with the fluid phase. Knowledge of the water-mineral fractionation factors at temperatures of formation permits an estimation of the isotopic composition of the paleowaters and allows to reconstruct paleoaltitude, paleoclimate and paleotopography.

The isotope analysis of clay minerals, however, proves to be a challenging task. In particular members of the smectite family are highly hygroscopic, leading to potentially falsified results of the isotope measurements if the adsorbed water is not removed. A number of tests and experiments were conducted in order to validate the most accurate as well as economical procedure of sample preparation. While $\delta^{18}O$ values are readily analyzed using a CO_2 laser fluorination line, the adsorbed water fraction may pose problems for the hydrogen isotope analyses using the TC/EA method. Prior to H-isotope analyses, it proves advantageous to evacuate the samples at elevated temperatures before rapidly transferrring them to the TC/EA for measurements. Additional analytical methods including XRD, TGA, SEM, and studies of organic matter within the sample material have been applied for actual samples as well as for standard materials in order to evaluate the effects of sample treatment on final measured values. The results were also cross-checked through an inter-laboratory comparison of the results obtained.

Once established, this modified preparation technique will be applied to clay mineral separates from stratigraphically distinct Molasse sediment horizons, as well to samples from recent soil profiles in the Swiss Alps, and bentonites from volcanic ash layers in Switzerland. The present results from Molasse clay minerals are in agreement with proxies of changes in paleoclimate from marine sediments and also with related isotope studies on material from high-Alpine fault zones of similar age.

Which emission sector is winning the mitigation competition when direct, indirect and semi-direct effects are investigated seperately?

SUSANNE E. BAUER[1] AND SURABI MENON[2]

[1]Columbia University and NASA Goddard Institute for Space Studies, New York NY, (sb2273@columbia.edu)
[2]Lawrence Berkeley National Laboratory, Berkeley CA, (smenon@lnbl.gov)

Attention has been drawn to black carbon aerosols, as a target for short-term mitigation of climate warming. Regulating soot emissions could, as a short-term action, potentially buy time by slowing global warming until regulations for long-lived greenhouse gases are set in place. The scientific community debates the impacts of such mitigation measures, and mitigation modelling studies show incoherent answers. One of the main reasons for the disagreement are semi-direct aerosol effects, that are neglected in some studies and included and dominating the overall results in others. In this study we apply the GISS/MATRIX model, a global climate model including detailed aerosol microphysics, to understand the single contributions of aerosol forcings and feedbacks. The study goes beyond black carbon mitigation by investigating the whole suite of aerosol sources and sectors of the CMIP5 emission data sets.

Our study finds a regionally divers picture. For example aerosol-cloud effects over the United States lead to reduced cloudiness through semi-direct effects and increased cloudiness by the indirect effect and the reversed phenomena is simulated over Europe. This response will be explained by the chemical composition of the emission mix in the different regions and its impact on black carbon coatings. The most promising emission mitigation sectors differ greatly between geographically regions and even among industrialized countries.

D_2O as tracer to study diffusion processes through the quartz crystal

M. BAUMGARTNER, G. DOPPLER AND R.J. BAKKER

University of Leoben, 8700 Leoben, Austria
(*correspondence: miriam.baumgartner@unileoben.ac.at)

Laboratory synthesised fluid inclusions in natural quartz are used to study diffusion processes of H_2O and D_2O molecules through the quartz crystal. Feedstock of re-equilibration experiments are pure H_2O inclusions synthesised at 600°C and 337 MPa which correspond to a molare volume of 25 cm^3/mole of the liquid phase. Those inclusions are exposed to a D_2O fluid at equal experimental conditions. Due to the concentration gradient (chemical potential) diffusion is induced and fluid exchange between the "pore fluid" and the fluid inclusions is expected. D_2O is used for re-equilibration experiments because it is easily identified in the inclusions due the increase of the melting temperature of ice (pure D_2O at +3.8 °C) and its typical Raman spectrum between 2200 – 2800 cm^{-1}. After five days of re-equilibration the inclusions shapes are strongly modified and ice melting temperatures up to +1.8 °C are observed, which corresponds to about 47 mass% D_2O. In addition, Raman spectra taken from those inclusions reveal high amounts of D_2O (see Figure below). Nevertheless, the concentration of D_2O vary significantly and inclusions with low and high contents can be found. This variation is mainly caused by the position of the inclusion in the quartz sample (3-dimensional distance from the quartz surface) and the total volume of the inclusion itself. In addition structural effects, like nano cracks and crystal defects affect the fluid flow through the quartz crystal.

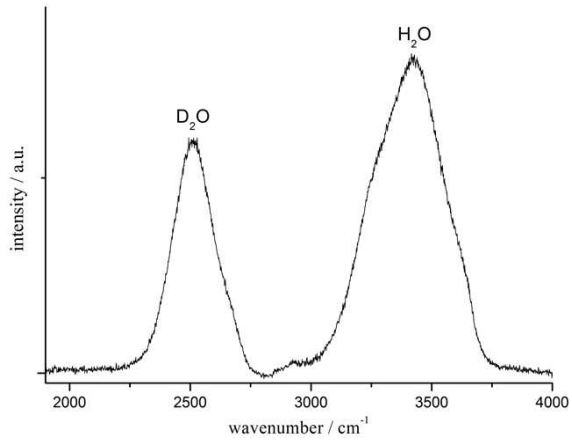

Figure 1: Raman spectrum of a fluid mixture of H_2O and D_2O measured in an inclusion after re-equilibration.

Microbially induced corrosion of depleted uranium metal in oxic soil

A.C. BAXTER[1,2] S. SHAW[3] M.N GARDNER[1] AND I.P. THOMPSON[4]

[1]Department of Earth Sciences, University of Oxford, UK
[2]AWE, Aldermaston, UK
[3]School of Earth and Environment, University of Leeds, UK
[4]Department of Engineering, University of Oxford, UK

To determine the enviomental impact of corroding depleted uranium (DU) munitions in oxic soils, fundamental information regarding the mechanisms and kinetics of DU breakdown are required. In particular, the key geochemical and microbiological factors which control the rate of corrosion. Previously, a study was conducted on DU metal pieces left *in situ* in two soil types (quartz rich dune sand and organic rich clay) for ≈8 years [1]. This concluded that a significant biological repsonse, e.g. oxalate production, was instigated from the indigenous microbes in response to the DU corroding in the soil, suggesting that microbes may have a significant influence on DU breakdown.

To detemine the microbial impact on the corrosion of DU metal, microcosm experiments were set up containing DU metal piece in a slurry containing either sterile soil or soil with the intact indigenous microbial communities.

After 5 months *in situ* corrosion had only occured in the microcosms containing the viable indigenous microbes (Figure 1).

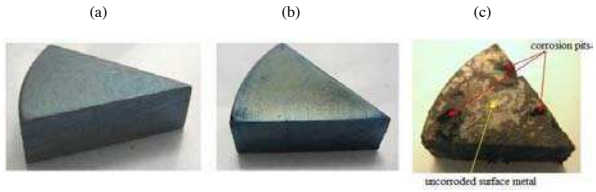

Figure 1: Digital photograph of the DU metal pieces (a) before addition to the microcosms, and after 5 months in situ in (b) sterile soil and (c) soil with viable indigenous microbial communities.

Imaging the DU metal pieces showed considerable pitting corrosion had occured on the surface. Within these pits bubble-like structures were observed which may have been caused by hydrogen generation at the metal surface. Fluorescent staining of the DU metal demonstrated diverse microbial communities had colonised within the corrosion pits.

[1] S. Shaw, *et al*. (2007) Geochemical and microbiological controls on the corrosion and transport of depleted uranium in soil. *Geochim. Cosmochim. Acta* **71**(15) A925

Causes of pulsed mineral growth during metamorphism

ETHAN F. BAXTER*[1,2], MARK J. CADDICK[2], ALAN B. THOMPSON[2], BESIM DRAGOVIC[1], ANTHONY D. POLLINGTON[1,3] AND JAY J. AGUE[4]

[1]Boston University, Department of Earth Science, Boston MA, 02215, USA (*correspondence: efb@bu.edu)
[2]ETH Zurich, Institute for Geochemistry and Petrology, 8006 Zurich, Switzerland
[3]University of Wisconsin, Department of Geoscience, Madison, WI, 53706, USA
[4]Yale University, Department of Geology & Geophysics, New Haven, CT, 06520-8109, USA

A growing set of observations suggests that metamorphic processes and conditions frequently are pulsed or episodic in nature rather than steady and long-lived. We recognize a "pulse" as any process, condition, or manifestation thereof that persists or dramatically accelerates for a brief period of time (relative to the general timescale of background tectonic/geologic forcing). Such pulses may include some or all of the following, which may not always be genetically linked: increased temperature, fluid influx, magmatism, and deformation, any of which may also promote mineral growth (and thus potentially be recorded therein).

Mineral growth pulses can have different causes. We describe three end-member possibilities here. First, rapid changes in *P* or *T* can drive more rapid mineral growth by quickly moving rocks through sets of reaction isopleths requiring compositional or modal change. Thermal pulses require mechanisms for rapid heating followed by focused heat dissipation, not possible via conductive heat transfer alone. For example, advective heat flow, provided by migrating syn-orogenic magmas and/or related fluids can contribute to thermal pulses. Or, rapid changes in P (and T) may accompany deformation during vertical motion in shear zones or thrusts. Second, steadily changing *P* and *T* can also produce pulsed mineral growth if reaction isopleths become closely (and/or orthogonally) spaced along portions of the *P-T* path. Third, a kinetic trigger (such as the introduction of a catalyzing fluid, which itself may be related to a pulse of dehydration or deformation) can permit a thermodynamically overstepped reaction to suddenly activate. Using vividly documented examples of mineral growth pulses [1,2] and thermal pulses [3], we explore different pulses, their possible causes, and the likely extent of their interactions.

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A global distribution map for Nd isotopes in European watersheds

G. BAYON*, S. TOUCANNE*, N. FRESLON AND E. PONZEVERA

Département Géosciences Marines, IFREMER, Plouzané, France (* correspondence : gbayon@ifremer.fr; stoucann@ifremer.fr)

The Nd isotopic composition of the detrital fraction of a sediment provides information on the geographical provenance of that material. Aplication of the ε_{Nd} proxy to sedimentary records can be used to deduce sediment input variations, and hence to constrain fluctuations in transport mechanism.

In this study, we have compiled literature data for Nd isotopes in river sediments from all over Europe. This compilation was completed by analysing an extensive series of fine-grained sediments collected from various european rivers, estuaries, upper continental shelves and endorheic basins. For each sediment, the obtained ε_{Nd} value was taken as representative of the corresponding drainage basin signature. The result of this work is a global distribution map for Nd isotopes in european watersheds, which covers about 70% of the continent.

Based upon this map, we will discuss on the potential of using Nd isotopes for adressing some of the key issues related to the Late Quaternary environmental history of Europe.

Zinc and cadmium behavior in low-density fluids

E.F. BAZARKINA[1]*, G.S. POKROVSKI[2], N.N. AKINFIEV[1] AND A.V. ZOTOV[1]

[1]IGEM RAS, 119017 Moscow Russia (*correspondence: elenabaz@igem.ru)
[2]GET, Géoscience, Environnement Toulouse , 31400 Toulouse, France

Low-density fluids and vapors (density ≤ 0.5-0.3 g/cm^3) are ubiquitous in the Earth crust from moderate depth (vapor-brine immiscibity) to the surface (volcanic degassing). Quantitative understanding the transport capacity of such fluids for metals is, however, weak owing to both experimental difficulties and imperfections of classical thermodynamic models (e.g., HKF) when applied to the low-density aqueous phase. Our study is aimed at quantifying the transport of Zn and Cd, typical base metals, in such phases. We combined solubility measurements of ZnO and CdO in H_2O and H_2O-NaCl-HCl fluids and vapors and Zn and Cd vapor-liquid partitioning experiments in water-salt systems across a wide range of temperature, pressure and density (T = 350-450°C, P = 150-600 bar, d = 0.01-0.5 g/cm^3) with physical-chemical modeling.

Results reveal significant differences in the behavior of Zn versus Cd in low-density fluids in the presence of chloride. For example, the Cd/Zn ratio in the H_2O-NaCl-HCl vapor in equilibrium with CdO and ZnO increases with increasing Cl content, which demonstrates a stronger stability of Cd-Cl complexes compared with their Zn analogs. Our thermodynamic model [1] allow accurate description of the obtained solubility data using the neutral chloride and hydroxide species of Zn and Cd. These findings in homogenous fluids are in agreement with our data in dense aqueous solution [2], and vapor-liquid distribution measurements, which demonstrate that although both Zn and Cd partition in favor of the dense Cl-rich brine, vapor-liquid partition coefficients ($K = m_{vapor}/m_{liquid}$) for Cd are much lower than for Zn (e.g., log K ~ -5.5 and -3.3 at 450°C/280 bar for Cd and Zn, respectively). The different stabilities of Cd- and Zn-Cl complexes may play a key role in Cd fractionation by low density fluids, and explain the elevated Cd/Zn ratios in volcanic gases compared to the mean Earth crust value.

[1] Akinfiev and Diamond (2003) *GCA* **67,** 613–627. [2] Bazarkina *et al*. (2010) *Chem. Geol*. **276**, 1-17.

Reactive transport modelling of natural carbon sequestration in ultramafic tailings

S.A. BEA[1,2], K.U. MAYER[1], S.A. WILSON[1,3] AND G.M. DIPPLE[1]

[1]Department of Earth and Ocean Sciences, University of British Columbia, 6339 Stores Road, V6T 1Z4, Vancouver, BC, Canada.
[2]now at: Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA (sabea@lbl.gov)
[3] now at: Department of Geological Sciences, Indiana University, Bloomington, IN, USA

Anthropogenic CO_2 is naturally sequestered in ultramafic mine tailings as a result of the weathering of serpentine minerals [$Mg_3Si_2O_5(OH)_4$] and brucite, and subsequent mineralization of CO_2 in hydrated magnesium carbonates such as hydromagnesite, $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$ [1]. Understanding the CO_2 trapping mechanisms is key to evaluating the capacity of such tailings for carbon sequestration.

Natural CO_2 sequestration in ultramafic tailings at a mine site near Mount Keith, Australia is assessed with a modified version of the process-based reactive transport code MIN3P [2]. The model formulation includes energy and vapor transport fully coupled with fluid conservation in the aqueous phase and geochemical reactions. Atmospheric boundary conditions accounting for the effect of climate variations are also included. Kinetic dissolution of chrysotile, dissolution-precipitation of brucite [$Mg(OH)_2$] and primary carbonates [i.e. calcite, $CaCO_3$; dolomite, $MgCa(CO_3)_2$; magnesite, $MgCO_3$] as well as the formation of hydromagnesite, halite (NaCl), gypsum ($CaSO_4{\cdot}2H_2O$), blödite ($Na_2Mg(SO_4)_2{\cdot}4H_2O$) and epsomite ($MgSO_4{\cdot}7H_2O$) are considered.

Simulation results at ten years are consistent with field observations. Precipitation of hydromagnesite is predicted, and is mainly controlled by the dissolution of chrysotile (the source of Mg) and the equilibrium with the CO_2(g) ingressing from the atmosphere. The predicted rate for CO_2 entrapment in these tailings is 1.2 kg m^{-2} year^{-1}. Modeling results suggest that this rate is sensitive to CO_2 fluxes through the mineral waste and may be enhanced by several mechanisms, for instance by atmospheric pumping.

[1] Wilson, S. A., Dipple, G. M., Power, I. M., Thom, J. M., Anderson, R. G., Raudsepp, M., Gabites, J. E., Southam, G., (2009). *Economic Geology*, **104**, 95–112. [2] Mayer, K. U., Frind, E. O., Blowes, D. W., (2002). *Water Resources Research*, **38**, 1174.

Distribution and activity of iron-oxidizing microorganisms in acidic geothermal environments

J.P. BEAM[1], H.C. BERNSTEIN[2], M.A. KOZUBAL[1], R. P. CARLSON[2] AND W.P. INSKEEP[1]*

[1]Department of Land Resources and Environmental Sciences and Thermal Biology Institute, Montana State University, Bozeman, MT 59717, USA (*correspondence: jacob.beam@msu.montana.edu, binskeep@montana.edu)

[2]Department of Chemical and Biological Engineering and Center for Biofilm Engineering, Montana State University, Bozeman, MT 59717, USA

Iron oxide mats of acidic geothermal springs in Norris Geyser Basin, Yellowstone National Park are inhabited by numerous deeply-rooted members of the domain *Archaea*. Microorganisms of the order Sulfolobales (e.g., *Metallo-sphaera yellowstonensis* and other novel phylotypes) have previously been shown to be important community members and are likely responsible for the oxidation of Fe(II) and subsequent formation of Fe(III)-oxide mats. Iron-oxidizing microorganisms are hypothesized to thrive in more oxic regions of Fe(III)-oxide mats and are likely most abundant at the water/mat interface where oxygen concentrations are high relative to deeper mat positions. The current study investigated the relationship among vertical distribution of specific microorganisms, mRNA transcript levels of genes involved in Fe(II)-oxidation, and corresponding oxygen gradients measured *in situ*.

Quantitative PCR primers designed around specific phylotypes were used to determine the vertical distrbution of organisms within the Fe(III)-oxide mats. Similarly, mRNA transcripts of genes, thought to be important in Fe(II)-oxidation (i.e., Fe-specific heme copper oxidases), were amplified with primers designed for various Fe(II)-oxidizing microbial populations.

Results suggest that the spatial distribution of aerobic Fe(II)-oxidizing microbial populations correspond with measured oxygen gradients. Specifically, Fe(II)-oxidizing microorganisms become less abundant at depths below ~600 μm corresponding to depths where dissolved oxygen concentrations approach detection. Transcripts of genes (mRNA) previously shown to be involved in Fe(II)-oxidation are well represented in the top 600 μm-layer. This study highlights the important linkage among hydrodynamics, oxygen in-gassing and diffusion, and the spatial location of active Fe(II)-oxidizing microorganisms (and associated transcription of specific genes) in the biomineralization of Fe(III)-oxide phases in acidic geothermal environments.

Residence time analysis of metal-desorption and mineral-dissolution kinetics using a Damkohler approach

LINDSAY BEARUP[1], ALEXIS NAVARRE-SITCHLER[2], REED MAXWELL[3] AND JOHN MCCRAY[1]

[1]Hydrologic Science and Engineering, Colorado School of Mines, Golden CO; (lindsaybearup@gmail.com)

[2]Environmental Science and Engineering Division, Colorado School of Mines, Golden CO

[3]Department of Geology and Geological Engineering, Colorado School of Mines, Golden CO

Understanding processes that control coupled reaction and transport in contaminated and natural systems is important for predicting the behavior of metals. Mineral dissolution and metal desorption are two important processes that govern metal behavior. Reactive transport studies often assume that desorption occurs instantaneously and therefore apply thermodynamic equilibrium models, or that mineral dissolution is so slow that it is not relevant. This study investigates groundwater time scales where kinetic metal desorption and/or mineral dissolution are important mechanisms for accurate modeling of metal fate and transport. Compiled desorption reaction times for metal and metalloid rate constants show large variations, spanning over six orders of magnitude. Mineral dissolution rate constants span over thirteen orders of magnitude and overlap with the range of desorption rate constants.

The Damkohler number was used to calculate residence times where kinetic formulations for dissolution and desorption may be more accurate representations of metals behavior. According to this method, metal desorption kinetics are influential at residence times from a few days to ~ 2 years. For longer residence times, metal desorption should behave according to equilibrium desorption models. In constrast, kinetic mineral dissolution should be considered over nearly all residence times and length scales relevant to groundwater modeling. Groundwater models with residence times of minutes up to ~600 days should potentially consider both metal desorption and mineral dissolution rates, with greater residence times exhibiting equilibrium behavior and shorter residences resulting in negligible change in metal concentrations. Ultimately, this Damkohler analysis provides constraints on relevant metal release mechanisms for models of metal fate and transport, such as those used in the fields of carbon sequestration and acid mine drainage. Additionally, the results can be used in experimental design to determine the setup required to measure the desired variable, i.e. kinetic or equilibrium characteristics.

Fe kinetics of marine particle uptake and desorption determined from laboratory experiments

ANNA BECK* AND JESS ADKINS

Caltech, Geological and Planetary Sciences, Pasadena, CA 91125 (*correspondance: abeck@caltech.edu)

Particle residence times in the ocean are short enough for the adsorption and desorption of Fe(III) from marine particles to control the dissolved [Fe] profile. Previous laboratory experiments measured Fe(III) uptake rates using radiotracers under simulated natural conditions and in the presence of various particles. However, since at least 99.9% of dissolved Fe(III) in the ocean is bound to organic ligands, we carried out similar laboratory experiments with Fe(III) bound to desferryoxamine B, a naturally occurring siderophore, and used ^{54}Fe as a tracer.

We find the adsorption of ^{54}Fe onto a fresh, labile iron oxide (ferrihydrite) to be first order dependent on particle concentration and has a rate of -0.17 (±0.05) pmol Fe/(mg particle)/day. Experiments with ferrihydrite concentrations of less than 200 mg/L reach steady state after 100+ days, a time period two orders of magnitude larger than particle residence times in the water column, underscoring the significance of the adsorption kinetics on the profile of [Fe]. The uptake of ^{54}Fe onto clay (montmorillonite) has a very fast (<10 min) initial uptake followed by a slower, possibly first order, absorption that are both dependent on particle concentration. In stark contrast to clay and ferrihydrite, there is insignificant absorption of ^{54}Fe onto 3 other types of marine particles—stable iron oxide (goethite), opal (pulverized diatoms), and carbonate shells (forams). In desorption experiments, we find that 1) all particle types reach steady state in 1 week or less, and 2) the uptake mechanism onto ferrihydrite is irreversible. Fe cycling models currently lack these differences in particle preference and their respective rates.

Reconciling abundances of highly siderophile elements and major volatiles in the silicate and near-surface Earth

H. BECKER[1]* AND M. FISCHER-GÖDDE[2]

[1]Institut für Geologische Wissenschaften, Freie Universität Berlin, Malteserstrasse 74-100, D-12249 Berlin, Germany (*correspondence: hbecker@zedat.fu-berlin.de)

[2]Institut für Planetologie, Universität Münster, Wilhelm-Klemm-Strasse 10, D-48149 Münster, Germany

Ratios of highly siderophile element (HSE) abundances permit to distinguish between different classes of chondrites and may help in tracing the presence and evolution of differentiated metal and the differentiation of planetary crusts and mantles. The HSE can also play an important role in constraining the origin of the more abundant highly volatile elements in the terrestrial planets, in particular, if both groups of elements were added after core formation and the magma ocean stage. Recent constraints from peridotites and komatiites suggest that the relative abundances of Ru and Pd in the silicate Earth are suprachondritic. In contrast, other HSE show chondritic relative abundances, with Re/Os and Rh/Ir more similar to ratios in ordinary or enstatite rather than carbonaceous chondrites. HSE abundances and geochronological data for pre-3.8 Ga lunar impact rocks indicate that at least two ≥4.2 Ga old meteoritic components occur widely dispersed across the lunar nearside: a somewhat volatile element depleted (carbonaceous?) chondritic component in granulitic impactites and in some impact melt rocks, and a differentiated metal component, similar to some IVA iron meteorite compositions. The Earth may have accreted similar materials after 4.5 Ga, however, much larger quantities would be necessary to explain the HSE abundances in the Earth's mantle. Late accretion of 80-85 % of a slightly volatile depleted carbonaceous chondrite composition and 15-20 % of differentiated metal reproduces integrated abundances of the HSE, S, H, C and N in the silicate Earth + atmo- and hydrosphere, remarkably well, and would be consistent with the isotopic composition of S, H, C and N. Small discrepancies in abundances may reflect poorly known partition coefficients (Rh) and volatile loss (N). Reqired HSE abundances in the metal are equivalent to abundances in liquid metal that has fractionated 40-60% solid metal in the core of a ~2000 km diameter protoplanet. In order to prevent segregation of metal into the Earth's core, the bulk of this material should have accreted some time after the giant impact and solidification of the terrestrial magma ocean.

Atomistic approaches to determine redox reaction mechanisms of U, Np, and Pu on mineral surfaces

U. BECKER, L. SHULLER, D. RENOCK AND R. EWING

University of Michigan, Department of Geological Sciences, 2534 CC Little, Ann Arbor, MI 48109

The rich redox chemistries of U, Np, and Pu control the chemical and physical properties of nuclear materials at different stages in the nuclear fuel cycle from extraction to disposal. The redox chemistry of the actinides can be predicted based on the Eh-pH conditions; however, adsorption to mineral surfaces and redox reactions on the surface are impacted by the physicochemical properties of the mineral surface itself.

In recent studies, our research groups as well as others have been challenging the traditional way redox processes are being treated in the near-surface environment. One example that has been studied is the complicated interplay between uranyl complexes, sulfide/oxide surfaces, and organic and inorganic reductants. Our findings indicate that, despite many decades of research, the key controls of surface-mediated mechanisms and, hence, the rates of environmentally-important redox processes are still poorly understood. There are a number of reasons for this: 1) these processes almost always involve a complex series of elementary reactions, each involving the transfer of one electron at a time, 2) it can be unwieldy to resolve the influence of individual environmental parameters (pH, pe, pO2, concentration of other oxidants and reductants, other ions in solution, temperature, etc.) in rate experiments, 3) it can be challenging to differentiate rate constants for heterogeneous (surface) processes and homogeneous (solution) processes in order to assess the catalytic effects of the surface itself, and 4) rate-limiting processes such as spin transitions have been widely ignored so far. Our calculations address fundamental questions with regard to many different redox systems: Does the mineral surface directly participate in the redox event or indirectly participate by acting as a heterogeneous catalyst or an electron shuttling device for the transport of charge (and/or spin) between co-adsorbates.

Methane formation in abandoned coal mines: Role of acetogens and acetoclastic *Methanosarcinales*

S. BECKMANN[1]*, T. LÜDERS[2], M.KRÜGER[3], F. VON NETZER[2], B. ENGELEN[1] AND H. CYPIONKA[1]

[1]ICBM, Univ. of Oldenburg, Oldenburg D-26129, Germany (*correspondence: s.beckmann@icbm.de)
[2]IGOE, Helmholtz Zentrum Munich, D-85764, Germany
[3]BGR, Geomicrobiology, Hannover D-30655, Germany

Mine gas has come into the focus of the power industry and is being used increasingly for heat and power production. Worldwide, about 7% of the annual methane emissions originate from coal mining. In abandoned coal mines, stable carbon and hydrogen isotopic signatures of methane indicate a mixed thermogenic and biogenic origin. While thermogenic methane is a remainder of geological processes, biogenic formation is still going on [1]. Besides hard coal, possible sources for methane are large amounts of mine timber left behind after the end of mining.

In two abandoned coal mines in Germany, methanogenic archaea are responsible for the production of substantial amounts of methane [2]. The mines are characterised by low O_2 concentrations at high humidity and fungal mats mainly on the mine timber. We analysed active methanogens as well as the active bacteria involved in the trophic network by stable isotope probing (DNA-SIP). Therefore, the ^{13}C-labeled precursors of methane (acetate and H_2+CO_2) were fed to liquid cultures from hard coal and mine timber. Directed by the methane production kinetics, samples for DNA-SIP coupled to subsequent quantitative PCR and DGGE analyses were taken from long term incubations over 6 months. Surprisingly, the formation of ^{13}C-methane was linked to acetoclastic methanogenesis in both, the ^{13}C-acetate and H_2+$^{13}CO_2$-amended cultures of coal and timber. H_2+$^{13}CO_2$ was mainly used by acetogens related to *Pelobacter acetylenicus* and *Clostridium* species. Active methanogens, closely affiliated to *Methanosarcina barkeri*, utilized the readily available acetate rather than the thermodynamically more favourable hydrogen. Thus, the methanogenic microbial community appears highly adapted to the environment where acetate is a much more prominent intermediate than H_2.

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PGE reference material heterogeneity – Estimating minimum analytical mass

L. PAUL BÉDARD[1], KIM H. ESBENSEN[2] AND SARAH-JANE BARNES[3]

[1]Sciences de la Terre, Université du Québec à Chicoutimi, Chicoutimi, Qc Canada; (pbedard@uqac.ca)
[2]Geological Survey of Denmark and Groenland, Copenhagen, Denmark; (ke@geus.dk)
[3]Sciences de la Terre, Université du Québec à Chicoutimi, Chicoutimi, Qc Canada; (sjbarnes@uqac.ca)

Very small analytical masses (mg to ng) are dictated by modern analytical instruments, either because of their high sensitivity, analytical protocols or because of the small sampling volume of micro-beam techniques. But small sample masses can create problems when trace elements are major constituent in some minerals (e.g. PGE as PGM) and are irregularly distributed in samples or reference materials. Accidental inclusion or exclusion could change the spatial concentration realised simply due to spatial heterogeneity issues [1,2]. Such effects influence mass balance calculation and element budgets. Recommended minimum mass for reference materials is generally determined by analysing smaller sample mass until variance become unacceptable. Is there a way to determine minimum sample mass directly related to RM heterogeneity? And is it identical for all analytes, or unique for each analyte, in each sample? In order to systematically investigate these questions, pressed-pellets of PGE-bearing reference materials (CHR-Bkg, CHR-Pt+, MASS-1, MASS-3, WMS-1, WMS-1a) were analysed with an EDAX EAGLE III micro-XRF. Approximately 10 000 contiguous measurements were made with a beam of 50 μm covering a total area of about 25 mm^2. Up to 25 analytes were measured including precious metals. Reproducibility was determined by analyzing the same location 1 000 times. In order to express the empirical heterogeneity, Angle Measure Technique (AMT) was employed [2]. The AMT transform describe the elemental map complexity as a function of geometrical scale from local to global. AMT provides a quantitative measure of the empirical heterogeneity for each element, RM, or analytical sample. From such results a minimum analytical mass for each analyte is proposed to ensure that analytical results are representative all the way down to the scale of RM fields-of-view. The proposed technique offers the advantage of defining the *effective* minimum mass for each analyte with better elemental sensitivity by allowing for a more meaningful estimation of the *global* minimum analytical mass.

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Groundwater flow impacts on sediment biogeochemistry: A multivariate statistical approach

J. BEER[1,*], C. NEUMANN [1], J.H. FLECKENSTEIN[2], S. PEIFFER[1], AND C. BLODAU[3]

[1]Department of Hydrology, University of Bayreuth, Germany (*correspondence julia.beer@uni-bayreuth.de)
[2]Department of Hydrogeology, Helmholtzzentrum für Umweltforschung, Leipzig, Germany
[3]Department of Environmental Geology, University of Guelph, Kanada

Lakes in (former) mining areas are strongly affected by Pyrite oxidation leading to high loads of iron and sulfur and the acidification of local waterbodies. Whereas the groundwater surrounding such lakes is mostly only weakly acidic, the pH of acidic mine lakes (AML) often lies below about 3 due to iron oxidation and subsequent Schwertmannite precipitation. It has been described that advective and diffusive flow through AML sediments affect the distribution of solutes and the biogeochemical driver pH in such sediments (e.g. Beer *et al*., 2009).

To study the influence of groundwater – lake water – exchange on sediment biogeochemistry, we measured exchange rates along with sediment composition at 19 sites at an anthropogenic AML near Lauchhammer, Germany.

The pattern of the exchange rates was temporally and spatially heterogenous. Groundwater inflow dominated in the northern part of the lake and often exfiltration of acidic lake water was measured in the southern part.

To analyze the effects on the sediment, we cut sampled sediment cores according to color and textur into 3-5 layers and measured pH, sulfate reduction, contents of reduced sufur species and carbonate, etc., and analyzed the results by multivariate statistical analysis. E.g. using cluster analysis, samples were grouped into 7 clusters which showed two different spatial patterns: 1) vertically, samples representing “fresh” sediment were observed in upper layers whereas “older” sediment samples were present at depth 2) clusters combining samples with higher biogeochemical activity and higher amounts of e.g. reduced iron sulfur species, and thus trapped acidity, prevail in the northern part of the lake. This second cluster could be related to the predominance of groundwater inflow in this part of the lake.

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Water content and OH speciation in natural Fe-bearing pyroxenes

K. BEGAUDEAU[1], Y. MORIZET[2] AND J-C.C. MERCIER[1]

[1]LIENSs, University of La Rochelle, La Rochelle, France
[2]LPGN, University of Nantes, Nantes, France
(*correspondence: yann.morizet@univ-nantes.fr)

H in NAMs plays a crucial role on the physical and chemical properties of the Earth's mantle [1]. FTIR and NMR analyses were used to measure H contents and constrain OH dissolution mechanisms for natural Fe-bearing pyroxenes of 40 mantle xenoliths brought up by alkaline basalts magmas. Crystal chemistry was analyzed by EMPA. Equilibrium P-T conditions were determined by a new geothermobarometer developped yielding T°C=644-1151 and P(GPa)=0.85-2.7. Polarized FTIR spectra display the main absorption bands in OH species region. H_2O estimates [2] range between 38-450 ppm H_2O for cpx and 19-184 ppm H_2O for opx. Cpx/Opx partionning coefficients range to 0.6-3.7. H_2O variations seem correlated to fO_2, P, T and crystals chemistry allowing us development of geohygrometers.

^{1}H, ^{27}Al, ^{29}Si MAS NMR were also carried out with different magnetic fields. ^{1}H spectra are not exploitable because of paramagnetic components [3]. Their influences on the change of NMR spectral features are tested with mixtures of kaolinite + magnetite. ^{29}Si and ^{27}Al spectra are slightly affected. Tests on pyroxenes show an Al species distinction. Additional data reveals H proximity around Al species confirming relationships described by FTIR [4]. Thus, the use of both spectroscopic methods opens new perspectives for mineralogy and geochemistry of mantle's peridotites.

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Decarboxylation of fatty acids during petrogenesis: Qualitative and quantitative analyses of bitumen NSOs by FTICR-MS

F. BEHAR[1], E. SALMON[2], A.W. KAMGA[2] AND P.G. HATCHER[2]*

[1]IFP Energies Nouvelles, 1-4 avenue de Bois Préau, Rueil-Malmaison 92500, France.
(Francoise.BEHAR@ifpenergiesnouvelles.fr)
[2]Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529. (esalmon@odu.edu, akamga@odu.edu, *correspondence: phatcher@odu.edu)

The NSO compounds generated during the artificial maturation of kerogen from Green River Formation were collected by successive *n*-pentane and dichloromethane (DCM) extractions and analyzed using electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FTICR-MS). Compounds containing only CHO elements in their make-up are dominant in each spectrum and are comprised mostly of the series $C_nH_{2n}O_2$, $C_nH_{2n-2}O_2$, $C_nH_{2n-2}O_4$, and $C_nH_{2n-10}O_2$ which all correspond to carboxylic acid-containing compounds. By calibrating the FTICR-MS with internal standard, it was possible to assign a response factor for the carboxylic acids and consequently get better quantification of the total carboxylic acids content. This response factor is invariant in the carbon number range of C_{20} to C_{40}. Also, after calibration, the carboxylic acid yield remains dominant among the other peaks detected by FTICR-MS. The same quantitative strategy was used for determining the response factor of the alcohols and dicarboxylic acids in order to determine the quantitative proportions of these functional groups in the NSOs.

Results clearly demonstrate that hydrocarbon generation from kerogen is mainly attributed to decarboxylation of the NSOs compounds. Moreover, there is a strong qualitative and quantitative relationship between the hydrocarbon distributions and the fatty acid distributions. For example, the carbon preference index for hydrocarbons matches exactly that observed for the fatty acids.

Combined WAXS/XAFS measurements for studying the reaction of S(-II) with lepidocrocite

T. BEHRENDS[1], K. HELLIGE[2], M. SILVEIRA[3] AND S. PEIFFER[2]

[1]Utrecht University, Faculty of Geosciences, NL-3508 TA Utrecht, The Netherlands (behrends@geo.uu.nl)
[2]Department of Hydrology, University of Bayreuth, D-95440 Bayreuth, Germany
[3]Katholieke Universiteit Leuven, DUBBLE beamline, ESRF, 38043 Grenoble, France

The reaction of sulfide (S-II) with iron oxides is an important process linking the redox cycles of iron and sulfur in many subsurface environments. Here, we studied the reductive dissolution of lepidocrocite (γ-FeOOH) by S(-II) in batch reactors at constant pH. A combination of wide angle X-ray scattering (WAXS) and X-ray absorption spectroscopy (XAS) at the Fe K-edge (about 7.1 keV) was used to follow on line the progress of the reaction.

Addition of Na_2S solution to the lepidocrocite suspension led to a fast decrease in intensity of the characteristic lepidocrocite diffraction peaks. This change in the WAXS signal was larger than expected from the stoichiometric amount of consumed lepidocrocite and indicates that the long range order of the crystals was profoundly disturbed upon the attack of sulfide.

Principle component analysis of all collected XANES spectra revealed that the combination of two spectra is sufficient to reproduce the major features of all spectra. The two components can be attributed to the spectrum of Fe(III) in lepidocrocite and to that of Fe(II) tetrahedrally coordinated with S. The stoichiometry of the reaction regarding the consumption of H^+ and S(-II) per reacted Fe(III) was derived from relating the change in XANES spectra to the amount of acid, which was added during the experiment, and to the different amounts of initially added sulfide, respectively.

Analyses of EXAFS spectra demonstrated that mackinawite was not the product of the reaction, while mackinawite was shown to form when Na_2S solution was added to Fe^{2+} solution under the experimental conditions.

These observations suggest, that the reaction of lepidocrocite with S(-II) does not follow a surface controlled mechanism in which the release of Fe(II) from the surface is required for the reaction to proceed. An alternative mechanisms will be presented and the differences between observed and expected stoichiometric coefficients will be discussed.

Lithospheric control on geochemical composition of the Louisville Seamount Chain

CHRISTOPH BEIER[1], MARCEL REGELOUS[1], JOHN MAHONEY[2], LOŸC VANDERKLUYSEN[2] AND KARSTEN HAASE[1]

[1]GeoZentrum Nordbayern, Universität Erlangen-Nürnberg, Schloßgarten 5, D-91054 Erlangen, Germany. (Christoph.Beier@gzn.uni-erlangen.de)
[2]Department of Geology and Geophysics, University of Hawai'i Mānoa, 1680 East-West Road, Honolulu, HI 96822, USA

Chemical changes with time in lavas erupted on long-lived seamount chains can be used to test models for the origin of intraplate magmatism and examine the effect of sub-seamount lithosphere on volcanism. Major and trace element and Sr, Nd, and Pb isotope data for lavas from 12 seamounts along the westernmost 1500 km of the Louisville Seamount Chain (LSC) in the SW Pacific show that magmatism was compositionally remarkably uniform between 80 and 40 Ma. All 56 samples analysed are alkalic or transitional; most are basalts. The youngest lavas from a given seamount tend to have the least enriched incompatible element compositions. Unlike Hawaiian volcanoes, Louisville volcanoes appear not to pass through a tholeiitic shield-building stage. The oldest Louisville seamounts formed close to the Osbourn Trough fossil spreading centre, but there is no obvious effect on the composition of LSC lavas. Nor do Osbourn Trough MORB contain any contribution from Louisville mantle, which suggests that spreading at the Osbourn Trough ceased well before the construction of Osbourn Guyot at 79 Ma. Lavas from volcanoes in the central part of the LSC are more variable and extend to more enriched compositions. These volcanoes tend to be smaller and more widely spaced, and were underlain by the oldest, thickest oceanic lithosphere. Smaller degrees of melting of heterogeneous mantle may explain the more variable compositions of these volcanoes.

On carbonatization fronts in serpentinite: Implications for *in situ* CO_2 storage

A. BEINLICH[1,2,*], O. PLÜMPER[1], J. HÖVELMANN[1], H. AUSTRHEIM[1,2] AND B. JAMTVEIT[1]

[1]Physics of Geological Processes (PGP) University of Oslo, Norway (*correspondence: andreas.beinlich@fys.uio.no)
[2]Department of Earth Sciences, University of Oslo, Norway

In situ storage of CO_2 in ultramafic rocks is considered as a promising strategy to counteract global warming. In order to identify positive and negative feedback mechansims for the reaction, examination of natural analogues is essential. Here we present observations from a massively carbonatized serpentinite complex in northern Norway. The investigated area is comprised of several ultramafic fragments of a dismembered ophiolite complex. Individual fragments are hydrothermally altered to varying degrees resulting in coexisting serpentinite, ophicarbonate, soapstone, and listvenite. Generally, reaction fronts between the soapstone and the serpentinite presursor are extremely sharp and can be traced for hundreds of meters. Locally, soapstone forms m-wide reaction halos around talc veins that cross-cut the serpentinite. The reaction fronts are defined by the complete replacement of the former antigorite by talc and magnesite. Where present, listvenite is spatially related to soapstone and cross-cut by abundant subparallel quartz-magnesite veins. The vein minerals exhibit a homogeneous O-isotopic composition and indicate a formation temperature of ~ 300 ˚C. The corresponding isotopic signature of the fluid ($\delta^{13}C_{PDB}$ = 2.2(5)‰; $\delta^{18}O_{SMOW}$ = 7.8(1)‰) suggests an interaction with crustal rocks and devolatilization of associated carbonates as a possible source for the CO_2. Assuming that during alteration temperature differences between directly adjacent soapstone and listvenite units are insignificant, thermodynamic phase stability modeling suggests that the conversion of serpentinite to listvenite requires a higher PCO_2 than that of conversion to soapstone.

In situ carbon storage schemes should aim to convert peridotite to listvenite as the complete inventory of divalent metal cations would be incorporated into the carbonates. However, our observations show that listvenite is distinctly less frequent than soapstone, implying that a high PCO_2 was not maintained during the natural alteration. Furthermore, alteration with a lower PCO_2 developed sharp fronts between the reacted and unreacted rocks, indicating that the carbonatization reaction ceased abruptly before completion.

Oxygen overshoot and recovery during the early paleoproterozoic

A. BEKKER[1]* AND H. D. HOLLAND[2]

[1]Department of Geological Sciences, University of Manitoba, Winnipeg, MB R3T 2N2, Canada (*correspondence: bekker@cc.umanitoba.ca)
[2]Department of Earth and Environmental Science, University of Pennsylvania, Philadelphia, PA 19104 USA

During the Lomagundi Event, >2.22 to 2.06 Ga, marine carbonates recorded the largest and longest positive carbon isotope excursion, the earliest extensive marine sulfate evaporites were deposited, and the average Fe_2O_3/FeO ratio of shales increased dramatically. At the end of the Lomagundi Event, the first economic sedimentary phosphorites were deposited, and the carbon isotope values of marine carbonates returned to ~0‰ VPDB. Thereafter marine sulfate evaporites and phosphorites again became scarce, while the average Fe_2O_3/FeO ratio of shales decreased to intermediate values between those of the Archean and Lomagundi-age shales. We propose that the large isotopic and chemical excursions during the Lomagundi Event were caused by a positive feedback between the rise of atmospheric O_2 level, the weathering of sulfides in pre-2.3 Ga sedimentary rocks, and the flux of phosphate to the oceans. The rise in the terrestrial phosphate flux led to an increase in the burial rate of organic carbon and a major transfer of oxygen from the carbon to the sulfur cycle.

The end of the Lomagundi Event was probably caused by a decrease in the terrestrial phosphate flux related to the weathering of low-pyrite sediments that were deposited during the Lomagundi Event. The rate of deposition of organic matter and burial rate of sulfate evaporites decreased, the isotopic and chemical excesses of the Lomagundi Event were eliminated, and the ocean-atmosphere system entered the period frequently called the Boring Billion.

Chloride degassing and its effects on the evolution of magmatic redox state

AARON S. BELL[1], ADAM SIMON[2] AND JAMES D. WEBSTER[1]

[1]Department of Earth and Planetary Science, American Museum of Natural History. New York, NY. USA (abell@amnh.org)

[2] Department of Geoscience, UNLV, Las Vegas, NV. USA

Magmatic fO_2 is a parameter that plays an important role in ferromagnesian and sulfide phase equilibria, the speciation of redox sensitive volatiles, and the physical properties of silicate liquids. We have performed redox controlled experiments to investigate iron partitioning behavior between a coexisting chloride rich volatile phase and silicate liquid. The results of these experiments suggest that volatiles with relatively modest chloride contents may contain several wt % Fe as a chloride species. These experimentally generated data suggest that the degassing of chloride rich volatiles may reduce the concentration of the FeO component of the melt. Notably, the preferential scavenging of ferrous iron from the melt must increase the $Fe^{3+}/\sum Fe$, consequently causing the fO_2 residual degassed melt to also increase.

These data support a model wherein the degassing of a chloride-rich volatile phase may significantly increase the oxidation state of the residual melt. Model calculations indicate that the magnitude of the induced oxidation ranges from 0.5 to 1.0 log unit; where this value depends on the partition coefficient value and the volatile phase-melt ratio used in the calculation. The oxidation of magmas during degassing and ascent may have marked effects on the identity and composition of the hypersolidus phase assemblage. Most saliently, this oxidizing effect may be manifested in sulfide saturated arc magmas as the destabilization of coexisting immiscible sulfide liquids or crystalline magmatic suflides. Such an iron scavenging based oxidation process has important implications for the remobilization of sulfide bound chalcophile metals as well as the petrologic interpretation of compositional zoning patterns in crystallizing ferromagnesian phases.

Carbonatites and Pb isotopes – Insights into terrestrial evolution

K. BELL

Earth Sciences, Carleton University, Ottawa, Ont. K1S 2W8, Canada (kib@magma.ca)

Information concerning the depleted mantle has come from studies of oceanic basalts but these cover only a small amount of geological time, at best back to a few hundred million years. Carbonatites, however, ranging in age from 3.0 Ga through to the present, provide a means of monitoring the secular evolution of the sub-continental mantle. Initial Pb isotopic ratios in carbonatites and alkaline complex rocks from the Canadian and Fennoscandian Shields appear to trace the evolution of "depleted" subcontinental mantle over the past 2.7 Ga. $^{87}Sr/^{86}Sr$ and $^{206}Pb/^{204}Pb$ ratios from Archean carbonatites from Canada tend to cluster closely around model "bulk silicate Earth" values in isotope correlation diagrams suggesting a mantle not yet depleted. A marked depletion event >3.0 Ga indicated by the Sm-Nd and Lu-Hf systems indicates sampling of considerably older, depleted mantle sources. Mantle differentiation processes appear to have changed in some fundamental way around 3 Ga with extraction of sialic crust. The similarity in isotopic compositions of young carbonatites (<100 Ma) to some OIB components (FOZO, HIMU, EM1) with little or no involvement with DMM suggests similar sources, and sub-lithospheric, deep-seated magmatism. Analogues to present day mantle components are not recognized in Archean carbonatites. Binary mixing of mantle sources (e.g. HIMU and EM1 for many young carbonatites) can be traced back to at least 1900 Ma.

Dissolution rate of bunsenite (NiO) in acid solution to 130°C

A. BELLEFLEUR[1], M. BACHET[1], P. BENEZETH[2] AND J. SCHOTT[2]

[1]EDF R&D, Site des Renardières, Avenue des Renardières, Ecuelles 77818 Moret Sur Loing Cedex (alexandre.bellefleur@edf.fr ; martin.bachet@edf.fr)
[2]GET, 14 Avenue Edouard Belin, 31400 Toulouse (benezeth@get.obs-mip.fr ; jacques.schott@get.obs-mip.fr)

Rates of proton-promoted dissolution of bunsenite (NiO) were measured from 50 to 130°C in hydrochloric acid solutions (pH 3 and 4.5) in a titanium mixed flow reactor. Measurements were also realized at 25°C with the stationary pH method [1] to confirm data from literature [2]. Pure bunsenite powder (Alfa Aesar Puratronic, Lot n°23430) was used for dissolution rate measurements, after beeing calcinated for 2*20 h at 1000°C in air. To avoid plug up of the outlet filter by fine particles, the powder was not directly introduced in the titanium reactor but in a specifically designed cell with walls made of a porous membrane. Measured bunsenite dissolution rate at 25°C are $2.4\pm0.3.10^{-10}$ and $7.5\pm0.6.10^{-11}$ $mol.m^{-2}.s^{-1}$ at pH 3 and 4.5, respectively. Apparent activation energies for dissolution rate (25-130°C) are equal to 59.7 ± 5.3 $kJ.mol^{-1}$ and 32.9 ± 2.4 $kJmol^{-1}$ at pH 3 and 4.5, respectively. Bunsenite proton-promoted dissolution rate can be expressed as $R_H=k_H\{>NiOH_2^+\}^n$ where, k_H, $\{>NiOH_2^+\}$ and n stand for the dissolution rate constant, the concentration of protonated surface sites and the order of reaction with respect to adsorbed protons, respectively [3]. A two pK, one site surface speciation model which assumes a constant capacitance of the electric double layer was used to calculate $\{>NiOH_2^+\}$ as a function of pH and temperature. The variation of the apparent activation energy with pH can be explained by the contribution of the enthalpy of protonation of surface sites to the dissolution reaction ([4], [5]). However, the variation in dissolution rate observed between pH 3 and 4.5 is not compatible with the surface protonation constant of $10^{8.17}$ from [2], suggesting a lower constant for the powder studied here. Therefore, more work on surface properties of NiO is foreseen.

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Experimental studies on cesium retardation on Brazilian crystalline rocks: Petrography, porosity and distribution coefficients

J.B. BELLINE[1]*, M. SIITARI-KAUPPI[2], M. KELOKASKI[2], P. SARDINI[3], M.E.B. GOMES[4] AND M.L.L. FORMOSO[1]

[1]Post-Graduate Program in Geosciences. IG/UFRGS. Brazil. (*correspondence: jean.belline@ufrgs.br)
[2]Laboratory of Radiochemistry. Univ. of Helsinki. Finland
[3]Laboratory HydrASA. Univ. of Poitiers. France
[4]Dep. of Mineralogy and Petrology.IG/UFRGS.Brazil

Cesium is an important radionuclide in the waste from the nuclear power plant [1,2]. The diffusion and sorption of cesium into rock is important to the safety of the radiowaste disposal. The mechanisms of sorption onto the minerals are important mechanisms to predict migration rates in the host rocks [3, 4]. The low porosity of granites is considered to prevent the radionuclides migration from repository site to the biosphere. This work discusses ^{134}Cs diffusion in three brazilian granites of São Sepé Complex Granitic, Rio Grande do Sul, Brazil, in the laboratory conditions. One sample comes from an outcrop and the two others (fresh and altered) are borecores from Camaquã mine. The porosities and densities of the each sample were measured by a water saturation method (pycnometry and water immersion techniques [5]). The porosity was measured also by C-14-PMMA autoradiographic method [6, 7]. Batch experiments and in diffusion test were made on crushed rock samples with several size fractions and blocks having volumes of about $8cm^3$, respectively, to obtain the distribution coefficients (K_d values) of cesium-134 and diffusion paths from ^{134}Cs autoradiographs.

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Short residence time and fast transport of fine-grain detritus – From ^{7}Be in settled dust in the Judean desert

R. BELMAKER[1,2], B. LAZAR[1], M. STEIN[2] AND J. BEER[3]

[1]The Institute of Earth Sciences, Hebrew University of Jerusalem, Givat-Ram Campus, Jerusalem 91904, Israel; (reuven.belmaker@mail.huji.ac.il)

[2]Geological Survey of Israel, 30 Malkhe Israel St,. Jerusalem 95501, Israel; (motistein@gsi.gov.il)

[3]Swiss Federal Institute of Environmental Science and Technology (EAWAG), Uberlandstrasse 133, CH-8600, Dübendorf, Switzerland; (Juerg.Beer@eawag.ch)

The short-lived cosmogenic isotope ^{7}Be ($t_{1/2}$=53.3 d) was measured in dust collected from dust traps placed in the Judean Desert. This enabled us to: (a) Determine the ^{7}Be dry deposition flux in the Dead Sea region; (b) Estimate the residence time of dust in the Dead Sea drainage basin and (c) Estimate the recycled component of the long-lived cosmogenic isotope ^{10}Be ($t_{1/2}$=1.39·10^{6} y) of Judean desert dust. These estimations constrain the rate of transport of fine detritus material that is washed from the marginal terraces of the Dead Sea basin into the lakes that occupied the basin during the late Quaternary. The data show that: (a) the ^{7}Be flux in the Dead Sea regions is 2.0±0.6×10^{4} atoms·cm^{-2}·y^{-1} during summer and winter months and 5.3±0.7×10^{4} atoms·cm^{-2}·y^{-1} during fall months; (b) the residence time of dust in the drainage basin is less than one year and (c) the recycled ^{10}Be component in Judean desert dust is small. It appears that the inventory of ^{7}Be in dust settled in the Dead Sea drainage basin increases as a function of time and does not reach steady state. Thus, ^{10}Be may be used for reconstructing paleo-flood frequency and dust transport

Behaviour of dissolved silica (adsorption and coprecipitation) in the presence of calcite

D.A. BELOVA[1]*, O.N. KARASEVA[2], L.Z. LAKSHTANOV[2] AND S.L.S. STIPP[1]

[1]Nano-Science Center, Department of Chemistry, University of Copenhagen, Denmark. (*correspondence: db@nano.ku.dk)

[2]Institute of Experimental Mineralogy RAS, Chernogolovka, Russia (leonid@iem.ac.ru).

The replacement of carbonate minerals in sediments by silica is common during carbonate rock diagenesis. Silica, as well as organic material and clays, can be one of the inhibitors of chalk (>95% calcite) recrystallization process [1]. However, the mechanism of selective substitution of carbonate sediments by silica and the influence of different factors on silica uptake by adsorption and coprecipitation with calcite are still not clear. In this work, we studied the interaction between dissolved silica and calcite under a variety of experimental conditions to estimate the role of SiO_2 in chalk diagenesis.

The experiments were performed at 25 ºC, different CO_2 partial pressures (pCO_2=1 atm, pCO_2=10$^{-3.5}$ atm and no access to CO_2) and various SiO_2 concentrations (≤ 2 mM). In monomeric silica solutions, no SiO_2 removal by adsorption was observed. The uptake of SiO_2 correlates with the amount of silica polymers and has its maximum value at basic pH, where some polysilicates are present.

Coprecipitation experiments were carried out by the constant addition method. The silica partition coefficient was calculated to be less than 1 and found to be dependent on calcite precipitation rate. The results of coprecipitation studies support that of adsorption experiments and also show that only insignificant amount of silica can be coprecipitated with calcite (maximum SiO_2 uptake is 4.8 μmol g^{-1}). This value increases with increasing dissolved silica concentration, increasing pH and the amount of silica polymers. Using the data from the adsorption study, namely, that polysilicic acid depolymerizes at the calcite surface, we can suggest two models for solid solution formation during coprecipitation.

We can conclude that interaction between dissolved SiO_2 at concentrations below the saturation with respect to amorphous silica and calcite is very weak and depends on adsorption of silica polymers.

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The volatile content of subduction zone melts and fluids

A. BÉNARD[1]*, D.A. IONOV[1], N. SHIMIZU[2] AND P.Y. PLECHOV[3]

[1]Univ. J. Monnet, St Etienne & UMR6524-CNRS, France (*correspondence: antoine.benard@univ-st-etienne.fr)
[2]Woods Hole Oceanographic Institution, Woods Hole, USA
[3]Moscow State University, Moscow, Russia

Harzburgite xenoliths from the andesitic Avacha volcano (Kamchatka, Russia) contain two types of spinel-hosted melt inclusions: (a) high-T inclusions (homogenized at 1200°C) containing opx±cpx+glass and (b) low-T inclusions (homogenized at 900°C) containing amph±sulf+glass. Homogeneous glass in the high-T inclusions is similar in major element composition to basaltic andesite experimentally produced by high-degree, hydrous melting of peridotite [1]. Homogeneous glass in low-T is silica oversaturated, Al- and Ca-rich, enriched in $LREE_N$ and $LILE_N$ relative to $MREE_N$-$HREE_N$; it displays a strong slab-related chemical overprint. The xenoliths also contain melt pockets originating from local, fluid-assisted melting, produced shortly before the entrapment of the xenoliths.

We analyzed the volatile content of melt inclusions and pockets by Secondary-Ion Mass Spectrometry (SIMS) with Cameca IMS 1280. Most inclusions contain much more CO_2 and H_2O than predicted by saturation curves for these species in silicate melt at 600 bar, implying that the melt entrapment occurred at mantle depth. High-T inclusions have 0.20±0.02 wt.% CO_2, 2.05±0.01 wt.% H_2O and 130±1 ppm S. Low-T inclusions display a wide range of CO_2 (0.01-0.57±0.01 wt.%) and H_2O (0.86-7.45±0.02 wt.%). The abundances of CO_2 and H_2O are positively correlated. The low-T inclusions define also an F-enrichment trend (from 50 to 672±5 ppm) with less variable Cl (540-759±14 ppm) and are strongly enriched in S (up to 0.59 wt.%). Glass in the melt pockets has the lowest CO_2 and H_2O contents (respectively ≤0.03±0.01 and ≤1.58±0.02 wt.%). The $\delta^{34}S$ range of +7.0 to +11.0‰ (±0.6‰, 2σ) in the melt inclusions indicates the presence of heavy oxidized sulfur, likely with surface provenance [2].

The results suggest and/or confirm that (1) the high-T inclusions trapped a mantle-derived primary melt, (2) the low-T inclusions are produced by polybaric entrapment of fluid-rich, hydrous melts in the lithospheric mantle; and provide the first "in situ" evidence for volatile recycling in the lithospheric mantle above a subducting slab.

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Laser-induced photo-luminescence spectroscopies: Probes for sulfide crystal-chemistry

A. BÉNARD[1]*, T. OLIVIER[2], B.N. MOINE[1], D.A. IONOV[1], L.-S. DOUCET[1] AND M. BOYET[3]

[1]Univ. J. Monnet & UMR6524-CNRS, St Etienne, France (*correspondence: antoine.benard@univ-st-etienne.fr)
[2]Centre de Microscopie Confocale et Multiphotonique, Univ. J. Monnet, St Etienne, France
[3]Univ. B. Pascal & UMR6524-CNRS, Clermont-Ferrand, France

We combine Two-Photon Fluorescence (TPF), Confocal Laser Scanning Microscopy (CLSM) and Confocal Laser-Induced Luminescence (LIL) to acquire 2-D and 3-D-resolved luminescence emission spectra from transition metal- and (Ca, REE)-bearing mantle-derived and meteoritic (enstatite chondrite) sulfides. The latter include primary condensates and high-degree metamorphic crystals. A wide range of excitation λ (442-800 nm) is tested; Raman micro-spectrometry adds qualitative constraints on sulfide crystallinity. Despite the small amount of luminescence emitted by the sulfides, TPF and CLSM are sensitive enough to perform 3-D imaging with a resolution of ~0.5 μm laterally and ~5 μm axially, in particular using Near Infra-Red (NIR) femtosecond excitation (TPF). Versatile concofal microscopes allow to scan collected luminescence with a 20 nm spectral window to record spectra of roughly 10 x 10 μm regions of interest.

All sulfides emit a characteristic band at 710 nm under TPF NIR radiation that can be related to the sulfur 3sσ state [1]; its increased sharpness may be due to higher crystallinity degree. Pyrrhotite has a continuous emission along a broad λ range (400-710 nm) that allows to distinguish it both from lower temperature, NiAs-type monosulfide polymorphs with two individualized Gaussian-shaped bands (centered at 460 and 650 nm) and troïlite (one major band at 710 nm). We seek to identify *4d*- and *5d*-metal monosulfide heterogeneities (PtS and PdS clusters) with the super-resolution of the TPF.

Under a 633 nm LIL excitation, CaS emits the 710 nm band characteristic of sulfur while below 442 nm, the *4f* and *5d*-derived levels of $^{VI}Ce^{3+}$ are excited with the appearance of the $\Gamma_8(^2T_{2g}) \rightarrow {}^2F(\Gamma_7, \Gamma_8(^2F_{5/2}); \Gamma_6, \Gamma_7, \Gamma_8(^2F_{7/2}))$ transitions. With the use of point charge crystal-field modelling at constant Ce valency, we infer a direct correlation of the *5d* orbitals (t_{2g}-e_g set) splitting parameter Δ_0 to the CaS lattice spacing, controlling in turn Ce partitioning. We investigate REE fluorescence mapping with the TPF super-resolution.

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On the radiogenic ^{40}Ca anomaly in seawater and limestone

MICHAEL L. BENDER* AND JOHN A. HIGGINS

Department of Geoscience, Princeton University, Princeton, NJ 08544, USA
(*correspondence: bender@princeton.edu)

Caro *et al*. [1] estimate that the silicate upper continental crust has a radiogenic ^{40}Ca anomaly of 2.5 epsilon units from ^{40}K decay. Surprisingly, Caro *et al*. show that epsilon ^{40}Ca of seawater and limestone is indistinguishable from the mantle value (epsilon ^{40}Ca~0, since the mantle has low K/Ca), with an uncertainty of about ± 0.3 units. To balance the modern oceanic ^{40}Ca budget, they suggest that the riverine flux of radiogenic crustal Ca is balanced by a small nonradiogenic flux from high-temperature hydrothermal processes at mid-ocean ridges, and a larger flux of nonradiogenic calcium from low-temperature hydrothermal systems on ridge flanks. If correct, waters in ridge flank hydrothermal systems must play a major role in the chemical mass balance of the oceans.

We discuss 3 factors that, without invoking ridge flank exchange, help explain the enigma that limestone and seawater Ca are much less radiogenic than the silicate crust. First, radiogenic ^{40}Ca is diluted into the large mass of limestone. Second, the time-averaged hydrothermal flux would be twice the present value if it scaled with past heat production. Third, nonradiogenic hydrothermal Ca would have been retained in the limestone and (via metamorphism) in the silicate crust; it would be recycled by subsequent weathering, thereby lowering epsilon ^{40}Ca in rivers. These three factors together can account for about two-thirds of the difference between the estimated ^{40}Ca anomaly of the silicate continental crust and the nonradiogenic Ca composition of seawater and limestone.

[1] Caro, Papanastastassiou & Wasserburg (2010), *Earth and Planetary Science Letters* **296**, 124-132.

Limited early continents from the chemistry of eoarchean rocks

VICKIE C. BENNETT[1] AND ALLEN P. NUTMAN[2]

[1]Research School of Earth Sciences, The Australian National University, Canberra, Australia (vickie.bennett@anu.au)
[2]School of Earth and Environmental Sciences, University of Wollongong, NSW, Australia (allen.nutman@gmail.com)

Continuing and fundamental questions in Earth history focus on the timing and mechanisms of early continent formation. These questions take on additional significance in consideration of potential early life habitats and early tectonic regimes. Key approaches used to argue for, and against, massive early continents, have centered on the signatures of long-lived isotopic systems, i.e. initial εNd and εHf, preserved in the oldest rocks. For example, positive deviations from bulk silicate Earth compositions have been equated with massive early crust formation. Such interpretations contain the assumption that continental crust has been the primary complement to the depleted mantle throughout Earth history. However, using an expanded ^{142}Nd,^{143}Nd,^{176}Hf database derived from Eoarchean rocks worldwide we demonstrate that Nd and Hf isotopic data do not record the distinctive correlations observed in younger granitic terranes; these correlations are generated in the mantle by long term crust extraction. Furthermore, positive ^{142}Nd anomalies (relative to modern terrestrial compositions) measured in some Eoarchean rocks require extremely early (4.53 Ga - 4.4 Ga) Sm/Nd fractionation. Overall, neither Sm-Nd or Lu-Hf fractionation in the >3.7 Ga mantle can be linked to continental crust extraction.

Other types of observations from ancient rocks further support the case for limited crustal volumes. Eoarchean rocks are now recognised in 8 gneiss complexes worldwide. In each area, the oldest felsic rocks (ca. 3.7-4.0 Ga) are typically tonalites, with no evidence of pre-existing crust in the form of inherited zircon grains with older U-Pb ages. Where data are available, the initial εNd and εHf values range from chondritic to positive and δ^{18}O isotopic compositions are mantle-like; thus there is no chemical evidence for reworking of older components. In contrast, younger (≤3.65 Ga) granites (*sensu stricto)* often contain inherited zircons whose U-Pb ages match the oldest crust in each region; initial εNd and εHf values become more negative with decreasing rock age, reflecting incorporation of older felsic components. We consider that, at present, there is no compelling evidence for the existence of extensive early continents, prior to ~3.65 Ga.

An experimentalist call to theoreticians about XANES spectra theoretical simulation at the C K-edge, Ca and Fe $L_{2,3}$ edges

KARIM BENZERARA[1], OLIVIER BEYSSAC[1], MATTHIEU GALVEZ[1], SYLVAIN BERNARD[2] AND JULIE COSMIDIS[1]

[1]Institut de Minéralogie et de Physique des Milieux Condensés, UMR7590, CNRS, UPMC & IPGP, 4 Place Jussieu, 75005 Paris, France
[2]LMCM, UMR 7202, MNHN & CNRS, 61 rue Buffon, 75005 Paris, France

Scanning transmission x-ray microscopy (STXM) is increasingly used in geobiology and more generally in Earth sciences [1-5]. It is a transmission microscopy providing images with 25-nm spatial resolution and a x-ray absorption near-edge structure (XANES) spectrum for each pixel of this image. The few beamlines that are available worldwide (e.g., 11.0.2 at the ALS or 10ID-1 at the CLS) give the opportunity to scan over a large energy range (e.g. 70-2200 eV) with high energy resolution enabling the study of elements such as C, N, O, Mg (using K-edges), or P, Ca, Fe or As (using L-edges). XANES spectra coupled with high spatial resolution can thus provide unique information on the speciation of diverse elements which is a 1st order interest for a variety of applications. However, very often, the use of the spectroscopic information is limited to a fingerprinting approach. We believe that theoretical developments would help retrieving significantly more information from these spectra. Here we will review some of the experimental work that we have done over the last few years in order to identify some key needs that we have and that might be adressed by theoreticians. In particular, we will discuss the use of XANES spectroscopy at the C K-edge to study the chemical composition and structure of organic carbon in (ancient) rocks and mention the implications for the study of metamorphism and/or search for ancient traces of life. Absorption variations due to linear dichroism in particular will be presented. The use of XANES spectroscopy at the Fe $L_{2,3}$ edges and difficulties to retrieve Fe redox state values will be adressed.

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Arsenic contamination of ground-water in Vietnam: Delta-wide survey and 3D geospatial modelling

M. BERG[1]*, L.H.E. WINKEL[1], P.T.K. TRANG[2], V.M. LAN[2], C. STENGEL[1], M. AMINI[1], N.T. HA[3], AND P.H. VIET[2]

[1]Eawag, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland (*correspondence: Michael.Berg@eawag.ch)
[2]Centre for Environmental Technology and Sustainable Development (CETASD), Hanoi, Vietnam.
[3]Centre for Water Resources Monitoring and Forecast (CWRMF), Hanoi, Vietnam.

Arsenic contamination of shallow groundwater is among the biggest health threats in the developing world. The Red River Delta was recognized to be affected in 1998, but the spatial extension remained unknown [1]. Here we present the results of a groundwater survey of the entire Red River Delta combined with a unique probability model based on 3-dimensional (3D) Quaternary geology. Our investigations reveal that ~7 million delta inhabitants use groundwater that contains unsafe levels of As, Mn, Se, and Ba.

Global and sub-continental arsenic risk maps based on surface geology were recently shown to be a successful tool to initiate mitigation measures [2,3]. For the Red River delta we now established a 3D model based on stratigraphy of Quaternary geology, which visualizes As hot-spots at depths and identifies safe regions for drinking water production.

This 3D model further reveiled anomalities of As enrichment in the aquifers. Particularly in the Hanoi area, depth-resolved probabilities and As concentrations indicate drawdown of As-enriched water from Holocene aquifers to naturally As-safe Pleistocene aquifers, most likely as a result of more than 100 years of groundwater abstraction. Vertical As migration induced by large-scale pumping from deep aquifers has been discussed to occur elsewhere, but has never been shown to occur at the scale seen here. The present situation in the Red River Delta is hence a warning for other As-affected regions where groundwater is extensively pumped from uncontaminated aquifers.

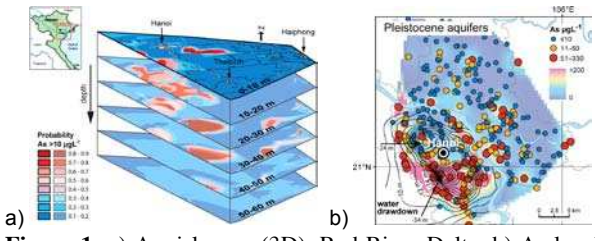

Figure 1: a) As risk map (3D), Red River Delta. b) As levels in the Pleistocene aquifers, and water drawdown in Hanoi [4].

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Volatile release from crustal-xenolith during subvolcanic magma transport

S. BERG[1]*, V. R. TROLL[1,2], H. ANNERSTEN[1], C. FREDA[2], L. MANCINI[3], L. BLYTHE[1], E. MUÑOZ JOLIS[1] AND A. BARKER[1]

[1]Department of Earth Sciences, Uppsala University, Villavägen 16, 752 36 Uppsala, Sweden (*correspondance: e.sylviaberg@gmail.com)
[2]Istituto Nazionale di Geofisica e Vulcanologia, Rome, Italy
[3]SYRMEP Group, Sincrotrone Trieste, Basovizza, Italy

Magma-crust interaction in magma reservoirs and conduits is a crucial process during magma evolution and ascent. This interaction is recorded by crustal xenoliths that frequently show partial melting, inflation and disintegration textures. Frothy xenoliths are widespread in volcanic deposits from all types of geological settings and indicate crustal gas liberation. To unravel the observed phenomena of frothy xenolith formation we experimentally simulated the behaviour of crustal lithologies in volcanic conduits. We subjected various sandstones to elevated temperature (from 810 to 916 °C) and pressure (from 100 MPa to 160 MPa) in closed-system autoclaves. Experimental conditions were held constant for 24h up to 5 days, then controlled decompression simulated xenolith ascent. Pressure release was a function of temperature decline in our setup. Temperature lapse rate proceeded exponentially; the first 20 minutes experienced an enhanced decline of 24-20°C/min, whereafter 6-8 hours of slow cooling followed towards room temperature. The experimental xenoliths have been analysed by synchrotron X-ray μ-CT at a resolution of 3.4 – 9 microns/pixel. This method permits visualisation and quantification of internal vesicle volumes, -networks and -connectivity in 3D.

Experimental products closely reproduced the textures of natural frothy xenoliths in 3D and define an evolutionary sequence from partial melting to gas exsolution and bubble nucleation that eventually leads to the development of three-dimensional bubble networks. The lithology proved decisive for degassing behaviour and ensuing bubble nucleation during decompression. Increased volatile content (chiefly water) and amount of relict crystals in the partial melt promote bubble nucleation and subsequent bubble coalescence to form interconnected bubble networks. This, in turn, enables efficient gas liberation. Our results attest to significant potential of even very common crustal rock types to liberate volatiles and develop interconnected bubble networks upon heating and decompression. Volatile input from xenoliths may therefore considerably affect explosive eruptive behaviour, and our experiments offer a detailed mechanism of how such crustal volatile liberation is accomplished.

Cr-isotopes and REE variations in a laterite profile: Implication for redox processes and element mobility during weathering

ALFONS BERGER AND ROBERT FREI

University Copenhagen, Denmark (*correspondence: ab@geo.ku.dk)

The isotope composition of redox sensitive elements are a powerful tool to reconstruct transport of elements depending on their oxidation state. One major application is the study of element transfer from weathering to redeposition. However, the understanding of the "output" during weathering requires insights to processes during erosion and soil development. In this context, the mineralogy and oxidate state of certain elements in weathering profile are key informations.

We will give some insights into a modern laterite profile of Madagascar. The profile is taken in an quarry near RN7 south of Antisrabe, including bed rock, saprolith and top soil. The fresh rock are a Panafrican tonalite. The sample site is characterized by minor topography and groundwater flow is controlled by small rivers. The fresh rock is dominated by two feldspars, quartz, biotite, hornblende, ilmenite, magnetite, apatite, allanite and chevkinite. Weathering starts along cracks and is accompined by change mineralogy and major elements abundances. Trace element concentrations and Pb isotopes indicate no or only minor solid mass transport. The profile reflects an *in situ* weathering profile with a water level horizon above the saprolith. The water flow horizon includes a change in Ce concentrations related to deposition of ceriate. This is most likely related to insolvable Ce(IV) in this part of the profile. In contrast, transformation during weathering from allanite/chevkinite to rhabdophane did not change the REE whole rock pattern. Cr is strongly depleted in the soil and in the saprolith and reflects mobilization of Cr by oxidation to the hexavalent state. This change of oxidation change is corroborated by fractionated Cr isotopes in the saprolith (δ^{53} Cr -0.4 – -0.5‰), relative to the δ^{53}Cr value of ~0.15‰ of the tonalite

The different behaviour of the redox sensitive elements Ce and Cr is either related to the redox potential of the elements and/or is kinetically controlled by the respective host minerals. The REE´s are predominantly hosted by accessory minerals (chevkinite, allanite, apatite), whereas Cr are incorporated rock forming silicates and oxides. Comparison of Ce anamolies and Cr isotopes provide important insights to the behaviour of these elements during weathering and consequently to the relative concentrations in the solvent.

Hydrothermal synthesis of cubanite under conditions relevant to the CI-chondrite parent body

E. L. BERGER*[1], D. S. LAURETTA[1] AND L. P. KELLER[2]

[1]Lunar & Planetary Laboratory, Tucson, AZ 85721 (*correspondence: elberger@lpl.arizona.edu)
[2]NASA Johnson Space Center, Houston, TX 77573

The low temperature form of $CuFe_2S_3$, cubanite, has been identified in the CI chondrites and in samples returned from Comet Wild 2 by the Stardust Mission [1]. We report the first synthesis of this mineral under aqueous conditions consistent with predictions for the CI-chondrite parent body.

An aqueous system can be described as the interplay between pH, temperature, oxygen and sulfur fugacities [2]. We form cubanite at 150 and 200ºC (fig. 1) by controlling oxygen fugacity (fO_2), pH and T. Oxygen isotope measurements and modeling of aqueous conditions on asteroidal bodies [3, and ref. therein] predict: T of 20-150ºC, pH of 7-10 and log $fO_2 > 10^{-55}$ -10^{-70}.

EMPA and FIB-TEM techniques are used to determine composition and crystal structure.

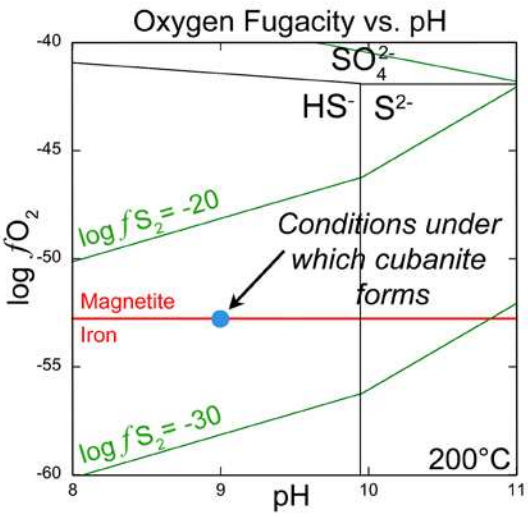

Figure 1: Oxygen fugacity vs. pH for an aqueous system containing 0.025M S. Major S species (aq), lines of constant sulfur fugacity and the iron-magnetite buffer are indicated.

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Fluoride patterns in a boreal stream influenced by bedrock and hydrology

T. BERGER*, P. PELTOLA, H. DRAKE AND M. ÅSTRÖM

Department of Natural Sciences, Linnaeus Univ., Kalmar, Sweden (*correspondence: tobias.berger@lnu.se)

The spatial and temporal variation of fluoride in the Kärrsvik catchment (27 km^2) in SE Sweden has been monitored monthly for up to 6 years (2002 - 2009). The bedrock is characterized by 1.8 Ga old granite to quartz monzodiorite. However, in the lower reaches the F-rich, 1.45 Ga old, Götemar granite crops out.

Fluoride increased significantly at this intrusion and showed a strong negative relationship with flow, ranging between 0.6 and 4.2 mg L^{-1} (median 1.04 mg L^{-1}). In the upper reaches the concentrations were lower, <0.20 - 0.85 mg L^{-1} (median ~0.4 mg L^{-1}). The spatial concentration pattern of fluoride in well waters was concordant with that of the surface waters within the catchment.

On a continental scale, European streams (n=808, 25 countries) have median fluoride concentrations of 0.1 mg L^{-1} [1]. The Kärrsvik catchment is therefore an area with anomalous fluoride concentrations. Stream waters can be major sources of drinking water and the World Health Organization guideline value is set to 1.5 mg L^{-1}.

The fluoride pattern can be explained by three main sources associated with weathering processes in the lower reaches of the catchment: 1, glacial deposits partially enriched in weathering products from the Götemar granite, 2, larger input of baseflow water (longer interaction time with F-bearing minerals) and 3, intrusion-related fractures strongly enriched in fluorite.

Detailed studies of near-surface groundwaters in the region will further increase the understanding of the dynamics of this element in these kinds of environments.

[1] Salminen *et al*. (2005) *Geochemical Atlas of Europe*. *Part 2*, 161-162.

Early Neoproterozoic arc magmatism along the northwestern margin of the Yangtze craton and its connection with the South China Block evolution during the Rodinia assembly

W. BERKANA[1,2] ,W-L. LING[1,2]*, X-F. QIU[1,2] AND S-S. LU [1,2]

[1]State Key Laboratory of Geological Process and Mineral Resources, China University of Geosciences, Wuhan 430074, P R China (lingwenli2008@126.com)

[2]Faculty of Earth Sciences, China University of Geosciences, Wuhan 430074, P R China (wafaberkana@yahoo.fr)

The South China Block (SCB) comprises the Yangtze craton and the Cathysian block, welded during ~1.0-0.95 Ga. Neoproterozoic igneous activities of ~830-750 Ma are widely recorded in the SCB. However, their origin and tectonic setting have long been debated, resulted in competing models for the correlation of the SCB with Rodinia supercontinent.

The Wangcang igneous complex occurs along the northwestern Yangtze craton, which has long been regarded as early Precambrian basement. Our present study reveals that both the intrusive and volcanic suites were formed at ~880 Ma. The mafic rocks show tholeiitic geochemistry with initial ε_{Nd} values of +2.1 to +7.7, whereas the felsic samples are calc-alkaline series with a ε_{Nd} range of -2.1 to +4.7. These suites are suggested to have an arc magmatic origin, and their intensive deformation and high metamorphism occurred during ~880-820 Ma.

Integrating with proofs such as Nd isotope stratigraphic studies of the Yangtze craton, we suggest that the Yangtze craton had experienced a continent growth during the Rodinia assembly by microcontinent merging before the SCB unification. This study was supported by National Nature Science Foundation of China (Grants 40873017, 40673025).

The advantage of the use of Focused Ion Beam technique to specify the mantle fluid inclusions

M. BERKESI[1]*, T. GUZMICS[1], C. SZABÓ[1] AND J. DUBESSY[2]

[1]Lithosphere Fluid Research Lab, Institute of Geography and Earth Sciences, Eötvös University Budapest, 1117 Pázmány Péter sétány 1/C, Budapest, Hungary (correspondence: martaberkesi@caesar.elte.hu)

[2]UMR G2R and CREGU, Nancy University, BP-70239, 54506-Vandœuvre-les Nancy Cedex, Nancy (France) (jean.dubessy@g2r.uhp-nancy.fr)

The Focused Ion Beam (FIB) coupled with scanning electron microscopy (SEM) technique has became one of the most promising tools for many geochemical studies in the last decade [1].

It is known that within the fluid inclusions solids (referred to as daughter phases) may crystallize as a result of cooling and/or reaction with their host mineral. If the volume proportions of the daughter phases are not known, the fluid composition determined can be misinterpreted. However, *in situ* measurement of the daughter phases can be complicated and ambiguous with conventional techniques because of their size and/or composition. In this study we report our results using FIB-SEM technique on investigation of daughter phases in orthopyroxene-hosted fluid inclusions in mantle xenoliths from the Pannonian Basin (Hungary).

Solid phases such as magnesite and quartz have been found within the fluid inclusions. They have a size between 200 – 2000 nm occurring as cluster on some parts of the inclusion walls. In addition, S-bearing solid phase (probably sulfide) has also been identified. One of the most interesting feature observed was a thin film covering the wall of the studied fluid inclusions. This film has a feature that is typical for the volcanic glasses, containing numerous spherical-shaped holes (vesicles) on the surface as a result of the exsolution of volatiles. It is to emphasize that previous works on fluid inclusions have already proposed the presence of the glass film on the wall [2] in mantle fluid inclusions, however, in this work the glass film has been found *in situ*.

The acquired results of this study contribute to 1) quantification of the bulk fluid composition and 2) better understanding the mechanisms of the post-entrapment processes in fluid inclusions entrapped at lithopheric mantle condition.

[1] Wirth (2009) *Chem Geol* **261**, 217-229. [2] Hidas *et al.* (2010) *Chem Geol* **274**, 1-18.

Can we use variations in volatile concentrations in volcanic glass to study degassing?

KIM BERLO[1], DAVID PYLE[1], JENNI BARCLAY[2], TAMSIN MATHER[1] AND HUGH TUFFEN[3]

[1]Department of Earth Sciences, University of Oxford, Oxford, UK. (kim_berlo@inbox.com, David.Pyle@earth.ox.ac.uk, Tamsin.Mather@earth.ox.ac.uk)
[2]School of Environmental Sciences, University of East Anglia, Norwich, UK. (J.Barclay@uea.ac.uk)
[3] Lancaster Environment Centre, Lancaster University, Lancaster, UK. (h.tuffen@lancaster.ac.uk)

Decompression of volatile rich magma results in the exsolution of a separate gas phase. Major volatile species, H_2O, CO_2, SO_2, as well as many minor volatile species, $PbCl_2$, $ZnCl_2$, Hg, AsS etc, will be partitioned between the gas and the melt phase. However, the rate of magma ascent and eruption does not always allow for the equilibrium distribution between gas and melt of such species to be reached. Instead elements are quenched in transition towards an equilibrium that constantly changes as the magma ascends. Volatile elements can thus display diffusive profiles towards gas escape features, such as bubbles, tubes or fractures. This exploratory study aims to map out the extent of heterogeneity in rhyolitic glasses. Samples with different gas pathways, bubbles, fractures, channels and tuffisite veins have been selected and will be mapped for H_2O and selected trace metals (Cu, Zn, Bi, Pb) using synchrotron FTIR and XRF. The results of this study will allow us assess the extent to which volcanic gases can be in equilibrium with a melt shortly before eruption.

Calcium isotopes in lunar crust

K. BERMINGHAM[1], T. MAGNA[1,2], N. GUSSONE[1] AND K. MEZGER[3]

[1]Universität Münster, Germany
[2]Czech Geological Survey, Prague, Czech Republic
[3]Universität Bern, Switzerland

Calcium isotope compositions were determined in lunar crustal rocks in order to quantify possible mass-dependent (MDF) and mass-independent (MIF) isotope fractionation. Anorthosites show ~0.4‰ variation in $\delta^{44/40}$Ca; pristine anorthosite 60025 has an identical value to previous reports [1] but appears to be slightly heavier than the other anorthosites ($\delta^{44/40}$Ca=0.65–0.91‰) which may reflect a larger proportion of isotopically heavy olivine. Norite 77215 has $\delta^{44/40}$Ca=1.06‰, which is identical to pristine terrestrial mantle rocks [2] and likely represents a mixture between isotopically light plagioclase and heavy orthopyroxene. In general, anorthosites and norite mimic the range of terrestrial and Martian basalts [2–4] as well as lunar low-Ti and high-Ti lithologies [4]. The $\delta^{44/40}$Ca uniformity of lunar crust and mantle-derived rocks is dissimilar to the Ca systematics of major terrestrial reservoirs with predominantly light Ca isotope signature in continental crust and may suggest cessasion of magmatic activity early in the lunar history without further material exchange with deeper parts of the Moon. A tight negative correlation of $\delta^{44/40}$Ca with K contents could reflect either the chemical development of the magma ocean or a collateral effect of immiscibility between Ca and K feldspars. However, only a detailed experimental investigation could provide tight constraints on the role of plagioclase in lunar Ca budget. This may be particularly important for the Moon considering that, in contrast to the Earth where >99% Ca budget is dominated by mantle, lunar crust is a significant Ca repository and hosts ~11% of the total lunar Ca. New data for lunar mare basalts coupled with data for anorthosites could help constrain the lunar Ca evolu-tion in the context of lunar magma ocean crystallization.

The MIF effects are indiscernible for individual Ca isotopes in all investigated lunar rocks in this study. This is in agreement with previous findings for some Solar System material [5–7]. In particular, lack of resolvable MIF variations in lunar samples may imply Ca isotope homogeneity on the planetary scale.

[1] Farkaš *et al*. (2010) *LPSC* **41**, #2266; [2] Amini *et al*. (2009) *GGR* **33**, 231-247; [3] Huang *et al*. (2010) *EPSL* **292**, 337-344; [4] Simon & DePaolo (2010) *EPSL* **289**, 457-466; [5] Huang *et al*. (2010) *LPSC* **41**, #1379; [6] Moynier *et al*. (2010) *ApJ* **718**, L7-L13; [7] Simon *et al*. (2009) *ApJ* **702**, 707-715

Nanoscale study of the mineralogical and geochemical evolution of black shales with increasing maturity

S. BERNARD[1,*], B. HORSFIELD[2], H-M. SCHULZ[2], A. SCHREIBER[2], R. WIRTH[2] AND N. SHERWOOD[3]

[1]LMCM, MNHN, CNRS, Paris, France (sbernard@mnhn.fr)
[2]Deutches GeoForschungsZentrum GFZ, Potsdam, Germany (horsf@gfz-potsdam.de, schulzhm@gfz-potsdam.de, schreiber@gfz-potsdam.de, wirth@gfz-potsdam.de)
[3]CSIRO, North Ryde, Australia (Neil.Sherwood@csiro.au)

Gaseous hydrocarbon generation processes occur within gas shales as a response to increases in thermal maturation. While efforts have been directed at unravelling the resource potential of these unconventional systems [1], their spatial variability in chemistry and structure is still poorly understood at the sub-micrometer scale. For instance, intra-particle nanoporosity has been documented within overmature gas shale samples but has not yet been attributed to any specific organic macromolecule [2]. Here, we have characterized samples of the Lower Toarcian Posidonia Shale from northern Germany at varying stages of thermal maturation using a combination of compositional organic geochemistry and spectromicroscopy techniques, including synchrotron-based scanning transmission X-ray microscopy (STXM). We document geochemical and mineralogical heterogeneities down to the nanometer scale within the investigated samples at all levels of thermal maturity [3,4].

In particular, authigenic albite crystals containing nanometric halite inclusions have been documented within the investigated mature and overmature samples. The presence of such tracers of palaeobrine-carbonate interactions supports a maturation scenario for the Lower Toarcian Posidonia Shale intimately related to ascending brine fluids. In addition, various types of asphaltene- and NSO-rich bitumen have been detected within the same samples, very likely genetically derived from thermally degraded organic precursors. Furthermore, the organic macromolecules displaying intra-particle nanoporosity have been identified as pyrobitumen residues, such nanoporosity likely resulting from the formation of gaseous hydrocarbons. By providing *in situ* insights into the fate of bitumen and pyrobitumen as a response to the thermal evolution of the macromolecular structure of kerogen, the results reported here constitute an important step towards better constraining hydrocarbon generation processes during natural gas shale maturation.

[1] Jarvie *et al*. (2007), *AAPG* **91**, 475-499. [2] Loucks *et al*. (2009), *J. Sediment. Res*. **79**, 848-861. [3] Bernard *et al*. (2010), *Chemie der Erde - Geochemistry* **70(S3)**, 119-133. [4] Bernard *et al*., *Marine and Petroleum Geology*, in review.

Does the electron transfer process determine the product of U(VI) reduction?

RIZLAN BERNIER-LATMANI[1], DANIEL S. ALESSI[1], HARISH VEERAMANI[1], JONATHAN O. SHARP[1], ELENA DALLA VECCHIA[1], ELENA I. SUVOROVA[1], JOANNE E. STUBBS[2], JUAN S. LEZAMA-PACHECO[3] AND JOHN R. BARGAR[3]

[1]École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland (*correspondence: rizlan.bernier-latmani@epfl.ch)
[2]University of Chicago, Chicago, IL 60637, USA
[3]Stanford Synchotron Radiation Lightsource, Menlo Park, CA 94025, USA

The bioremediation of uranium-contaminated sites is based on the amendment of an electron donor to stimulate microbial activity. Typically, Fe(III) and U(VI) serve as electron acceptors for microorganisms with the former supporting microbial growth. However, this biostimulation process may generate competing mechanisms of uranium bioreduction. While direct enzymatic reduction of U(VI) by microbes is a possible route of immobilization of U(IV), Fe(II) produced by the reduction of Fe(III) also is thermodynamically capable of abiotically reducing U(VI).

Here we investigate the question of whether different U(IV) products are expected from these various U(VI) reduction processes. Specifically, we consider the reduction of U(VI) via direct enzymatic reduction by both Gram-positive and Gram-negative bacteria, via abiotic reduction by Fe(II)-bearing minerals as well as through a potential combination of these direct and indirect processes in sediment columns.

The results indicate that geochemical conditions dictate the product of U(VI) reduction. For example, the same microorganism produced a monomeric sorbed U(IV) complex in the presence of particular solutes but nanoparticles of the mineral uraninite in their absence. A phosphate-reacted magnetite (Fe_3O_4) suspension produced a similar monomeric U(IV) product while unreacted magnetite produced uraninite. Finally, in studying U(VI) reduction in sediments, both laboratory and field-run columns yielded non-uraninite U(IV), suggesting that *in situ* geochemical conditions favor monomeric U(IV) formation.

This work shows that, while the kinetics of U(VI) reduction have been shown to depend on the reduction mechanism, the end-product of the reduction is largely determined by the geochemical conditions under which the reduction–biotic or abiotic- takes place.

Solubility of fluorine and chlorine in nominally anhydrous mantle minerals: Implications for mantle metasomatism and arc magmas

D. BERNINI[1], D. DOLEJŠ[1,2], N. DE KOKER[1], A. AUDÉTAT[1], H. KEPPLER[1] AND M. WIEDENBECK[3]

[1]Bayerisches Geoinstitut, University of Bayreuth, 95440 Bayreuth, Germany
[2]Institute of Petrology and Structural Geology, Charles University, 12843 Praha 2, Czech Republic
[3]Deutsches GeoForschungsZentrum, 14473 Potsdam, Germany

Subduction fluxes and recycling of halogens are important for interpreting the fate of halogen budget of altered subducting slab, availability of ligands for complexing in aqueous fluids, origin of high-pressure brines, and volatile signatures of arc magmas. We investigated solubilities of fluorine and chlorine in forsterite, enstatite and pyrope, and halogen partitioning between aqueous fluids and these minerals by piston-cylinder experiments at 1100 °C and 2.6 GPa. The chlorine solubility in forsterite, enstatite and pyrope is very low, 0.2-0.9 ppm, and it is independent of the fluid salinity (0.3-40 wt. % Cl). The fluorine solubility is 16-31 ppm in enstatite and 24-52 ppm in pyrope, also independent of fluid salinity. Forsterite dissolves 246-267 ppm up to a fluid salinity of 1.6 wt. % F. At higher fluorine contents in the system, forsterite is replaced by the minerals of the humite group. The fluid-mineral partition coefficients are 10^1-10^3 for fluorine and 10^3-10^6 for chlorine. The latter values are approximately three orders of magnitude higher than those for hydroxyl partitioning suggesting a gradual increase in the fluid salinity during fluid percolation through the mantle wedge. Energetics of fluorine incorporation in forsterite and the forsterite-humite chemical equilibria in the system Mg_2SiO_4-MgF_2 were further explored by first principles computations. The fluorine solubility in forsterite strongly increases with temperature, from 0.01 ppm F at 500 K up to 0.33 wt. % F at 1900 K and 0 GPa. By contrast, the effect of pressure on the fluorine solubility is very small, producing a decrease by a factor of two to three at 12 GPa. Consequently, partition coefficients of fluorine between forsterite and aqueous fluid (or silicate melt) are expected to increase with increasing temperature and decreasing pressure. When fluids or melts pass through the mantle wedge, fluorine will most efficiently be stored in the high-temperature portions of the wedge, promoting mantle metasomatism beneath the arc, and it will be released when the metasomatized mantle is advected to colder regions or to higher pressures.

Diffusion and microbial consumption of oxygen in an acidic geothermal iron-oxide mat

H C. BERNSTEIN[1], J. P. BEAM[2], R. P. CARLSON[1] AND W.P. INSKEEP[2]*

[1]Department of Chemical and Biological Engineering, Montana State University, Bozeman, MT 59717, USA (*correspondence:hans.bernstein@biofilm.montana.edu,binskeep@montana.edu)
[2]Department of Land Resources and Environmental Sciences, Montana State University, Bozeman, MT 59717, USA

The role of dissolved oxygen as a primary electron acceptor for microbially mediated iron oxidation was investigated within the primary flow path of an acidic geothermal spring in Norris Geyser Basin, Yellowstone National Park. Previous data has suggested that Fe(II)-oxidizing microbial populations (e.g., Metallosphaera yellowstonensis and potentially other novel members of the domain Archaea) represent the primary-producers within these microbial communities. Consequently, the availability of oxygen is hypothesized to limit microbial Fe(II)-oxidation and primary-productivity in this system. In situ measurements of oxygen profiles were obtained perpendicular to the direction of convective flow across the aqueous phase-Fe(III)-oxide interface using oxygen microsensors. Dissolved oxygen concentrations drop below detection by ~ 600 μm into the Fe(III)-oxide mat, indicating reactive oxygen consumption and defined spatial gradients. Evaluation of the oxygen flux across the liquid-mat boundary showed that convection was negligible compared to diffusive transport in the mat. Reaction-diffusion models were evaluated assuming both zero and first-order reaction kinetics. The in situ measurements and models suggest that the rate of oxygen consumption exceeds the rate of diffusion. Thus, microbially mediated Fe(II)-oxidation in this system is likely limited by oxygen diffusion, resulting in an active surface layer of Fe(III)-oxide biomineralization.

Quantitative mapping of the oxidation state of iron in mantle garnet

A.J. BERRY[1]*, G.M. YAXLEY[2], B.J. HANGER[2], A.B. WOODLAND[3], M.D. DE JONGE[4], D.L. HOWARD[4] AND D. PATERSON[4]

[1]Department of Earth Science and Engineering, Imperial College London, South Kensington, SW7 2AZ, UK (*correspondence: a.berry@imperial.ac.uk)
[2]Research School of Earth Sciences, Australian National University, Canberra, ACT 0200, Australia
[3]Institut für Geowissenschaften, Universität Frankfurt, Frankfurt am Main, D60438, Germany
[4]Australian Synchrotron, Clayton, VIC 3168, Australia

The garnet structure can accommodate both Fe^{2+} and Fe^{3+} and $Fe^{3+}/\Sigma Fe$ of garnets in garnet peridotite can be used to determine the oxygen fugacity (fO_2) of the cratonic lithosphere. This is important as an indicator of diamond (versus carbonate) stability. Post-formation metasomatic processes in the upper mantle, or during transport in kimberlites, may impose high fO_2s that result in diamond breakdown or resorption. Such events will usually be recorded by the coexisting garnet.

$Fe^{3+}/\Sigma Fe$ of garnets has traditionally been determined by Mössbauer spectroscopy of powdered samples. This lacks spatial resolution and the data for each measurement take several days to acquire. X-ray absorption near edge structure (XANES) spectroscopy is now commonly being used to determine $Fe^{3+}/\Sigma Fe$, is capable of micron spatial resolution and spectra can be recorded in ~15 minutes. We have recently reported a new method for quantifying $Fe^{3+}/\Sigma Fe$ from the XANES spectra of mantle garnets with an accuracy and precision comparable to Mössbauer spectroscopy [1].

XANES spectra were recorded in fluorescence mode from garnets prepared as either polished thin sections or electron probe mounts. A calibration curve relating the XANES spectra to $Fe^{3+}/\Sigma Fe$ of mantle garnets previously analysed by Mössbauer spectroscopy allowed garnet unknowns to be quantified. By recording the fluorescence intensity at a small number of energies as a function of position $Fe^{3+}/\Sigma Fe$ maps could be produced. It is possible to quantitatively map the oxidation state of Fe with a spatial resolution and acquisition time comparable to elemental mapping using the electron microprobe. This allows zonation of $Fe^{3+}/\Sigma Fe$ due to metasomatic processes to be identified.

[1] Berry *et al*. (2010) *Chem. Geol*. **278**, 31-37.

Carbonation of Steel Slag I

ELEANOR J. BERRYMAN[1]*, ANTHONY E. WILLIAMS-JONES[1], ARTASCHES A. MIGDISOV[1] AND SIEGER VAN DER LAAN[2]

[1]Department of Earth and Planetary Sciences, McGill University, Montreal, Quebec, Canada *(berryman.eleanor@gmail.com)
[2]Tata Steel RD&T, Ceramics Research Centre, IJmuiden, The Netherlands

Mineral carbonation provides a durable and environmentally inert method of sequestering CO_2 emissions. Larnite (Ca_2SiO_4), a major constituent of steel slag, is highly reactive with aqueous CO_2 [1]. Consequently, carbonation of steel slag offers an opportunity to reduce CO_2 emissions while recycling an industrial waste product. This study investigates the reactions taking place during the dissolution and carbonation of steel slag, and is part of a larger study designed to determine the conditions under which conversion of larnite and other calcium silicates to calcite is optimized.

Experiments were conducted on 2 – 3 mm diameter steel slag grains supplied by Tata Steel RD&T. A H_2O-CO_2 fluid mixture (XCO_2 = 0.05) was pumped through a flow-through reactor containing these grains. Temperature ranged from 120°C to 200°C, the pressure was 250 bar and the flow rate was 3.00 mL/min. The duration of experiments varied from 3 to 7 days.

The slag grains reacted to form Ca-carbonate and –phosphate phases upon contact with the CO_2-saturated fluid. These phases subsequently dissolved, forming a porous aluminium and iron oxide framework around the edges of the grains. The compositions of the reacted fluid reflect the observed dissolution of Ca-bearing phases and the buffering of Si by the formation of opaline silica. These results are in good agreement with predictions from thermodynamic calculations, indicating that the system achieved local equilibrium.

[1] Santos et al. (2009) *Journal of Hazardous Materials* **168**, 1397-1403.

Effect of CO_2-enriched fluid on three argillite type caprocks

G. BERTHE[1,2]*, S. SAVOYE[3], C.WITTEBROODT[1] AND J.-L. MICHELOT[2]

[1]IRSN, DEI/SARG/LR2S,92260 Fontenay-aux-Roses, France (*correspondence: guillaume.berthe@cea.fr)
[2]IDES,CNRS-Université Paris-Sud F-91405 Orsay, France
[3]CEA, DEN/DANS/L3MR, F-91191 Gif-sur-Yvette, France

The sequestration of CO_2 under impervious caprocks as argillite is proposed to reduce the greenhouse effect. CO_2 impact on the containment properties of argillite has to be assessed, as performed by [1] on Upper Toarcian rocks from Tounemire site (France). In the current study, we widened the approach to two other levels from Tournemire (Lower Toarcian and Domerian), displaying distinct carbonate contents (30% and 8%, resp.).

^{36}Cl, HTO, Br^- and D_2O were used as tracers in through-diffusion experiments carried out with and without CO_2-enriched fluids. The through-diffusion technique consists in imposing a concentration gradient of the tracer between the two faces of the sample. For the cells simulating an acidic fluid attack, dissolved CO_2 was injected inside the upstream reservoir. Chemistry evolution was also monitored in the up and downstream reservoirs.

Tracer data analyses indicated a degradation of the containment properties of the samples, increasing from the Paper Shale (unaffected) up to the Toarcian (Fig.1)

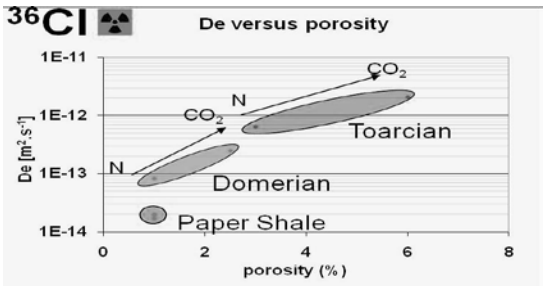

Figure 1: evolution of the diffusive parameters for the 3 levels

Such a difference can be accounted for by the distinct kinetics for achieving the chemical equilibrium regarding carbonates as shown by [Ca2+], [Mg2+] and alkalinity monitoring. This demonstrates the role played by the initial petrophysical properties of the rocks, in addition to their carbonate content.

[1] Berthe *et.al*. (2011) *Energy Procedia* **4**, 5314-5319.

On the use of nucleation barriers in numerical simulation of water-rock interactions

P. BERTIER*, C. WEBER AND H. STANJEK

Clay and Interface Mineralogy, RWTH-Aachen University, Bunsenstrasse 8, D-52072 Aachen Germany, (*correspondence: Pieter.Bertier@cim.rwth-aachen.de)

Numerical simulations of water-rock interactions in diagenetic or CO_2 sequestration systems generally predict mineral alteration processes that are considerably faster than those observed in experiments or diagenetic environments. This has been attributed to several reasons, among which the common disregard for nucleation of precipitating mineral phases in such models.

The effect of the implementation of nucleation barriers was evaluated on a kinetic reaction path model of sandstone diagenesis. Critical levels of supersaturation required for precipitation, based on literature data of formation water compositions, substantially slow down reaction kinetics due to their feedback on the dissolution rates of the minerals supplying the component species of the precipitating phase.

The implementation of nucleation barriers and rates based on classical nucleation theory have a similar effect, but often predict unrealistically high levels of supersaturation. One of the crucial parameters in classical nucleation theory is the mineral-water interface tension. Literature data on mineral-water interface tension is scarce and ambiguous. Different methods for measuring or calculating interface tensions produce very different results.

A methodology, based on capillary rise in powder beds as described by Washburn's equation, was developed for quantifying mineral water interface tensions under conditions typical of diagenetic systems. The interface tensions of several common rock forming minerals were determined. Application of these new data in the classical nucleation theory based kinetic reaction path model results in more realistic levels of supersaturation.

Interactions between precipitation and sea surface temperature in Northern Chilean Patagonia during the Late Holocene

S. BERTRAND[1,2,*], K. HUGHEN[2], J. SEPÚLVEDA[3] AND S. PANTOJA[4]

[1]Renard Centre of Marine Geology, University of Ghent, Ghent, Belgium (* correspondence: sbertrand@whoi.edu or sebastien.bertrand@ugent.be)
[2] Woods Hole Oceanographic Institution, Woods Hole, MA, USA
[3] Massachusetts Institute of Technology, MA, USA
[4] COPAS, University of Concepción, Concepción, Chile

The climate of Chilean Patagonia is highly influenced by the Southern Westerlies, which control the intensity and latitudinal distribution of precipitation in the Southern Andes. In austral summer, the Westerly Wind Belt (WWB) is restricted to the high latitudes (> 47°S). It expands northward in winter, which results in a strong seasonal signal in precipitation between ~47 and ~30°S. In addition, the area is characterized by a steep latitudinal Sea Surface Temperature (SST) gradient, which reflects the regional influence of the Antarctic Circumpolar Current (ACC). Here, we present a new precipitation proxy record from the Chilean fjords at 45°S, and we compare our results with regional SST records to assess the ocean-continent interactions in Chilean Patagonia during the last 2 millennia. Our precipitation record is based on a high-resolution inorganic geochemical analysis of a 2m long sediment core from Quitralco fjord (45°S), using ICP-AES and XRF core scanning techniques. Since our coring site is located in front of a small river that drains the Patagonian Andes (Rio Pelu), it is particularly sensitive to changes in river discharge, and therefore precipitation. Our data demonstrates a significant increase in Fe/Al and Ti/Al between ~700 and ~50 cal. yr BP, which corresponds to a decrease in mean sediment grain-size from ~30 to ~20 μm. This shift is interpreted as a decrease in the energy of river sediment discharge, which most likely reflects a decrease in seasonal floods. The comparison of our precipitation record with published SST records from the region demonstrates that lower (higher) SSTs are systematically coeval with a decrease (increase) in seasonal floods in the Patagonian Andes. The decrease in seasonal floods at 700-50 cal. yr. BP corresponds to a SST decrease of ~1°C. We argue that the synchronicity of changes in precipitation and SST during the last two millennia likely reflects concomitant migration of the zonal systems, i.e., the WWB and the ACC.

Evolution of the macromolecular structure of biopolymers during pyrolysis: A C-XANES study

O. BEYSSAC[1], S. BERNARD[2], K. BENZERARA[1] AND G.E. BROWN JR.[3]

[1]IMPMC, UPMC, CNRS, Paris, France (Olivier.Beyssac@impmc.jussieu.fr, Karim.Benzerara@impmc.jussieu.fr)
[2]LMCM, MNHN, CNRS, Paris, France (sbernard@mnhn.fr)
[3]SAGG, DGES, Stanford University, Stanford, USA (Gordon@pangea.stanford.edu)

Identifying traces of life in ancient rocks can be challenging as they may have experienced significant structural and chemical transformations during diagenesis and metamorphism. Natural organic matter may indeed evolve during fossilization processes and hence lose all chemical and textural information relative to its original precursor. Recently, advanced spectromicroscopy techniques have allowed evidencing that morphological, textural and chemical bio-signatures might be preserved in some contexts despite intense metamorphism [1,2], notably depending on the chemical nature of the organic precursor [3]. Synchrotron-based techniques are thus increasingly used to *in situ* characterize natural kerogens and study fossilization processes although standard data sets are still only scarcely available [4,5]. Therefore, information obtained from these recently developed techniques remains barely exploited.

Here, we have investigated the evolution of reference organic biocompounds more or less resistant to biodegradation (e.g. sporopollenin, lignin and cellulose) heat-treated at different temperatures up to 1000°C at ambient pressure using X-ray absorption near edge structure (XANES) spectroscopy at the Carbon K-edge. In addition to evidencing the differential evolutions of these precursors during carbonification and early steps of graphitization, quantitative information extracted from our results provide a calibration for the spectroscopic evolution of reference biocompounds with increasing temperatures. By providing new insights into the thermal evolution of the macromolecular structure of reference biopolymers, the present results constitute a new step towards better constraining the fate of natural organic matter during burial.

[1] Schiffbauer *et al*. (2007), *Astrobiology* **7(4),** 684-704. [2] Bernard *et al*. (2007), *EPSL* **262**, 257-272. [3] Bernard *et al*. (2010), *GCA* **74**, 5054-5068. [4] Solomon *et al*. (2009), *Soil Sci. Soc. Am. J.* **73**, 1817-1830. [5] Bernard *et al*. (2010), *Carbon* **48**, 2506-2516.

Seasonal shifts in concentration, age, and lability of carbon exported from the Greenland ice sheet (GrIS)

M.P. BHATIA[1]*, S.B. DAS[2], M.A. CHARETTE[3], L. XU[3], AND E.B. KUJAWINSKI[3]

[1]MIT-WHOI Joint Program, Woods Hole Oceanographic Institution (WHOI), Woods Hole MA, 02543 (*correspondence: mayab@mit.edu)
[2]Department of Geology and Geophysics, WHOI, Woods Hole MA, 02543 (sdas@whoi.edu)
[3]Department of Marine Chemistry and Geochemistry, WHOI, Woods Hole MA, 02543 (mcharette@whoi.edu, lxu@whoi.edu, ekujawinski@whoi.edu)

Active microbial communities at the base of glaciers and ice sheets provide a mechanism for (a) subglacial organic carbon metabolism on various timescales, and (b) the present-day export of labile carbon to downstream ecosystems. Prior studies point towards the importance of both these processes in modulating carbon cycling. Here we describe for the first time the bulk-level carbon composition of meltwater draining the GrIS. We investigate the dissolved (DOC) and particulate organic carbon (POC) concentration, age, and lability in the subglacial discharge throughout the summer. The early season discharge contains higher organic carbon concentrations, and exports younger DOC (~ 2 kyr ^{14}C age) compared to the peak season discharge, where the concentrations are lower and the age is older (~ 4 kyr ^{14}C age). Conversely, the age of the exported POC (~ 2.5 kyr ^{14}C age) does not change throughout the meltseason. We hypothesize that overwinter subglacial microbial processes shift the type of DOC exported, and use the dissolved ion loads in the discharge to explore this idea. These results illustrate (1) that chemically-distinct organic carbon pools are accessed by seasonally-evolving hydrology and (2) that the GrIS may deliver labile, old carbon to the North Atlantic Ocean.

Sr-Nd isotopic studies of Narcondam Volcanics, India: Constraints on Andaman-Indonesian arc magmatism

RAJNEESH BHUTANI*[1], R.S. SMITHA[1], JYOTIRANJAN S. RAY[2], HETU C. SHETH[3], S. BALAKRISHNAN[1], ALOK KUMAR[2] AND NEERAJ AWASTHI[2]

[1]Department of Earth Sciences, Pondicherry University, Puducherry-605014, India (*rbhutani@gmail.com)
[2]Geosciences Division, Physical Research Laboratory, Navrangpura, Ahmedabad-380009, India
[3]Department of Earth Sciences, Indian Institute of Technology Bombay, Powai, Mumbai-400076, India

Narcondam island, part of Andaman group of islands of India is a dormant volcano of Andaman-Indonesia island arc related to oblique subduction of Indian plate beneath the SE Asian plate.

Unlike the active Barren Island volcano of Andaman arc, which erupts basaltic to basaltic-andesite lavas, Narcondam samples, studied during the present study, range from basaltic-andesites to dacites with majority of them plotting in andesitic field of Total Alkali Silica (TAS) classification diagram.

Origin of andesitic lavas has been explained variably, ranging from models of hydrous melting of mantle-wedge to models of mixing of basaltic magma with rhyolitic magma at shallower depths [1].

Narcondam andesites show mineral textures, such as resorbed rims of plagioclase phenocrysts, Na rich layers sandwitched between Ca rich layers of plagioclase crystals and at least two generations of phenocrysts, indicating compositional changes in magma not related to fractional crystallization. Presence of rhyolitic glass inclusions, and olivine and quartz crystals together are reported from Narcondam samples in an earlier study [2]. It is therefore suggested that andesitic lavas are not primary melt but probably resulted from mixing of basaltic and rhyolitic magmas.

Sr and Nd isotope ratios are used to quantify the mixing and it appears that andesites of Narcondam and also other andesitic volcanoes of Sunda arc may have resulted from variable but small inputs of sediments (<5%) to the mixed magma which has 70 to 80% contribution from Barren Island type basaltic melt and 15-20% of rhyolitic melt similar to that erupted in Sunda arc elsewhere [3].

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U-Pb cassiterite dating by LA-ICPMS and a precise mineralization age for the superlarge Furong tin deposit, Hunan Province, Southern China

XIANWU BI[1], HU RUIZHONG[1], LI HUIMIN[2], DONG SHAOHUA[1,3], CHEN YOUWEI[1] AND PENG JIANTANG[1]

[1]State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China (bixianwu@vip.gyig.ac.cn)

[2]Tianjin Institute of Geology and Mineral Resources, Tianjin, 300170, China

[3]Graduate School of Chinese Academy of Sciences, Beijing 100039, P.R. China

Cassiterite is an important tin mineral in the W-Sn deposit. Furthermore, it is also a common accessory in a variety of deposits, and the successful use of cassiterite as a geochronometer would resolve many genetic questions. The direct dating of cassiterite with U–Pb and Pb–Pb methods was initially attempted by Gulson and Jones. In recent years, the U–Pb isotope data on cassiterite from tin deposits using TIMS were reported and the potential of cassiterite as a geochronometer for directly dating hydrothermal mineralization was evaluated. This study aims to directly date the U-Pb age on cassiterites from the Furong tin deposit using LA-MC-ICPMS techniques, to validate the utilization of cassiterites for precise dating of ore formation.

The Furong deposit is a newly-discovered superlarge tin deposit in the central Nanling district, South China. In this study, cassiterite from the Furong tin deposit has been successfully dated by LA-MC-ICPMS and it is the first report of the U–Pb isotope dates on cassiterite using LA-MC-ICPMS. In situ analysis of two cassiterites (WCP2-1 and WCP2-2), yield U–Pb isochron age of 155.8±1.6Ma (MSWD=20). This U–Pb age from the cassiterites in skarn type ores which is the main type ore in Furong tin deposit, yielded indistinguishable mineralization ages with U–Pb isochron age of 160.0±5.5Ma (MSWD=1.74) by TIMS and published Ar–Ar dating on hydrothermal muscovite, hornblende and phlogopite from greisen type tin ore and skarn-type ores, reveal the main stage age of Furong tin mineralization was around 155Ma. The dates obtained in this study indicated that the cassiterites with high content U are the potential directly dating minerals.

This work was supported jointly by the National Basic Research Program of China (2007CB411404)

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Investigation of atmospheric nitrate and ammonium and their impact on air quality and climate in GMI

HUISHENG BIAN[1,2], STEVE STEENROD[1,2], MIAN CHIN[3] AND JOSE RODRIGUEZ[3]

[1]Goddard Earth Sciences and Technology Center, University of Maryland, Baltimore County, Baltimore, Maryland, USA

[2]Also at Atmospheric Chemistry and Dynamics Branch, NASA Goddard Space Flight Center, Greenbelt, Maryland, USA

[3]Atmospheric Chemistry and Dynamics Branch, NASA Goddard Space Flight Center, Greenbelt, Maryland, USA

The capability to simulate nitrate and ammonium aerosols has been developed in NASA GMI model by implementing a thermodynamic equilibrium model that treats gas and aerosol multiphase chemical equilibrium reactions in a SO_4-NO_3-NH_4-H_2O system. Nitrate and ammonium can influence air quality and ecosystems substantially, and their importance will be increasing in the future due to the predicted increase of nitrogen emissions. An immediate outcome from the work is the possibility to improve tropospheric O_3 simulation. Currently, the model treats HNO_3 solely as a gas phase tracer. This semi-volatile species now partitions between gas and aerosol phases, and the tracer in each phase is subject to different chemical and physical processes. A preliminary analysis has been conducted by comparing results simulated with and without new nitrate package and by comparing model results with the ground station observations from CASTNET and EMEP.

High resolution minor and trace element study on mussel shells from coastal region of Tatoosh Island, Washington, USA

NANXI BIAN[1]*, PAMELA MARTIN[1], CATHERINE PFISTER[2], AND ALBERT COLMAN[1]

[1]Department of Geophysical Sciences, University of Chicago, Chicago, IL, USA (*correspondence: nanxibian@uchicago.edu

[2]Department of Ecology and Evolution, University of Chicago, Chicago, IL, USA

The successively deposited calcium carbonate layers and annual growth bands in mollusk shells could offer high resolution archives of the environmental conditions the mollusk has experienced during its life. Previous studies have shown that the elemental composition of mollusk shells is related to environmental parameters[1, 2, 3].

Here, we present high resolution data of a suite of minor/trace element/Ca ratios collected from shells of mussel species, *Mytilus californianus*, using laser ablation sector field inductively coupled plasma mass spectrometry (LA-ICP-MS) as well as an ICP-MS solution based method. The mussel shells were ~10 years of age and were collected live in 2009 and 2010 from Tatoosh Island, Washington, USA, where instrumental data of various enviromental parameters over the last decade are available. We also analyzed several shells present in middens on Tatoosh Island. Radio-carbon dating data of these mussels show they lived ~1000 years ago; shell banding suggests individual ages of ~12 years. Age models were constructed using annual banding, a growth model and high resolution stable isotope composition ($\delta^{18}O$) of the shell.

Our preliminary results show that several of a suite of trace elements exhibit promising correlation with nutrient concentration and oxygen level in the sea water, and could serve as proxies for coastal geochemical cycling and a means to probe rapid changes documented in seawater chemistry at this site[4]. Data for a suite of element/Ca ratios from different transects on the same shell generally show good reproducibility. Element/Ca data from midden shells and modern shells show different ranges of variation suggesting that there have been significant differences in geochemical cycling in this coastal environment over the last 1000 years.

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Carbonate rocks from fluid and gas expulsion sites of the Green Canyon, Gulf of Mexico: Analysis and interpretation

YOUYAN BIAN[1,3], HONGPENG TONG[1,3], DONG FENG[1,2], HARRY H. ROBERTS[2] AND DUOFU CHEN[1]*

[1]Key Laboratory of Marginal Sea Geology, Guangzhou Institute of Geochemistry, CAS, Guangzhou 510640, China (*correspondence: cdf@gig.ac.cn)

[2]Coastal Studies Institute, Louisiana State University, Baton Rouge, LA 70803, USA

[3]Graduate University of the Chinese Academy of Sciences, Beijing 100049, China

Cold hydrocarbon seepage is a frequently observed phenomenon in marine settings worldwide. Authigenic carbonates from hydrocarbon seeps are unique archives of past seepage and associated environmental parameters. Carbonate rocks were collected from fluid and gas expulsion sites of Green Canyon lease block 140 (GC 140) at 260 m water depth on the Gulf of Mexico continental slope during Johnson-Sea-Link dive 2591 in 1989. The carbonate rocks occur as blocks, crusts, and nodular masses incorporated in carbonate breccias. Most carbonates are composed of aragonite and high-Mg calcite as determined from X-ray diffraction. However, one sample was found to have compositoon of nearly 100% dolomite. Petrographically, high Mg-calcite peloidal matrix and acicular to botryoidal aragonitic void-filling cements are the most frequent associations. The carbon isotopic compositions of the carbonates ($\delta^{13}C_{Car}$) range from –36.5‰ to +4.9‰ V-PDB, indicating complex carbon sources that include ^{13}C-depleted methane, seawater CO_2, and ^{13}C-enriched residual CO_2 from methanogenesis. A similarly large variability in $\delta^{18}O_{Car}$ values (+1.6‰ to +5.5‰ V-PDB) demonstrates the geochemical complexity of the studied area. The considerable range of mineralogical and isotopic variations of the studied cold seep carbonate suggests that local controls on the fluid and gas flux, types of the local hydrocarbon reservoir may play an important role in determining carbonate mineralogy and isotope geochemistry. In addtion, the ^{14}C ages of bivalve shells incorporated in the carbonate matrix will be used to determine the timing and duration of fluid seepage in order to provide preliminary insight into probable factors governing seepage processes at the studied site.

Acknowledgements: The work was partially supported by the NSFC (40725011 and U0733003) and Chinese Academy of Sciences (KZCX2-YW-GJ03).

Pb-Hf-Nd isotopic decoupling in peridotite xenoliths from Mega (Ethiopia): Insights into the multistage evolution of the East African Lithosphere

G. BIANCHINI[1]*, J.G. BRYCE [3], J. BLICHERT-TOFT[4], L. BECCALUVA[1] AND C. NATALI[1],

[1]Università di Ferrara, Ferrara, Italy (bncglc@unife.it)
[2] CNR - Istituto di Geoscienze e Georisorse, Pisa, Italy
[3]UNH Earth Sciences, Durham NH, USA
[4]Ecole Normale Supérieure de Lyon, Lyon, France

New Hf and Pb isotopic data from clinopyroxenes from East African Rift (EAR) mantle xenoliths (Mega, Sidamo region, southern Ethiopia), coupled with recently published Nd isotope and trace element compositions, provide compelling evidence for multiple episodes of mantle depletion and metasomatic enrichment. Radiogenic values (ε_{Nd} up to +22.5 and ε_{Hf} up to +1076) suggest mantle domains currently located beneath the Main Ethiopian Rift suffered extreme melting regimes, possibly in the presence of residual (majorite?) garnet, effectively fractionating Sm/Nd, Lu/Hf and Nd-Hf systematics. Positively correlating Lu/Hf and $^{176}Hf/^{177}Hf$ provide an apparent ingrowth of 1.96 Ga, close to the CHUR model age of the most radiogenic sample (1.95 Ga, consistent with other local records of Proterozoic melting events). Pb isotopes are clearly decoupled from the Nd-Hf systematics, displaying $^{206}Pb/^{204}Pb$ up to 20.1, $^{207}Pb/^{204}Pb$ up to 15.70, and $^{208}Pb/^{204}Pb$ up to 39.8. These data suggest vigorous convection cells, possibly triggered as a far afield dynamic consequence of the Afar plume impingement, preferentially occurred beneath this site, where important lithospheric discontinuities exist between the Archean/Early Proterozoic Tanzanian craton and the Late Proterozoic Panafrican mobile belt. Such deep mantle dynamics may contribute to stabilizing distinct EM1 and HIMU metasomatic components in the EAR lithospheric mantle.

Early Archean crust of the Ukrainian Shield – Evidence from detrital zircons

E. BIBIKOVA, L. SHUMLYANSKYY, C.J. HAWKESWORTH, S. CLAESSON, C. STOREY, B. DHUIME AND A. FEDOTOVA

Data on continental sediments remain the basis for many models for the generation and evolution of the crust [1]. Detrital zircons from old metasedimentary rocks can provide valuable contributions to the knowledge of the Early Earth crust. We have studied geochronologically (U-Pb, zircons, Sm-Nd) and geochemically (Hf-isotopes and REE) detrital zircons from two greenstone structures in the Azov domain, Ukrainian Shield. U-Pb isotopes of zircons from five samples of mica schists from the Soroki and Fedorof greenstone belts were analysed on ion microprobe NORDSIM at the Swedish Museum of Natural History, focusing mainly on cores identified by CL. The data include a group of ages in the range 3.5-3.6 Ga, and some zircon cores older than 3.7 Ga.

The REE patterns of metasediments and zircons are similar to those of TTG Archaean rocks [1]. Lu-Hf isotopic system was studied by La ICP-MS at University of Bristol [2] at the same spots inside zircons where the most concordant ages were obtained. In our interpretation of Hf isotope data, we follow the model proposed by [3]. The majority of granites have isotope signatures that preclude direct mantle genesis, rather we constrain the $^{176}Lu/^{177}Hf$ ratio of the crustal material that was initially extracted from the mantle to be 0.22-0.25, typical for mafic magmas. In such interpretation, the age of this crust will be about 4.2 Ga. The model age of zircons in metasediments derived from the TTG rocks with low $\leq$ 0.01 $^{176}Lu/^{177}Hf$ ratio, is 3.8-3.6 Ga.

Sm-Nd model ages of 3.3-3.4 Ga and εNd (T) for the analysed samples are in a good agreement with the zircon data. Our new results indicate that Eo and Paleoarchean crust in the Azov domain was widely distributed.

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Geological carbon storage: Geochemical processes

MIKE BICKLE

Dept. Earth Sciences, University of Cambridge, Downing St., Cambridge CB2 3EQ, UK (mb72@esc.cam.ac.uk)

Modelling the complex physical and chemical processes that govern retention of CO_2 in geological reservoirs over long time scales present some interesting challenges, although not perhaps as challenging as coping with the consequences of unabated CO_2 emissions.

CO_2 may be held in geological formations by structural, capillary, dissolution and mineralisation trapping. CO_2 or CO_2-charged brines may corrode reservoir minerals and caprocks. Remote imaging of CO_2 reservoirs, such as at Sleipner [1,2], captures the complex physical behaviour of CO_2 but is unable to completely explain this behaviour or resolve alll potential trapping and escape mechanisms. Direct sampling of field small-scale injection experiments offers the best chance to do this [3]. Estimates of capillary trapping can be made by analysis of isotope spikes [4]. Dissolution trapping will be enhanced by the complexities of the flow processes and sampling of brines will be essential to monitor this. Prediction of the reaction rates between CO_2-charged brines and reservoir minerals or caprocks is even more difficult. Observations on geological analogue sites have recovered the rates of the sluggish reactions between silicate minerals and brines [5]. Curiously the much more rapid rates of dissolution of carbonate, evaporite and oxy-hydroxide minerals in field conditions seen in small scale injection experiments [6] are poorly known. These reactions may also release contaminants.

Modelling of fluid-mineral interactions currently uses averaged fluid properties in pseudo- 1 dimensional models [e.g. 7]. It is not clear if this is an appropriate way to approximate the complex flow paths. What is needed is a method for inverting geochemical data to constrain the key attributes of flow heterogeneities.

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A bond-valence view of interfacial structure and reactivity

B. R. BICKMORE*

Geological Sciences, Brigham Young University, Provo, UT 84602, USA
(*correspondence: barry_bickmore@byu.edu)

Studies of interfacial structures will be most useful in cases where we can relate structure to reactivity. However, a quantitative structure-activity relationship (QSAR) requires that structural information be couched in terms that are easily translatable into energy. The bond-valence model (BVM) [1] has proven fairly effective for this purpose, and it has been used to formulate a number of QSARs, including the MUSIC model for predicting surface functional group acidity on oxide surfaces [2]. Such BVM-based QSARs have had varying success, but they are typically applicable under a fairly restricted set of conditions [3].

It is not readily apparent when QSARs like MUSIC should work or fail, however, because nobody has yet worked out a full BVM-based accounting of the relationship between molecular structure and energy. E.g., the most commonly used aspect of the BVM involves summing bond valences calculated from the lengths of bonds to counter-ions surrounding a central ion. The valence sum is then compared to an ideal value, and the difference is taken to be indicative of some aspect of structural energy. But this does not account for directionality in bonding or interactions between co-ions.

We are currently using some lesser-known aspects of the BVM, including vectorial bond valence (VBV) sums [4] and "effective valence" between co-ions [1], combined with some concepts borrowed from the Valence Shell Electron Pair Repulsion (VSEPR) model of molecular geometry, to create a more complete BVM-based model of structure-energy relationships. By analyzing oxide crystal structures and *ab initio* molecular dynamics simulations of aqueous solutions, we have shown that ideal VBV sums have a fairly straightforward relationship with bond character and coordination number. VBV sums also exhibit a strong relationship with deviations from ideal valence sums.

In addition, we will be applying such analyses to simulated interfacial structures to see how our indicators of "structural energy" vary with distance from the interface, salinity, etc. Such information could then be related to double layer theory.

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Mineral and whole-rock chemical properties of pyroxenites in the peridotites of the Kop Ultramafics, NE Turkey

Ö. BILICI * AND H. KOLAYLI

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

The Kop ultramafic unit in NE Turkey is one of the largest Alpine type peridotites. Petrographic and field studies in the ultramafic unit indicate that there are widespread two main rock types as harzburgites and dunites. In addition to these, pyroxenites are also locally observed and associated with peridotites.

Pyroxenites crop out as veins/dykes in varying size within peridotites [1]. Orthopyroxenites (>500 m^2) cover larger area than clinopyroxenites (between 10 to 100 m^2) and websterites (<1 m^2). Clinopyroxenites and orthopyroxenites exhibit dyke-like body in dunites and harzburgite, respectively. Websterites are only observed as veins in harzburgitic zone. Orthopyroxenites show coarse grained texture whereas clinopyroxenite and websterites have porphyritic texture. Clinopyroxenites and websterites contain variable amounts of olivine, spinel and magnetite.

Both whole-rock and pyroxene mineral chemistry data of the pyroxenites are characterized by low contents of Al, Na, K, Ta, Zr, Hf, Ti and REE, high Mg-numbers and LILE enrichment relative to less incompatible elements. The mineral and petrochemical data suggest that clinopyroxenites and websterites from the pyroxenites have not been directly crystallized from primary magma(s) derived by partial melting of depleted mantle. Whole-rock and pyroxene compositions of orthopyroxenites are similar to those of ultra-depleted mantle-derived pyroxenites, whereas cliopyroxenites and websterites have very close chemical features to those of pyroxenites in suprasubduction zone mantle.

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In situ dating and investigation of remarkably depleted –26‰ SMOW "Slushball" Earth zircons

I. BINDEMAN[1], J. VAZQUEZ[2], A. SCHMITT[3], J. EILER[4], N. SEREBRYAKOV[5] AND D. EVANS[6]

[1]Geol Sci, U. Oregon, Eugene OR; (bindeman@uoregon.edu)
[2]USGS, Menlo Park, Ca;
[3]ESS, UCLA, Los Angeles, Ca;
[4]GPS, Caltech, Pasadena, Ca;
[5]IGEM-RAS, Moscow, Russia;
[6]Geol & Geophys., Yale Univ., New Haven, CT

Paleoproterozoic amphibolites and gneisses - that are remarkably depleted in ^{18}O are found in the Belomorian Belt in Karelia, Russia [1,2]. We mapped their extent to exceed 200x20km and affect metamorphosed mafic intrusions (est. ~2.4 Ga intrusion age) and host 2.6Ga gneisses found in this 1.9 Ga collisional belt. $\delta^{18}O$ values of –7 to –27.3‰ characterize minerals and rocks from several of these localities; some of these rocks are also remarkably depleted with respect to δD (-212 to –235‰ amphiboles). All have typical terrestrial $\Delta^{17}O$ values of 0‰. Based on previous paleogeographic reconstructions, we attribute the origin of these exotic O and H isotope compositions to the hydrothermal alteration associated with subglacial rifting during the Paleoproterozoic panglobal ice ages, but discuss additional possibilities: extremely low-$\delta^{18}O$ Paleo- proterozoic sea water, and excursion of Karelia to polar latitudes. Given that at high-T hydrothermal exchange equilibrium $\Delta^{18}O$(rock-water) is close to zero, but water-rock interaction is rarely 100% efficient, the lowest measured $\delta^{18}O$ value in silicates likely gives the upper $\delta^{18}O$ bound for the altering meteoric fluid; we thus continues our quest to find the lowest $\delta^{18}O$ material such as a mineral assemblage or a tiny zircon fragment that would provide record of $\delta^{18}O$water.

Zircons in these rocks have survived metamorphism and record normal $\delta^{18}O$ cores and extremely low $\delta^{18}O$ rims (down to $\delta^{18}O_{SMOW}$ = 26.2 ‰). The rims are in oxygen isotope exchange equilibrium with host metamorphic assemblages at each locality. We present data from the ongoing investigation of these zircons using large radius ion microprobes for *in situ* U-Pb ages and $\delta^{18}O$ values, ion microprobe profiling using a ~1 μm gallium beam, and NanoSIMS isotope mapping of the zircon with 23 to 34‰ and sharp (~3-5 μm) isotope gradients.

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High-precision Mg isotope measurements of inner solar system materials by HR-MC-ICPMS

M. BIZZARRO*, C. PATON, M. SCHILLER, K. LARSEN AND D. ULFBECK

Center for Star and Planet Formation, Natural History Museum, University of Copenhagen, Øster Voldgade 5–7, 1350, Copenhagen, Denmark (*correspondence: bizzarro@snm.ku.dk)

Magnesium has three naturally occurring isotopes - ^{24}Mg, ^{25}Mg and ^{26}Mg - with relative abundances of 79%, 10% and 11%, respectively. Variations in the isotopic composition of Mg can potentially occur in solar system materials through a number of processes including (*1*) stellar nucleosynthesis, (*2*) the former presence and decay of the ^{26}Al nuclide (half-life ~0.73 Myr) and (*3*) mass-dependent isotopic fractionation during high temperature processes such as partial evaporation and condensation as well as from low-temperature fluid/ rock interactions. Thus, studying the potential variability of ^{26}Mg/^{24}Mg and ^{25}Mg/^{24}Mg ratios in solar system solids can be used to infer genetic relationships between early solar system reservoirs and terrestrial planets.

We have developed novel methods for the chemical purification of Mg from silicate rocks, and high-precision analysis of Mg-isotopes by high-resolution multiple collector inductively coupled plasma source mass spectrometry (HR-MC-ICPMS) [1]. Based on the repeated analyses of international rock standards of variable matrices, we show that it is possible to routinely analyze the Mg-isotope composition of silicate materials with an external reproducibility of 2.5 and 20 ppm for the μ^{26}Mg* and μ ^{25}Mg values, respectively (μ notation is the per 10^6 deviation from the DSM-3 reference material).

Using these techniques, we have analyzed to unprecedented precision the Mg-isotope composition of a strategically-selected suite of inner solar system materials, including calcium-aluminium-rich inclusions and amoeboid olivine aggregates from the reduced Efremovka CV chondrite as well as bulk chondrite meteorites and meteorite samples originating from differentiated asteroids. These new data provide important constraints regarding the relative and absolute Mg-isotope composition of bulk inner solar system planetary reservoirs, the distribution of ^{26}Al in the solar protoplanetary disk, and the mechanism and timescale of asteroidal differentiation in the young solar system.

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Electrochemically-driven lithium isotopic fractionation

JAY BLACK[1]*, EMILIE PERRE[2], GRANT UMEDA[2], BRUCE DUNN[2], WILLIAM F. MCDONOUGH[3] AND ABBY KAVNER[1,4]

[1]IGPP
[2]Department of Materials Science and Engineering,
[3]ESS, University of California, Los Angeles, CA 90095 (*jayblack@ucla.edu, gumeda@yahoo.com, bdunn@ucla.edu, akavner@ucla.edu)
[4]Department of Geology, University of Maryland, College Park, MD 20742 (mcdonoug@umd.edu)

Lithium is a mobile element, with a high diffusion coefficient, and a large difference in solution diffusivities for the two stable isotopes, ^{6}Li and ^{7}Li [1], making it an ideal element for studying isotopic fractionation during electro-deposition processes. Rates of mass-transport and deposition can be dialed-in using experimental electrochemical techniques to study the competing isotopic fractionation effects of reduction/precipitation and diffusion. Previous experiments measured the equilibrium fractionation between Li metal and Li^+ in a propylene carbonate (PC) solvent [2], and large fractionations (up to -30 per-mil in ^{7}Li/^{6}Li) were observed between electrodeposited Li and stock solutions [3]. The magnitude of fractionation was largest closest to the equilibrium reduction potential, and decreased as the thermodynamic driving force (and thus deposition rate) was increased (Fig. 1) [3]. Two hypotheses for this trend are 1) mass-transport-limited supply of Li to the reactive interface resulted in an attenuated isotopic signature, and 2) the observed changing isotopic signature is an intrinsic rate-dependent kinetic effect. These competing hypotheses will be directly tested in models and experiments of temperature-depenedent isotopic fractionation during Li electrodeposition.

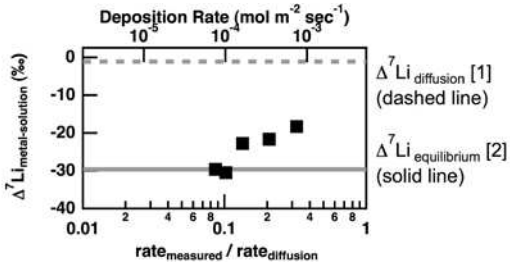

Figure 1. Lithium isotope composition of metal samples electroplated from 1M Li(PC) solutions, squares [3].

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A long-term record of continental lithosphere exhumation via U-Pb thermochronology of the lower crust

TERRENCE BLACKBURN[1]*, SAMUEL BOWRING[1], TAYLOR PERRON[1], KEVIN MAHAN[2] AND FRANCIS DUDAS[1]

[1]EAPS, MIT, Cambridge, MA, USA (*correspondance: terrence@mit.edu)
[2]Dept of Geol. Sci., Univ. of CU Boulder, CO, USA

Exposures of cratonic lithosphere (shields) are generally characterized by low long-term erosion and sediment accumulation. Seismic tomography and mantle xenolith studies of cratons reveal keels of seismically fast and relatively buoyant and viscous mantle; physical properties intimately linked with their long-term stability and topographic expression. Missing from these observations is a long-term record (>1000 Ma) of continental exhumation/burial that can be used to quantity the forces operating within these ancient regions. The exhumation or burial of the continent surface has a direct effect on the rate of heat loss within the lithosphere. By reconstructing the thermal history for the lithosphere using thermochronologic techniques, the magnitude of burial and exhumation through time can be estimated. Here we demonstrate how a long-term record of lithosphere exhumation or burial can be reconstructed using U-Pb thermochronology on lower crustal xenoliths. The U-Pb system is sensitive to cooling at temperatures of ~400-650 °C, corresponding to lower crustal depths of 20-50 km. Integration of this thermochronologic record with thermal models for the stable lithosphere allows one to reconstruct the magnitude of surface exhumation/burial during long-term cooling of the continents. In Montana, USA, lower crustal samples record extreme slow cooling consistent with low exhumation rates (<0.01 km/Ma) over time scales billions of years. Constraining the magnitude and variation of lithosphere exhumation over a billion years or more provides the opportunity to understand the degree of thermal and mechanical coupling between continental lithosphere and the underlying convecting mantle in the deep geologic past.

Are noble gases in the sediment pore water of Lake Van promising proxies for paleoclimate conditions?

R. BLÄTTLER[1], Y. TOMONAGA[1]*, M.S. BRENNWALD[1], O. KWIECIEN[1], R. KIPFER[1,2], AND THE PALEOVAN SCIENTIFIC PARTY

[1]Eawag, Swiss Federal Institute of Aquatic Science and Technology, CH-8600 Dübendorf, Switzerland (*correspondence: tomonaga@eawag.ch)
[2]Institute of Geochemistry and Petrology, Swiss Federal Institute of Technology (ETH), CH-8092 Zurich, Switzerland

As noble gases are chemically inert, they are ideal tracers to study physical processes in water bodies. The noble-gas partitioning between the atmosphere and the respective water body occurs according to Henry's Law, which is mainly controlled by the temperature and salinity of the exchanging water phase. Therefore, atmospheric noble gases (He, Ne, Ar, Kr, and Xe) have been successfully used in the past to reconstruct the physical conditions in aquatic systems such as groundwater, lakes, and oceans.

Several decades ago, noble gases in the pore water of unconsolidated sediments have been proposed as proxies for the reconstruction of environmental conditions in lakes and oceans. During sedimentation, a certain volume of the water overlying the sediment/water interface is trapped in the pore space of the growing sediment column. If the noble-gas diffusion within the pore water is sufficiently attenuated, the sediment column can conserve noble-gas concentrations over long time scales. However, only recently analytical methods allowing robust and reliable determination of noble-gas concentrations in the sediment pore water have been developed and improved. In Lake Issyk-Kul, a large closed-basin lake in central Asia, atmospheric noble gases in sediment pore water have been successfully applied for the first time as proxies for paleoclimate conditions.

In this study we present concentration profiles measured in the sediment column of Lake Van (Turkey). Lake Van is one of the largest terminal lakes and the largest soda lake on Earth. The lake is known to react very sensitively to changes in the local climate conditions.

We interpret the measured noble-gas concentrations in terms of possible changes in the physical conditions of the water body of the lake (i.e., changes in temperature and salinity). In particular we discuss the potential of noble gases as proxies for paleoclimate reconstruction considering the ongoing ICDP deep drilling project PALEOVAN (http://www.icdp-online.org).

First-principles simulation of arsenate adsorption on the (1 $\bar{1}$2) surface of hematite

M. BLANCHARD*, G. MORIN, M. LAZZERI, E. BALAN AND F. MAURI

MPMC, Univ. Paris VI, CNRS, IRD, Univ. Paris VII, IPGP, 4 Place Jussieu, 75252 Paris Cedex 05, France (*correspondence: marc.blanchard@impmc.upmc.fr, guillaume.morin@impmc.upmc.fr, michele.lazzeri@impmc.upmc.fr, etienne.balan@impmc.upmc.fr, francesco.mauri@impmc.upmc.fr)

Recent experimental studies [1, 2] revealed an unprecedented bimodal distribution of arsenate at the hematite (1 $\bar{1}$2) surface, with a simultaneous adsorption of inner-sphere and outer-sphere complexes. In the present study, first-principles calculations based on density functional theory were performed to make a detailed analysis of the structural and electronic properties of these inner-sphere and outer-sphere adsorption complexes on two hydroxylated terminations of the hematite (1 $\bar{1}$2) surface. For bidentate corner-sharing complexes, the most-stable adsorption configurations display interatomic distances in excellent agreement with EXAFS-derived data (i.e. As-Fe distances of ~3.3 Å). Our calculations also suggest that edge-sharing bidentate complexes can also form on clean (1 $\bar{1}$2) hematite surfaces and do not necessarily need step edges. These edge-sharing complexes would display two As-Fe distances at about 2.85 and 3.45 Å, instead of the unique short As-Fe contribution that is usually considered. For outer-sphere complexes, the most favorable adsorption configurations indicate the stabilization of the arsenate molecule by strong hydrogen bonds as well as the involvement of electrostatic forces. It is therefore essential to include these outer-sphere complexes in the thermodynamic models used to understand the arsenic fate in the environment.

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Response of vegetation and erosion dynamics to changes in precipitation in the Nile River drainage basin during the African Humid Period

CECILE L. BLANCHET[12], JANNE LORENZEN[3], RIK TJALLINGII[2], STEFAN SCHOUTEN[2] AND MARTIN FRANK[1]

[1]IFM-GEOMAR at the University of Kiel, Whischhofstrasse 1-3, 24148 Kiel, Germany
[2]NIOZ Royal Netherlands Institute for Sea Research, Landsdiep 4, 1797 SZ 't Horntje, The Netherlands
[3]University of Kiel, Ludewig-Meyn-Strasse 14, 24118 Kiel

During the mid-Holocene, the gradual decrease in summer insolation induced a decrease in monsoon strength and subsequent aridification of northern Africa. However, the timing of environmental and climatic responses to this slow orbital forcing is still being debated, with studies reporting either a gradual or an abrupt termination of the African Humid Period (AHP).

Here we use 6 m-long sediment core P362/2-33 that was retrieved at 700 m water-depth on the Nile deep-sea fan. Detailed ^{14}C dating shows that the core covers the last 9,500 years, with laminated sediments being deposited at very high rates (up to 600 cm/ka) during the AHP. These sediments allow to investigate the linkages and feedbacks between climate, vegetation and erosion dynamics at millennial to seasonal resolution. The variations in sediment and fresh-water input, as well as sediment provenance and vegetation changes are monitored using a combination of inorganic and organic geochemical proxies (major and trace elements ratios, $\delta^{18}O$ and $\delta^{13}C$ of planktonic foraminifera, radiogenic isotope compositions of sediments, foraminifera and seawater-derived ferromanganese coatings, and abundance and isotope composition of specific biomarker lipids). Massive amounts of fresh water and sediments were delivered by the Nile River to the deep-sea fan between 9.5 and 8 ka, as indicated by high sedimentation rates, high titanium/calcium ratios and sea-water εNd values similar to the Nile River. This time interval was also characterised by the dominance of C4 grasses and soil development, as indicated by heavier $\delta^{13}C$ values for higher plants n-alkanes and elevated concentrations in soil biomarker. A first rapid decrease in fresh-water and sediment delivery was recorded around 8.5 ka in sea-water εNd and sedimentation rate followed by a gradual decrease between 8 and 4 ka identified in all proxies. The transition from C4- to C3-dominated environment occurred between 8 and 6 ka, and might reflect the aridification of the Sahara, with n-alkanes mainly originating from southern sources after 6 ka. Sediment source tracing by mean of their radiogenic isotope composition is being processed.

A new calibration site for cosmogenic ^{3}He production rate in the Central Altiplano

PIERRE-HENRI BLARD AND JÉRÔME LAVÉ

CRPG-CNRS, Université de Lorraine, Vandoeuvre-lès-Nancy, France. (blard@crpg.cnrs-nancy.fr)

It is critical to refine the accuracy and precision of the *in situ* cosmogenic dating tool, especially for establishing reliable glacial chronologies that can be compared to other paleoclimatic records. Indeed, the fiability of this chronometer is highly dependent on the accuracy of the spatial and time dependent correcting factors. Potential bias are particulary important for the high altitude tropical area. There is thus a crucial need of well-dated calibration sites allowing to establish robust regional production rates.

We present here a new calibration site for cosmogenic ^{3}He that is located in the tropical Altiplano (20°S, 68°W), on the southern flank of the Tunupa volcano, in the vicinity of the Salar de Uyuni at ~3800 m. The calibration site consists in a fluvio-glacial outwash that has the remarkable characteristic to be stratigraphically bracketed by two successive lacustrine shorelines. These shorelines are well-dated by ^{14}C and U-series dating [1,2], allowing to define an absolute age of 15.1±0.3 ka for the outwash deposition. We sampled 10 andesitic boulders on this site and analyzed the cosmogenic ^{3}He contents in the pyroxenes phenocrysts. The measured ^{3}He concentrations are characterized by a very low scatter: 9 samples agree within analytical uncertainties, suggesting that pre-deposition or post-deposition processes dit not produce any detectable bias. If the nucleogenic contribution from ^{6}Li capture is lower than 2% (as measured in similar samples on the same volcano [3]), these clustered data will allow defining a new reference value for the local production rates of ^{3}He with a precision better than 5% (1σ).

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Changes in global weathering indicated by the Ca-isotope record of Oceanic Anoxic Events 1a and 2

C.L. BLÄTTLER[1]*, H.C. JENKYNS[1], L.M. REYNARD[2] AND G.M. HENDERSON[1]

[1]Department of Earth Sciences, University of Oxford, South Parks Road, Oxford OX1 3AN, U.K. (*correspondence: Clara.Blattler@earth.ox.ac.uk)

[2]Research Laboratory for Archaeology and the History of Art, University of Oxford, South Parks Road, Oxford OX1 3QY, U.K.

Oceanic Anoxic Events (OAEs) are huge perturbations to climate that offer an opportunity to observe the response of the Earth system to large and abrupt changes in the carbon cycle. Calcium-isotope ratios ($\delta^{44/42}$Ca) were measured by MC-ICPMS in carbonate-rich sedimentary sections deposited during OAE1a (Early Aptian) and OAE2 (Cenomanian–Turonian). A negative excursion in $\delta^{44/42}$Ca of ~0.20‰ is observed in two sections spanning OAE1a from Resolution Guyot (Mid-Pacific Mountains) and Coppitella (Gargano, Italy); a negative excursion of ~0.10‰ is observed in two sections spanning OAE2 from the English Chalk (at Eastbourne and South Ferriby, UK).

These Ca-isotope excursions occur at the same stratigraphic level as the C-isotope excursions that define the anoxic events, but they do not correlate with lithological changes or evidence for carbonate dissolution in the sections. Diagenetic and temperature effects on the Ca-isotope trends are discounted, leaving changes in global seawater composition as the most probable explanation for the change in $\delta^{44/42}$Ca in the carbonate records.

An oceanic box model with coupled Sr- and Ca-isotope systems indicates that a global weathering increase is likely the dominant driver of transient excursions in Ca-isotope ratios. Contributions from hydrothermal activity and carbonate dissolution are likely to be too small and short-lived to generate the observed changes in the oceanic Ca-isotope composition. A modelled increase in weathering flux, on the order of three times the modern flux, combined with increased hydrothermal activity due to formation of the Ontong-Java Plateau (OAE1a) and Caribbean Plateau (OAE2), can produce trends in both Ca- and Sr-isotope ratios that match the signals recorded in the carbonate sections. These data are the first major-element records of a weathering response to Oceanic Anoxic Events.

Aerobic methanotrophs drive the formation of a seasonal anoxic benthic nepheloid layer in a monomictic lake

H.J.R. BLEES[1]*, H. NIEMANN[1], C.B. WENK[1], J. ZOPFI[2], C.J. SCHUBERT[3], M.L. VERONESI[4] AND M.F. LEHMANN[1]

[1]Institute of Environmental Geosciences, University of Basel, Switzerland (*correspondence: jan.blees@unibas.ch)
[2]Laboratory of Microbiology, Institute of Biology, University of Neuchâtel, Switzerland
[3]Swiss Federal Institute of Aquatic Science and Technology (EAWAG), Kastanienbaum, Switzerland
[4]Institute of Earth Sciences, University of Applied Sciences of Southern Switzerland, Canobbio-Lugano, Switzerland

Monomictic lakes experience thermal stratification throughout most of the warmer seasons. Often this leads to seasonal bottom water anoxia, particularly if monomixis is paired with eutrophic conditions. The southern extension of Lake Lugano is a warm, monomictic basin with bottom water anoxia, and formation of a dense benthic nepheloid layer (BNL) during summer and fall. A sharp redox gradient marks the upper boundary of the BNL, which extends to up to 15m from the sediment into the water column. Previous work has revealed that the bulk organic matter in the BNL is strongly depleted in ^{13}C ($\delta^{13}C$ < -60‰), indicating that the BNL in the Lake Lugano South Basin is largely composed of methanotrophic bacteria. In this study we present radio-label rate measurement and compound specific C isotope data that confirm i) high rates of aerobic methane oxidation (MOx) at the redoxcline (i.e. just above the BNL) and ii) the dominance of bacterial methanotrophic biomass in the BNL of Lake Lugano's southern basin. MOx is restricted to a narrow zone at the top of the BNL reaching maximum rates of up to 1.8 μM/day. MOx activity leads to the formation of a sharp CH_4 concentration gradient (80 μM at 92 m; 100 nM at 82 m). The C kinetic isotope effect of methane consumption is strongly suppressed at the community level (ε = -2.4‰), highlighting the near perfect methane sink at the oxycline, where > 99.9% of the CH_4 diffusing from the sediment is oxidised. Fatty acids (FAs) indicative of type I aerobic methanotrophs are depleted in ^{13}C ($\delta^{13}C$ = -65 to -80‰) and are the dominant lipids in the FA fraction. In addition, preliminary molecular analysis of the microbial community provides further evidence that the formation of the BNL is driven by aerobic methanotrophs rather than by resuspension of sediments or accumulation of organic matter from the epilimnion, as is often observed in other lakes. Prior to water column mixing, these methanotrophs greatly limit the emission of accumulated methane to the atmosphere.

Hf isotope evidence for depleted and enriched reservoirs in the Hadean

J. BLICHERT-TOFT* AND F. ALBARÈDE

Ecole Normale Supérieure, 69007 Lyon, France (*correspondence: jblicher@ens-lyon.fr)

Chase and Patchett [1] and Galer and Goldstein [2] argued for the existence of a hidden enriched reservoir in the early mantle, a perspective that has since received strong support from Hf isotope [3] and ^{142}Nd [4] evidence. The geochemistry of the earliest magmatic minerals is critical in this context. The Jack Hills zircons (JHZ) have been analyzed for Pb and Hf isotopes by several groups using either *in situ* [5-7] or solution chemistry [5,8,9] techniques. The data support the presence of normal continental crust at 4.1±0.1 Ga, with Hf model ages and inferred Lu/Hf characteristics further suggesting a 4.35 Ga protocrust formed from KREEPy upper mantle [7,9]. Whereas all studies find the same predominantly enriched signature indicating apparently massive crustal recycling and reworking during the Hadean and the Archean, only the solution chemistry studies [5,9] see evidence for a depleted reservoir in the Hadean mantle. Statistical analysis of the *in situ* data sets strongly suggests that zircons with the most radiogenic Hf were mistaken for analytical artifacts such that the high-ε_{Hf} end of the distribution became unduly trimmed. We therefore conclude that, although the JHZ protolith seems to have been largely enriched, it also contained undifferentiated and depleted components. Hf and Nd isotopes in komatiites [10] likewise suggest that the Archean and Hadean mantle comprised long-term depleted sources, identical in terms of time-integrated lithophile trace element characteristics to the Early Depleted Reservoir [11] deduced from $^{146,147}Sm$-$^{142,143}Nd$ and Lu-Hf isotope studies of modern mantle material and chondrites. The uppermost KREEPy mantle likely held enough radioactive elements and water to have outlasted the crystallization of the magma ocean for 100s of Ma. If embedded within and between magma ocean cumulates and a thin hydrous lithosphere, such material may have jump-started early plate tectonics.

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Towards a resolution of the timing of Martian magmatism: Diffusion study of Hf in clinopyroxene and geochronological implications

E. BLOCH AND J. GANGULY*

Dept. of Geoscience, Univ. of Arizona, Tucson, AZ, 85721, USA (*correspondence: ganguly@email.arizona.edu)

The igneous crystallization age of the Shergottite suite of Martian meteorites has been a subject of considerable debate. While ^{147}Sm-^{143}Nd and ^{176}Lu-^{176}Hf mineral isochrons yield relatively young ages of ~150-225 Ma, ^{206}Pb-^{207}Pb ages from the same samples exceed 4.0 Ga. It has been proposed that the ^{206}Pb-^{207}Pb dates reflect the true crystallization age of the Shergottites and that the ^{147}Sm-^{143}Nd and ^{176}Lu-^{176}Hf "isochrons" represent either a mixing line with phosphate-hosted material or reflect the effect of thermal resetting at ~200 Ma [1,2]. Alternatively, it has been argued that the ^{206}Pb-^{207}Pb array is simply a mixing line arising from contamination by modern terrestrial Pb [3].

Lapen *et al*. [4] argued against the "mixing hypothesis" for younger Lu-Hf age on the basis of lack of correlation between ε(Hf) and 1/[Hf] of the samples defining Lu-Hf "isochron". In order to test the alternative hypothesis of thermal resetting via diffusion of Hf, we have determined the diffusion kinetic properties of Hf^{4+} in clinopyroxene, which is the primary host mineral of Hf. To evaluate thermal resetting due to a shock event, we assume a maximum estimate of post-shock temperature of ~1000°C. Using the average clinopyroxene radius (r) in the Shergottite RBT-04262 (0.5 mm), our diffusion data yield ~210 kyr as the time required for diffusive re-equilibration of Hf isotopes, which precludes resetting within a shock-heated and -ejected material. We have also addressed the problem of extended heating during a non-ejection impact event (or other thermal perturbation) by measuring and modeling Cr diffusion profiles in olivine in RBT-04262. Using Cr diffusion from [6], we obtain a time scale of ~1 year at the peak temperature of 1150 ºC [7]. This leads to a vlue of Dt/r^2 of ~$3x10^{-5}$ for Hf in clinopryoxene, which precludes any significant diffusive resetting of Lu-Hf chronometer for the sample [8].

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What defines a saline aquifer for CO_2 injection?

MADALYN S. BLONDES* AND MARGO D. CORUM

U.S. Geological Survey, 12201 Sunrise Valley Dr., Reston, VA 20192, USA (*correspondence: mblondes@usgs.gov, mcorum@usgs.gov)

The U.S. Geological Survey is currently assessing potential CO_2 subsurface storage formations in the United States. The U.S. Environmental Protection Agency requires that any U.S. CO_2 sequestration assessment or project avoid subsurface formations containing potential drinking water. The Underground Injection Control Program (UIC) for Class VI (CO_2 storage) wells protects fresh water, defined as water with a total dissolved solids (TDS) concentration < 10,000 mg/L. However, the UIC does not define how the limit must be interpreted statisically or spatially to determine potential storage formations. For example, if one analysis has a TDS concentration > 10,000 mg/L, is the entire formation considered a saline aquifer? Could a saline water analysis from a previous injection well in the same reservoir then be cited as evidence of a saline formation available for CO_2 injection? Other possibilities include using a median or mean within uncertainty for a water chemistry dataset. Though site-specific hydrogeological studies would be required before injection to predict CO_2 migration to aquifers, the concern is whether fresh water aquifers could be defined as saline based on existing subsurace water quality data.

For example, the Mesaverde Formation in the Southwestern Wyoming Province is a known aquifer with fresh water near the surface and saline water at depth. Using multiple water quality databases that cover the Rocky Mountain region, we find n = 789 independent analyses with non-null reported TDS concentrations between 72 and 249,838 mg/L at depths > 1 km. Whereas the mean TDS concentration is "saline" (13,240 ± 17,191 (1σ) mg/L), the median concentration is "fresh" (9,482 mg/L).

Since the scale of a sequestration project is not across an entire basin, we can also provide a spatial definition of salinity. If we see a region with suitably saline data, how far from those wells can we assume the formation is saline? Though this is a complex hydrogeologic problem, our interest is simply to define whether a potential storage region is "saline" or "fresh." Using 1-D Darcy flow (neglecting convection and dispersion) for a range of applicable reservoir properties and time-scales, we model length scales of saline water flux. These results then define the radial distance from a saline data region that could be considered saline at the time-scales relevant to long-term CO_2 storage.

Effects of sodium borohydride reduction and dioxygen concentration on the photochemical properties of humic substances

NEIL V. BLOUGH*[,1], KELLI GOLANOSKI[1], YI ZHANG[1], AND ROSSANA DEL VECCHIO[1,2]

[1]Department of Chemistry and Biochemistry University of Maryland College Park MD United States (*correspondence: neilb@umd.edu)

[2]Earth System Science Interdisciplinary Center University of Maryland College Park MD United States

Previous results have demonstrated that the reduction with sodium borohydride of Suwannee River humic and fulvic acids, a commercial lignin, and a series of solid phase C18 extracts from fresh, estuarine, coastal and offshore waters of the middle Atlantic bight produces a preferential loss of long wavelength (visible) absorption and enhanced, blue-shifted emission [1], consistent with a previously proposed electronic interaction model [2,3]. Here the effects of this reduction on the photosensitized oxidation of 2,4,6-trimethylphenol (TMP) and on the photoproduction of hydrogen peroxide is examined. For unreduced samples, the initial rate of TMP loss (R_{TMP}) increased with decreasing [O_2] concentration over the range from 1.2 mM to ~ 50 μM; below [O_2]~50 μM , R_{TMP} decreased precipitously, with no observable loss under N_2. Borohydride reduction substantial reduced R_{TMP} at all [O_2]. These results are consistent with the (aromatic ketone) triplet sensititization model of Canonica and co-workers [4,5]. In contrast, borohydride reduction only slightly decreased the intial rates of hydrogen peroxide production and similar dependencies of the initial rates on [O_2] were observed with both reduced and unreduced samples. Preliminary work, however, indicates interesting differences in peroxide yields between these samples under conditions in which they are first irradiated under N_2 followed by the introduction of O_2 at increasing delay times.

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Amendment of mill tailings for *in situ* treatment of mine drainage

D.W. BLOWES[1], M.B.J. LINDSAY[1], A.H.M. HULSHOF[1], C.J. PTACEK[1], P.D. CONDON[1] AND W.D. GOULD[2]

[1]Dept. Earth and Environ. Sci. Univ. Waterloo., ON, Canada, N2L 3G1 (blowes@uwaterloo.ca; matt.lindsay@uwaterloo.ca; ptacek@uwaterloo.ca)

[2] CANMET - Mining and Mineral Sciences Laboratories Ottawa, ON,K1A 0G1 (dgould@nrcan.gc.ca)

Field studies conducted at two mill-tailings impoundments suggest that amendment of sulfide-rich tailings with small masses of organic carbon has the potential to provide passive treatment of pore water through microbially-mediated sulfate reduction, metal-sulfide precipitation and alkalinity production. At the Kidd Creek Metallurgical Site, Timmins, Ontario, fine-grained mill tailings containing 15 – 20 wt. % sulfide minerals and 8 wt.% carbonates, were amended with 20 vol. % organic carbon in the form of pulp and paper sludge or wood chips. At the Greens Creek Mine, Alaska, mill tailings containing 34 wt. % pyrite were amended with 5 or 10 vol. % organic carbon as varied mixtures of peat, spent brewing grain and municipal biosolids. Increased populations of sulfate-reducing bacteria (up to 10^6 cells g^{-1}), and increased alkalinity concentrations were observed at both sites. These changes were accompanied by decreases in pore-water concentrations of SO_4, Zn and other metals as a function of time and relative to control cells. Mineralogical investigations indicate the precipitation of secondary Fe-S and Zn-S phases. However, increases in dissolved Fe and As concentrations were observed near the onset of the Greens Creek field experiments. Combined, these experiments demonstrate the potential for tailings drainage management using organic carbon amendments, but also indicate that care must be taken to limit the inadvertent release of dissolved constituents due to the reductive dissolution of Fe(III) and SO_4–bearing phases.

Cell permeability/senescence controls the reduction rate of iodate to iodide in marine phytoplankton

K. BLUHM[1], P. CROOT[2], K. WUTTIG[3] AND K. LOCHTE[4]

[1] IFM-GEOMAR, Kiel, Germany (kbluhm@ifm-geomar.de)
[2] Plymouth Marine Laboratory, Plymouth, United Kingdom (pecr@pml.ac.uk)
[3] IFM-GEOMAR, Kiel, Germany (kwuttig@ifm-geomar.de)
[4] AWI-Bremerhaven, Germany (Karin.Lochte@awi.de)

The role of marine organisms in the redox cycling of iodine in the ocean is not well understood presently. Previous studies have suggested that phytoplankton play an important role in the biogeochemical cycling of iodine, and were responsible for the appearance of the non thermodynamically favoured species iodide in the euphotic zone. A key question that arises however is how this reduction occurs; Is it driven by primary production, via direct biologically mediated uptake, or alternatively is it driven chemically by redox reactions related to the passive release of reduced substances from the decay of biological materials?

To directly address this question we have recently performed laboratory experiments and field measurements (Tropical Atlantic and Pacific, Southern Ocean) for this purpose. In culture experiments, including a variety of phytoplankton taxa (diatoms, dinoflagellates and prymnesiophytes), we observed changes in the speciation of iodine over the course of an experiment indicating the apparent ability to reduce iodate to iodide. Production rates were found to be species specific and not related to biomass. In all but one species tested the iodide production commenced in the stationary growth phase and peaked in the senescent phase of the algae. This indicates that iodide production is connected to cell senescence and suggests that iodate reduction results from increased cell permeability. We hypothesize that this is due to subsequent reactions of iodate with reduced sulphur species exuded from the cell. Combined with our field observations we suggest that cell senescence and other related processes that cause cell breakage (e.g. grazing, viral lysis) are responsible for the production of iodide.

Our data additionally suggest that the iodine redox cycle is completed via biological processes also. We observed that an experimentally induced shift from senescence back to the exponential growth phase resulted in a decline in the iodide concentrations, suggesting reoxidation back to iodate. Our new data help to provide a more complete picture of iodine cycling in the ocean.

Fault zone stability in cap rocks affected by CO_2

J. BLUME[1], J. D. ECKHARDT[4], H. G. STOSCH[1], TH. NEUMANN[2], K. BALTHASAR[3], TH. MUTSCHLER[3] AND TH. TRIANTAFYLLIDIS[3]

[1]Institute of Applied Geosciences,
[2]Institute of Mineralogy and Geochemistry,
[3]Institute of Soil Mechanics and Rock Mechanics,
[4]Laboratories for Materials Testing and Research, KIT, 76131 Karlsruhe, Germany (jennifer.blume@kit.edu)

A safe geological storage of CO_2 requires a better understanding of alteration processes in cap rock formations as a function of temperature, pressure, fluid and cap rock mineralogical composition. Alterations in the cap rock can influence the tightness and the stability of a storage site. With regard to fault zones it may lead to increases or decreases of permeability due to solution with widening of flow paths or precipitation with self-healing effects. Increased permeability and consequently leakage might also change the stress field and the rock mechanical properties.

To investigate these relationships, an experimental setup was designed within the BMBF-funded GEOTECHNOLOGIEN joint project CO_2SEALS, to study experiment-related shear planes in natural rock samples, the changes in the mineralogical and rock mechanical properties and their interactions.

Annular shear planes were produced within samples of several pelictic reference rocks by a punching process. The punched samples were installed in newly developed reaction vessels, in which they were continuously percolated with a CO_2-saturated NaCl-brine at a constant pressure (5 bar) and different constant temperatures (45 to 100°C). By varing temperature and reaction time (up to 24 months) it was expected to extract reaction rates from the experiments and also study the extent of alteration.

Results of the experiments with duration up to 6 months show that interactions between CO_2-saturated brine and cap rock are most visible at temperatures >75°C. Changes in the chemical composition of the effluent and in the solid phase show, that beside carbonate dissolution and precipitation, which is the dominant short term process, silicate alteration must have occured also. Thin-layer shear tests at high pressures up to 40 MPa normal stress on powder samples (before and after reaction with CO_2) will be carried out to characterise the change of the geomechanical properties due to alterations.

Geothermobarometric results at the northern tip of Antarctic Batholith: Tectonic implications

H. BOBADILLA[1]*, M. CALDERÓN[2] AND F. HERVÉ[1]

[1]Departamento de Geología, Universidad de Chile. Plaza Ercilla 803. Santiago, Chile. (*correspondence: hbobadil@ing.uchile.cl)
[2]SERNAGEOMIN. Av. Santa María 104. Santiago, Chile. (mccaldera@gmail.com)

The geological relationships between the Antarctic Peninsula (AP) and South America (SA) have been the subject of sustained study in recent decades. However, there are many problems unsolved yet [1]. This work provides new information that could be used to compare and relate the magmatic and tectonic processes occurring at the northern end of AP and southern tip of SA.

Using EPMA analysis in diorites from the northern Antarctic Batholith, we have determined the composition of a selected group of minerals. Knowing the compositions of amphiboles, we have estimated the temperature (T) and pressure (P) at which they crystallized, according to several geothermobarometers [2, 3].

The results indicate that minerals are not homogeneous, but most are zoned. Particularly for amphiboles, the difference of crystallization T for the many zones could reach 200ºC. These results are interpreted as crystallization in, at least, three stages.

The crystallization T and P of amphiboles in their many zones are revealed and, by extension, an approximation for the T-P crystallization conditions of the plutons. Using a preliminary approximation of lithostatic pressure we propose a specific range of depths of intrusion; they all have been emplaced at upper crust (less than 10-15 kms). Using SHRIMP zircon U-Pb crystallization ages, exhumation rates have been inferred. They seem to rise up since Eocene to Miocene in almost ten times.

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Boron, lithium and nitrogen isotope geochemistry of K- and NH_4-rich illite/smectite clays in fossil hydrothermal systems

I. BOBOS[1] AND L. B. WILLIAMS[2]

[1]Centre of Geology, University of Porto, 4169-007 Porto, Portugal (ibobos@fc.up.pt)
[2]SESE, Arizona State University, Tempe, Arizona 84287-1404, USA (Lynda.Williams@asu.edu)

Boron (B), lithium (Li) and nitrogen (N) transported by hydrothermal fluids may be incorporated into illite – smectite (I/S), as progressive illitization of smectite occurs [1]. Two illitic size fractions (<0.2μm; 0.2 – 2.0μm), distinct in age and composition, were selected corresponding to K-I/NH_4-I mixtures and to a continuous conversion series of smectite to NH_4-I via interstratified structures.

The $\delta^{11}B$ (‰) values range from -5.1 to -5.5‰ in the K-I/NH_4-I mixed phase samples and from -12.6 to -22.4‰ in the mixed-layered NH_4-I-S. The δ^7Li values measured in K-I/NH_4-I mixed phase ranges from +5 to +12.8‰ and in NH_4-I-S samples ranges from -0.5 to -12.3‰. Lower Li concentrations around few ppm were measured, whereas the B concentrations range from 400 to 1457 ppm. The $\delta^{15}N$ measurements in K-I/NH_4-I clays show a mean value of +5.4‰ and in NH_4-I-S series range from +4.8 to +14.6‰. Nitrogen contents range from 0.15 to 1.2 wt.%.

The results obtained have important implications for understanding sources of fluids cycling through subduction zones. The $\delta^{11}B$, δ^7Li and $\delta^{15}N$ values obtained on NH_4-I-S indicate two different fluids, one very high in B and N, confirming a contribution from sedimentary organic matter. The $\delta^{11}B$ and δ^7Li composition of fluids that produced older K-I/NH_4-I clays fits best with a magmatic source. The isotopically light composition of these trace elements provides an important contribution to subducted sediments in volcanic arcs.

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Na-bearing majoritic garnets in the system $Mg_3Al_2Si_5O_{12}$–$Na_2MgSi_5O_{12}$ at 11–20 GPa: Solid solutions and structural peculiarities

A.V. BOBROV[1]*, A.M. DYMSHITS[1], L. BINDI[2], K.D. LITASOV[3], A.F. SHATSKIY[3], E. OHTANI[3] AND YU.A. LITVIN[4]

[1]Geological Faculty, Moscow State University, Moscow, Russia (*correspondence: archi3@yandex.ru)
[2]Museo di Storia Naturale, Sezione di Mineralogia, Università di Firenze, Firenze, Italy
[3]Department of Earth and Planetary Materials Science, Tohoku University, Sendai, Japan
[4]Institute of Experimental Mineralogy, Chernogolovka, Russia

The phase with composition $Na_2MgSi_5O_{12}$ (Na-majorite), end-member of sodium-rich majoritic garnet [1], was synthesized and garnet/pyroxene *PT* phase boundary was determined in multi-anvil experiments at 11–20 GPa and 1500–2100 °C. Na-majorite was obtained at 16 GPa and 1500°C; its stability spreads to the high-temperature region with pressure (1900 °C at 17 GPa and 2100 °C at 19.5 GPa) [2]. Single-crystal study of Na-majorite provided evidence for its tetragonal symmetry, space group $I4_1/acd$, and cell parameters a = 11.3966(6), c = 11.3369(5) Å and V = 1472.5(1) Å^3 [3]. Experiments at 18 GPa and 1600 °C on the pyrope ($Mg_3Al_2Si_3O_{12}$)–Na-majorite join allowed us to study mixing peculiarities for sodium-rich majoritic garnet. The study demonstrated that the transition from cubic to tetragonal symmetry is observed for the starting composition with ~80 mol % $Na_2MgSi_5O_{12}$, which is consistent with the similar change of the structure in the pyrope–majorite ($Mg_4Si_4O_{12}$) system [4]. Significant Na-majorite solubility in pyrope, as well as findings of natural garnets with high Na concentrations (>1 wt % Na_2O) allow us to consider Na-bearing majoritic garnet as a phase accumulating sodium in the deep upper mantle and transition zone. Successful synthesis of the Na-majorite end-member and study of its structure are of key importance for obtaining of thermodynamic constants for this phase, which together with the computer modeling will allow us to suggest the new version of thermobarometer for mineral assemblages containing Na-bearing majoritic garnet.

Support: RFBR (09-05-00027), MD (534.2011.5).

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Application of the Linkam TS1400 X-Y heating stage to melt inclusion studies

R.J. BODNAR[1]*, R. ESPOSITO[1], R. KLEBESZ[1,2], Y.I. KLYUKIN[1,3], D. MONCADA[1] AND A. DOHERTY[1,2,4]

[1]Virginia Polytechnic Institute & State University, Department of Geosciences, Blacksburg, VA, USA (*correspondence: rjb@vt.edu)
[2]Università di Napoli Federico II, Dipartimento di Scienze della Terra, Naples, Italy
[3]Institute of Geology and Geochemistry of UB, RAS, Yekaterinburg, Russia
[4]Università degli Studi di Messina, Dipartimento Elementi e Ambiente, Messina, Italy

One of the major limitations in studying melt inclusions in natural samples has been the lack of availability of easy-to-use microscope-mounted heating stages that allow the user to heat the inclusion while it is being observed and to quench the sample rapidly to maintain a homogeneous glass and to avoid reequilibration during cooling.

The recently introduced Linkam TS 1400 X-Y stage has been tested and found to produce satisfactory results for many types of melt inclusions. Several experiments have been performed on recrystallized melt inclusions (MI) contained in olivine and sanidine phenocrysts from eruptions at Campi Flegrei, Italy, and in clinopyeoxene from the Sarno eruption at Monte Somma-Vesuvius Italy. During the heating experiment, a constant flow of argon gas was introduced into the sample chamber at a flow rate of 0.5 ±5% liter/min. During hating the temperature is easily controlled and the heating rate can be adjusted during the heating experiment. In all cases, it was possible to homogenize the MI and, importantly, to quench the melt to a glass after homogenization. In one experiment, the sample was heated to 1340°C. At that temperature, the field of view became a darkish-red and it was difficult to observe the behavior of the MI. At lower temperatures the optics were excellent. The quality of the optics during heating appears to be dependent on the sample characteristics, with samples containing matrix glass being most problematic.

In most of the experiments, the MI were homogenized completely (crystals + bubbles) and remained homogeneous during quenching to room temperature to produce a glass. In one case, the MI was heated to 1340°C and the solids all melted but the bubble did not dissolve back into the melt. When the MI was quenched, the single bubble remained in the MI and grew larger during cooling. The bubble in this MI may represent a trapped vapor bubble (i.e., the MI trapped a volatile-saturated melt plus a vapor bubble) and thus the bubble should not be expected to dissolve back into melt.

Tracing the late Paleozoic to early Mesozoic crustal evolution of coastal Southern Peru

F. BOEKHOUT [1]*, R. SPIKINGS [1], M. CHIARADIA [1], T. SEMPERE[2], A. ULIANOV [3] AND A. GERDES U. SCHALTEGGER[1]

[1]Earth and Environmental Sciences, University of Geneva, Switzerland
(*correspondence : Flora.Boekhout@unige.ch)
[2]IRD et GET, Toulouse, France
[3]University of Lausanne, Switzerland
[4]Goethe University, Frankfurt am Main, Germany

Subduction related magmatism along the Andean margin started as early as 550 Ma ago. Previous studies reveal a complex magmatic history from the late Paleozoic to the early Mesozoic that involved contributions from both mantle and crust.

This study aims to trace crustal growth and recycling through time along the South Peruvian margin with U-Pb laser ablation ICPMS dating on (Jurassic) plutonic and (Carboniferous – Jurassic) detrital zircons combined with a LA-MC-ICPMS Hf isotope study. This margin is especially suited for this type of study as no evidence is know of terrane accretion along this part of the margin since the Ordovician.

Our ages on detrital and plutonic zircons confirm periods of subduction related magmatism in the Ordovician, Permo-Carboniferous, and late Triassic-Jurassic, but also show periods of magmatic quiescence in the early Triassic and late Devonian.

A combination of Hf, Sr, Nd and Pb isotopes on the Jurassic plutonic rocks will be employed to quantify the relative contributions of mantle and crust to the melts formed along this part of the Andean margin. Additionally, Hf isotopes on detrital zircons will reveal periods of recycling and juvenile input. Preliminary results point towards crustal recycling as the dominant process of crustal evolution along the south Peruvian Andean margin between Carboniferous and Jurassic.

Aerosols, chemistry and the onset and evolution of fog layers

R. BOERS*

Royal Netherlands Meteorological Institute (KNMI) De Bilt, Netherlands (*correspondence: reinout.boers@knmi.nl)

In Western Europe, the occurrence of fog is on the decline since the 1980's. A reduction in the emission of anthropogenic aerosols due to increasingly strict regulatory measures and technological improvements on car and industrial exhaust seems a plausible reason for this decline. However, the onset and evolution of fog is the result of an interplay between a number of complex meteorological and aerosol – chemical factors. Here we model the evolution of fog and its sensitivity to atmospheric cooling rate, variation in aerosol size parameters and the aerosol chemical hygroscopicity parameter. First conclusions from these simulations can be summarized as follows:

1) Below RH=100% the three most important parameters controlling the visibility are the hygroscopicity parameter ($\varkappa$), the total number of aerosols and the relative humidity (RH) itself. For moderate to high values of $\varkappa$ (>0.4) and aerosol concentration typical for continental conditions (2000 - 4000 cm^{-3}), visibility can easily be reduced to below 1 km so that the meteorological condition for the occurrence of fog is satisfied, even though RH < 100%.

2) When RH > 100% and particle activation occurs, the parameter $\varkappa$ rapidly loses it significance in determining visibility. Rather it is the radiative cooling rate that exerts control over the value of visibility. The physical interpretation is that only a few particles (typically less than 150 cm^{-3}) are activated no matter what the value of $\varkappa$ is. Since these few particles grow rapidly upon activation they become increasingly more important in contributing to the reduction in visibility in the fog as the cooling progresses, so that the original sensitivity of visibility to $\varkappa$ when RH was still below 100% is quickly lost.

In atmospheres with RH<100% improved visibility may have been caused by reduced numbers of aerosols. However, for RH = 99% a reduction of $\varkappa$ from 0.9 to 0.5 yields an improvement of visibility from 1 to 2 km. Further work will be necessary to investigate whether changes in emission sources and land usage combined with possible changes in the relative humidity are contributing factors in explaining improved visibilities in the last three decades.

Structural distortion of $MgSiO_3$ perovskite and the influence of Fe and Al at pressures of the Earth's lower mantle

T. BOFFA BALLARAN[1], A. KURNOSOV[1], K. GLAZYRIN[1], M. MERLINI[2,3], M. HANFLAND[3] AND D.J. FROST[1]

[1]Bayerisches Geoinstitut, Universität Bayreuth, 95447 Bayreuth, Germany.

[2]Dipartimento di Scienze della Terra, Università degli Studi di Milano, Via Botticelli 23, 20133 Milano, Italy.

[3]ESRF - European Synchrotron Radiation Facility, 6 rue Jules Horowitz, BP 220, 38043 Grenoble, France.

The $MgSiO_3$ perovskite-type structure is considered the dominant phase in the Earth's lower mantle. As such a detailed understanding of its elastic properties and density as well as how such properties are affected by chemical substitutions are of great importance to mineral physics, seismology and geodynamics. Many studies have reported the compressibility of $MgSiO_3$ perovskite with or without additional element (mainly Fe and Al) substitution [1, 2, 3]. It has also been proposed that changes in the spin state of Fe at high-pressures may influence the compressibility of perovskite [4, 5]. Little is known, however, about the structural state of perovskite at very high pressures. Such knowledge is essential not only for constraining its physical-properties at lower mantle conditions, but also for understanding the structural instability leading to the perovskite to post-perovskite phase transition, which may cause complex seismic signatures within the D'' layer.

We have studied three single-crystals of $MgSiO_3$ with the end-member composition and containing either Fe^{2+} or Fe^{3+} and Al by means of X-ray diffraction at the ID09 beam line of the European Synchrotron Radiation Facility. Intensity data have been collected up to 90 GPa at room temperature with diamond anvil cells loaded with He as pressure transmitting medium and ruby chips as pressure calibrants. All perovskites display with increasing pressure only a small increase of the octahedral tilting, but undergo major octahedral distortions, which are more pronounced in the Fe^{3+}, Al-bearing perovskite. No evident structural changes associated with the Fe spin transition have been observed.

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Modelling the aqueous Al^{3+} System using Density Functional Theory

S. BOGATKO[1]*, E. CAUËT[2] AND P. GEERLINGS[1]

[1] Eenheid Algemene Chemie, Vrije Universiteit Brussel (VUB), Faculteit Wetenschappen, Pleinlaan 2, 1050 Brussels, Belgium (* sbogatko@vub.ac.be, pgeerlin@vub.ac.be)

[2] Service de Chimie Quantique et Photophysique CP 160/09, Université Libre de Bruxelles, 50 Av. F.D. Roosevelt, B-1050 Bruxelles, Belgium (ecauet@ulb.ac.be)

We have shown (1) that the speciation of aqueous Al^{3+} is well described over a wide range of solution pH by Density Functional Theory calculations on gas phase $Al(OH)_x(H_2O)_y^{(3-x)+}$ clusters embedded in a continuum solvent. Cluster geometry, electronic structure and Gibbs Free Energies all display similar trends suggesting increased acidity as the coordination number decreases. These results are in complete agreement with the observed cooperativity of Al^{3+} hydrolysis products (2).

Extending our model (3) to include coordination by an F^- counterion shows that this ligand coordinates the Al^{3+} cation in a similar way to the OH^- ligands thus inducing important changes in $AlF(OH)_x(H_2O)_Y^{(2-x)+}$ complexes in the direction of increased acidity, in agreement with the observed elevated acidity of natural waters in which AlF^{2+} species occur (4). Furthermore, in light of recent NMR observations (5) of a fast proton-coupled water exchange mechanism on Al^{3+} aqueous complexes, we suggest this mechanism is also present in the aqueous AlF^{2+} system.

Finally, a large array of $Al_2(OH)_x(H_2O)_y^{(6-x)+}$ aqua/hydroxo Al^{3+} dimer species have been investigated. Our results suggest that many species are possible and their stability may be understood in terms of the number of coordinating water and hydroxide ligands and the hydroxide bridging geometry. This novel approach thus provides a revealing picture of the extremely complex aqueous Al^{3+} environment and may thus be of great use to the geochemical and environmental chemistry communities.

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Element behavior in technogenic systems and methods of mine waste treatment

A.A. BOGUSH [1]*, E.V. LAZAREVA[1], V.G. VORONIN [2], O.G. GALKOVA [1] AND N.V. ISHUK [1]

[1]Institute of geology and mineralogy SB RAS, Koptyug Pr. 3, Novosibirsk 630090, Russia (*coresspondence: annakhol@gmail.com)

[2]Planeta-Ra Ltd., Lazurnay str. 4/3, Novosibirsk 630133, Russia

A huge amount of waste has accumulated in the world during the last century as a result of industrial activity. Research of element migration in technogenic systems and their accumulation on geochemical barriers is the important fundamental problem of the environmental geochemistry. The purpose was to describe migration, distribution, and redistribution of heavy metals by the example of the old tailings of the Lead Zinc Concentration Plant and Ursk tailings of the Gold Concentration Plant (Kemerovo region, Russia). The waste products of the ore mining and processing industry can be oxidized by atmospheric oxygen and microbial activity, forming acid mine drainage (AMD), with high concentrations of SO_4^{2-}, Fe, Zn, Cu, Cd, Pb, and other elements. The result obtained about element species in the sulfide tailings and the bottom sediments, using modified sequential extraction procedure, explain the main features of element migration and redeposition. In the mine waste and technogenic bottom deposits, there is vertical and horizontal substance transformation with formation of following geochemical barriers: 1) the evaporative barrier where secondary species of element, especially water-soluble, are redeposited; 2) the lithological barrier (Hardpan) which reduce migration of elements, pore water and pore gases such as O_2 and CO_2; 3) complex organic-mineral barrier on which heavy metals coprecipitate/sorb with/on iron oxy-hydroxides, organic matter and clay minerals. On the basis of the sulfide waste investigation, environmentally safe and cost-effective ways of liquid and solid waste treatment have been developing using natural (peat, clay, limestone, etc) and modified materials (peat-humic agent, organic-mineral complex, etc.), for example: 1) complex organic-mineral geochemical barriers for binding and long-term retention of pollutants; 2) methods of acid rock drainage treatment; 3) methods of solid waste conservation; 4) prevention of eolian transportation of tailings particles; 5) new method of metal extraction from acid mine drainage. This research was supported by the RFBR (grant 03-05-64529 and 06-05-65007).

Reconstruction of the Atlantic circulation back to the last interglacial by a combined proxy approach

E. BÖHM[1]*, J. LIPPOLD[1], S. WEYER[2], M. GUTJAHR[3] AND A. MANGINI[1]

[1]Heidelberger Akademie der Wissenschaften, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany (*correspondence: eboehm@iup.uni-heidelberg.de)

[2]Inst. für Mineralogie, Universität Hannover, Callinstr. 3, 30167 Hannover, Germany

[3]Dept. of Earth Sciences, University of Bristol, Wills Memorial Building, Queen's Rd., Bristol BS8 1RJ, UK

The Atlantic Meridional Overturning Circulation (AMOC) plays an important role in the global climate system, due to the transport of heat and carbon. Theoretical studies and measured data suggest that the AMOC underwent different circulation modes and the transitions between these modes can be triggered by variations of freshwater runoff into the North Atlantic [1, 2, 3].

The purpose of this project is to trace these transitions by creating a high resolution data set of ε_{Nd} and $^{231}Pa/^{230}Th$ for the last interglacial (Eemian) and the following glacial. ε_{Nd} gives information about the water mass provenance, signal $^{231}Pa/^{230}Th$ serves for reconstruction of AMOC export. Thus, the combination of $^{231}Pa/^{230}Th$ and ε_{Nd} from deep sea sediments is a promising tool to derive the past paleoceanography.

First measurements of ε_{Nd} have been accomplished for the time range from 60 to 154 ka with a temporal resolution of in average 3 ka. The data display the presence of Southern Source Water during MIS 6 to MIS 6.4 and indicates an active deep water formation in the North Atlantic at the beginning of the Eemian Interglacial (MIS 5.5). The transition between these two different modes in AMOC is marked by a distinct drop in the ε_{Nd} values (-11.5 to -14). This is consistent with ε_{Nd} results obtained from the same core [4] and from a neighbouring core [5] at the transition from MIS 2 to MIS 1.1. The similar temporal behaviour of ε_{Nd} during Termination I and II implies recurring millennial-scaled identical processes converting the AMOC from a Glacial mode into an Interglacial mode.

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Calcium isotope fractionation during dolomite formation

FLORIAN BÖHM[1]*, ANTON EISENHAUER[1], JAN FIETZKE[1], SVENJA RAUSCH[2], ANDREAS KLÜGEL[2] AND WOLFGANG BACH[2]

[1]IFM-GEOMAR, Kiel, Germany (*fboehm@ifm.geomar.de)
[2]Geoscience Department, University of Bremen, Germany

Dolomite is an important component of the global calcium cycle, being a source of Ca to the oceans [1]. Calcium released to the oceans by dolomitization of chalk and limestones can potentially be quantified using marine Ca isotope records [2]. However, little is known about Ca isotope fractionation and the Ca isotopic composition of dolomitic rocks. Theoretical calculations point to a -2 ‰ depletion in $\delta^{44/40}$Ca of dolomite relative to calcite at 25°C [3]. Ordovician dolostones interbedded with limestones were reported to be depleted in $\delta^{44/40}$Ca by -0.6 ‰ relative to the limestones [4].

We have investigated dolomites from an ODP core (Site 183-1140) drilled at the Northern Kerguelen Plateau (46.3°S 68.5°E, 2394 mbsl). The core penetrated 235 m of nannofossil ooze and chalk of early Oligocene to middle Miocene age, and 88 m of pillow basalts forming the basement for the sediments. The basalts erupted at about 34 Ma (latest Eocene) [5]. An interbedded chalk layer was found in the basalt, about 40 m below the top of the basement. The chalk was partly dolomitized at the contact with the basalt.

We measured oxygen, carbon, calcium and radiogenic strontium isotopes of bulk chalk and dolomite samples. The ^{87}Sr/^{86}Sr ratios indicate an age of dolomitization of about 10 Ma (late Miocene). Dolomitization obviously occurred about 20 Ma after eruption of the basalts, in a deep burial setting. Oxygen isotope values of chalk and dolomite demonstrate that dolomitization occurred at slightly elevated temperatures (10-20°C). The calcium isotopes of the dolomite are enriched in $\delta^{44/40}$Ca by about +0.5 ‰ compared to the chalk. This is in contrast to the depletion of $\delta^{44/40}$Ca in dolomite reported in the literature. On the other hand, dolomite veins in ocean crust basalts (DSDP/ODP Sites 37-332 and 129-801) are depleted in $\delta^{44/40}$Ca compared to calcite veins of similar age. Fluid composition, diagenetic history and kinetic isotope fractionation have to be considered when interpreting Ca isotope values of dolomite.

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Hydroxyl group reactivity at FeOOH/gas and FeOOH/water interfaces

JEAN-FRANÇOIS BOILY

Department of Chemistry, Umeå University, Sweden
(correspondence: jean-francois.boily@chem.umu.se)

Reactions involving mineral surfaces and their surrounding environments play important roles in atmospheric and geochemical processes. Knowledge of the types, distributions and orientations of reaction centers on minerals with different surface structures is notably essential for molecular-scale resolution of mineral/gas and mineral/water interactions.

This work is focused on properties of hydroxyl functional groups of important crystal planes of FeOOH minerals exposed to vacuum, gaseous as well as liquid water. Molecular dynamics simulations were carried out to identify hydrogen bonding patterns and calculate their properties in these different systems. These efforts formed the basis of an interpretative framework to our Fourier transform infrared measurements of α-, β-, and γ-FeOOH particles (Fig. 1). These measurements, which were limited to gaseous systems, were used to extract spectroscopic signatures for distinct isolate and hydrogen-bonded hydroxyl groups.

Our combined computational and experimental efforts are helping categorize different crystallographic terminations of FeOOH minerals on the basis of their site distributions, hydrogen bonding patterns and reactivity towards water.

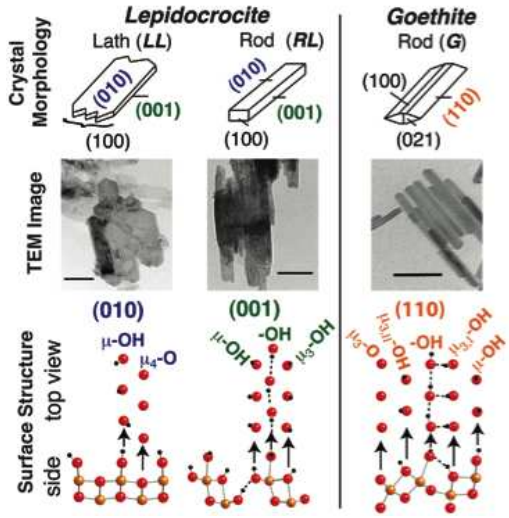

Figure 1: Morphology, TEM imaging (scale bar = 50 nm) and surface structures in three types of particle used for this work.

Trace elements in sediments of lakes in the Warta river basin

IZABELA BOJAKOWSKA*, TOMASZ GLIWICZ AND JAROSŁAW KUCHARZYK

Polish Geological Institute-National Research Institute, Warsaw, Poland (izabela.bojakowska@pgi.gov.pl)

The Warta River catchment (length 808.2 km), occupies an area of 54 529 km^2. The northern part of the catchment area covered by the Vistulian glaciation deposits, characterized by high abundance of lakes, while the southern part of the basin is practically without lakes.

The lake sediment samples taken from 5cm surface layer from profundal zone of 207 lakes, were analyzed for the content of As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sn, Sr, Ti, V, Zn, Al, Ca, Fe, K, Mg, Na, P and S using ICP-OES method after digestion in aqua regia. From solid samples the Hg content was measured by AAS method and C_{org}. was determined using coulometric method.

Geometric mean contents in the sediment were for: Ag - <0.5 mg/kg, Ba - 96 mg/kg, Cd - 0.5 mg/kg, Co - 2 mg/kg, Cr - 7 mg/kg, Hg - 0.10 mg/kg, Cu - 13mg/kg, Ni - 7 mg/kg, Sr - 148 mg/kg, V - 11 mg/kg and Zn - 72 mg/kg. Sediments of most of the studied lakes are characterized by low contents of trace elements, similar to the geochemical background values. Markedly increased levels of Cd, Cu, Hg, Pb, Sr and Zn were recorded in the sediments of several lakes located within the cities or their boundaries, e.g. Lakes Człuchów, Trzesiecko, Wierzysko and lakes which are used as places of recreation (e.g. Lake Jasień) and their maximum contents were for: Cd - 7.0 mg/kg, Cr - 135 mg/kg, Pb – 153 mg/kg, Zn – 1413 mg/kg, Hg - 1.163 mg/kg. High levels of Cu (579 mg/kg), Ba and Sr were detected in lake sediments, whose waters are included in the cooling system power plants Pątnów and Konin (among them Lake Goławskie and Licheńskie). Warta basin lake sediments compared to sediments of lakes, created on postglacial sediments associated with other glaciations show significantly higher contents Ba, Sr and Ca, and lower contents of Cr, Pb, Zn and Fe. Sediments from lakes of the Warta catchment are also characterized by lower contents of Ni and V as compared to the sediments of lakes of the Pomeranian phase of the Vistulian glaciation.

The presence of high amounts of Cd, Cu, Hg, Pb and Zn in sediments of some lakes in the basin of the Warta is linked to anthropogenic factors (the functioning of cities, recreation, industry). The differentiation has been observed in the contents of trace elements in sediments of lakes situated on postglacial deposits associated with various glaciations.

Submarine groundwater discharge, the subterranean estuary and climate change: *Quo vadis*?

H. BOKUNIEWICZ

School of Marine and Atmospheric Sciences, Stony Brook University, Stony Brook, New York 11794-5000 U.S.A.

The elusive role of submarine groundwater discharge (SGD), and groundwater in general, to global geochemical budgets has special importance in models of climate change. Conversely, geochemical fluxes *via* SGD can be expected to be altered significantly by a change in global climate. Our understanding is distilled from multifaceted case studies. Over the past several decades, the study of SGD has matured from being a fairly interesting novelty studied at a handful of sites before 1985; to a previously unrecognized nutrient source to coastal waters recognized in 45 studies at 39 sites worldwide by 2000 [1]; to a recognizably ubiquitous phenomenon of global importance investigated in over 300 studies and 160 sites, and counting, worldwide today. SGD is often, but not necessarily, confined to the shoreline and it is typically many times greater than the flow of terrestrial, fresh groundwater under the shoreline (i.e. the underflow). In special cases, other drivers might be considered, geothermal gradients, osmotic pressures and consolidation. Deciding its role in global geochemical budgets is, of course, compounded by variations in scale and geology. Nevertheless, issues, such as the flux of carbon, need to be addressed on the largest possible scale. Better distribution of sampling sites is warranted not only to better define current geochemical budgets, but also to anticipate future alterations. Research at sites in high latitudes, in arid environments and around oceanic islands are to be encouraged.

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Kinetics of coupled Fe(II)-catalysed ferrihydrite transformation and U(VI) reduction

D.D. BOLAND[1], R.N. COLLINS[1,2], C.J. GLOVER[3], T.E. PAYNE[1,2] AND T.D. WAITE[1,*]

[1]School of Civil and Environmental Engineering, The University of New South Wales, Sydney, NSW 2052, Australia. (*correspondance: d.waite@unsw.edu.au)

[2]Institute for Environmental Research, Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia.

[3]X-ray Absorption Spectroscopy Beamline, Australian Synchrotron Company Ltd, 800 Blackburn Rd, Clayton, VIC 3168, Australia.

The Fe(II) accelerated transformation of ferrihydrite to more crystalline Fe(III) oxides such as goethite has implications for the environmental mobility of uranium and other toxic elements. In this study we used X-ray absorption spectroscopy (XAS) on samples obtained from both batch and real time experiments to measure the kinetics of ferrihydrite transformation to goethite and U(VI) reduction across a range of Fe(II) concentrations.

Linear combination fitting of Fe K-edge Extended X-ray Absorption Fine Structure (EXAFS) and U L(III)-edge X-ray Absorption Near Edge Structure data revealed similar time scales of ferrihydrite transformation and U(VI) reduction to U(V) for each treatment, inversely proportional to Fe(II) concentration. The higher rate of U(VI) reduction by Fe(II) on pure goethite than the ferrihydrite/goethite system suggested that it is the associated enhanced rate of goethite formation, rather than the higher Fe(II) itself that causes faster U reduction. The use of quick-scanning XAS, which allowed the collection of Fe K-edge EXAFS spectral data to $k = 15$ Å^{-1} in < 1 minute for the real time experiments, provided improvements in experimental efficiency.

As predicted by calculations using the Nersnt equation and solubility products of the relevant Fe(III) oxides, the oxidation-reduction potential of the systems also declined on time scales similar to the transformation of ferrihydrite to goethite, further providing evidence for the strong reducing power of Fe(II) associated with goethite and that the presence of goethite is necessary for U(VI) to be reduced.

The effect of Sb(V) on the transformation of ferrihydrite to goethite, hematite, and feroxyhyte

R.M. BOLANZ[1], J. MAJZLAN[1] AND S. ACKERMANN[2]

[1]Inst. of Geosciences, Friedrich-Schiller-University Jena, Germany (ralph.bolanz@uni-jena.de)

[2]SGS INSTITUT FRESENIUS GmbH, Kölliken, Switzerland

Antimony is released into the environment in some natural and man-induced processes. [1]. Yet, its impact on the transformation processes of heavy metal-adsorbing minerals remains poorly understood. In acid-mine drainage systems and shooting ranges, the adsorption of antimony by iron oxides such as ferrihydrite can play a major role. The poorly crystalline 2-line ferrihydrite represents one of the most common Fe oxides in these settings and can transform to goethite (α-FeOOH) or hematite (α-Fe_2O_3) with time [2]. The rate of transformation depends on the pH, temperature, and on the ions and molecules present during the transformation process [3]. This study focuses on the transformation of synthetic ferrihydrite to crystalline iron oxides in the presence of Sb(V). Transformations were carried out for 1-16 days at 70 ºC and at pH 4, 7 and 12, with different concentrations of Sb(V) (0.00, 0.23, 0.75, 2.25 and 6.00 mM Sb). Samples taken from aqueous suspensions were washed, dried, and characterized by X-ray diffraction (XRD) and atomic absorption spectroscopy (AAS). At pH 12, goethite (Sb concentrations up to 3.7 mg Sb/g) is favored and the transformation is completed after one day. Only a concentration of 6 mM Sb retarded the transformation, where even after 8 days only 50 % of the ferrihydrite was transformed into goethite. Transformations at pH 7 led to a mixture of 75 % hematite and 25 % goethite (4.3 mg Sb/g). However, at concentrations of 6 mM Sb, feroxyhyte (δ-FeOOH) (9.1 mg Sb/g) was favored instead. At pH 4, hematite (32.3 mg Sb/g) was favored except for concentrations of 6 mM Sb, were again feroxyhyte (141.1 mg Sb/g) occurred. We assume that increased Sb concentrations favor feroxyhyte and indicate the incorporation of Sb into the structure of feroxyhyte.

[1] Filella *et al.* (2007) *Earth-Sci Rev* **80**, 195-217. [2] Cudennec & Lecerf (2006) *J Solid State Chem* **179**, 716-722. [3] Cornell (1987) *Pflanzenern Bodenk* **150**, 304-307.

Mineralogy and petrogenesis of the precambrian basement rocks, around Ede, Southwestern Nigeria

A.T. BOLARINWA[1], M.T. JIMOH[2] AND O.O. ODUSI[3]

[1]Department of Geology, University of Ibadan.
[2]Department of Earth Sciences, Ladoke Akintola University of Technology, Ogbomosho.
(*correspondence:jimohmustapha@yahoo.com)
[3]United Geophysical Nigeria Limited, Lagos.

Basement rocks around Ede southwestern Nigeria consist of Banded migmatite-gneiss, pegmatites, Amphibolites and lenses of charnockites. Petrographic studies revealed that the gneisses are composed of 50% quartz, 20% plagioclase. The pegmatite is made up of 50% quartz, 25% microcline, 20% muscovite and 5% microperthite.

The study is aimed at showing the compositional features, petrogenesis and tectonic setting of the rocks mentioned above by analysing the whole rock and trace element chemistry of the various rock types present.

Ten representative samples of the pegmatites and banded gneisses in the study area were collected and analysed for major, trace and rare earth elements. Geochemical analyses reflected the highest average SiO_2 value (72.43%) for the pegmatites while the lowest average SiO_2 content (62.48%) was obtained for the banded migmatite-gneiss. Mean Al_2O_3, Fe_2O_3, MnO, CaO and MgO are higher in the banded migmatite-gneiss than in the pegmatites. However mean Na_2O and K_2O values are higher in the pegmatites than in the banded gneisses.

Average bivariate plots indicates that the precursors of the gneisses are sedimentary while that of the pegmatites are igneous. Mode of occurrences involving partial melting seems to be compatible with the high Zr contents from the result of the trace element analytical data.

Geochemical discriminant diagrams show the rocks to have originated in a continental environment whose tectonic setting is similar to an active continental margin and a continental island arc. Geochemical studies and plots also indicate trends comparable to those typical of the calc-alkaline plutonic suites. Abundances and variations of major and trace elements suggest that part of the protoliths of the rocks are of sedimentary origin with an evolution involving partial melting and subsequent contamination by the plutonic episodes of the Pan African orogeny.

Ferric iron and water incorporation in wadsleyite under hydrous and oxidizing conditions

NATHALIE BOLFAN-CASANOVA[1], MANUEL MUÑOZ[2], CATHERINE MCCAMMON[3], E. DELOULE[4], ANAIS FÉROT[1], SYLVIE DEMOUCHY[5], LYDÉRIC FRANCE[5], DENIS ANDRAULT[1] AND SAKURA PASCARELLI[6]

[1]Laboratoire Magmas et Volcans, Université Blaise Pascal, France (N.Bolfan@opgc.univ-bpclermont.fr)
[2] ISTER, Grenoble, France
[3]Bayerisches Geoinstitut, Bayreuth, Germany
[4]CRPG, Nancy, France
[5]Géosciences Montpellier, France
[6]ESRF, Grenoble, France

Wadsleyite is the most hydrous nominally anhydrous mineral of the mantle transition zone (410-510 km depth). It also has a high affinity for trivalent cations such as Fe^{3+}. However the relationships between ferric iron and hydrogen incorporations in this mineral are unknown.

We conducted experiments at ~13 GPa and 1400°C, under oxidizing and hydrous conditions. The recovered samples were studied using micro-XANES (X-ray Absorption Near Edge Structure) to determine the ferric iron contents in polyphasic samples and SIMS (Secondary Ion Mass Spectrometry) to determine the water concentrations. XANES analyses show that ferric iron content increases with increasing total iron content, and reaches a maximum of 45 mol% of the total iron. The use of infrared spectroscopy highlights a new protonation scheme in wadsleyite, with most of the protons associated with the high frequency band near 3600 cm^{-1}. SIMS analyses show that water contents in wadsleyite vary from 0.5 to 0.7 wt% H_2O. Hydrogen content in wadsleyite is negatively correlated with ferric iron content. The divalent cations (i.e., $Mg^{2+} + Fe^{2+}$) and the Si content in wadsleyite decrease with increasing Fe^{3+} content, evidencing an incorporation mechanism via substitution into the metal sites with charge compensation by metal and Si vacancies.

These results bring new constraints on the contents of Fe^{3+} and H^+ defects in relation with the chemical environment. Such information is important in order to interprete electrical conductivity of wadsleyite in terms of hydrogen content.

Preliminary estimates on magma storage conditions of the Heise volcanic field, Snake River Plain

T. BOLTE[1]*, M. ERDMANN[1], B.P. NASH[2], H.E. CATHEY[2], R. ALMEEV[1] AND F. HOLTZ[1],

[1]Institute of Mineralogy, Leibniz University of Hannover, Germany (*t.bolte@mineralogie.uni-hannover.de)
[2]Department of Geology and Geophysics, University of Utah, Salt Lake City, UT, USA,

Tuffs and ignimbrites of the Heise and the Yellowstone Plateau eruptive centers, representing the silicic magmatism of the Snake River Plain – Yellowstone volcanic province, were studied to evaluate pre-eruptive storage conditions prevailing in rhyolitic magma chambers. We performed petrographic study of Blacktail Creek Tuff (6.62Ma), Tuff of Wolverine Creek (5.59Ma) and Kilgore Tuff (4.45Ma) of the Heise and the Huckleberry Ridge Tuff (2.05Ma) of the Yellowstone eruptive centers. Mineral and glass shard compositions obtained by electron microprobe were used to estimate temperatures, redox conditions and relative melt water contents.

In general, the set of mineral phases observed in studied rhyolites is similar to that of observed in BJR eruptive center [1] and are: Pl, ± Fsp, ± Cpx, ± Pig, Mt, ± Ilm, ± Qtz,± Fa, apatite and zircon. QUILF thermometry calculations performed on low- and high-Ca pyroxene pairs yield the ranges of temperatures between 818 and 830°C for Heise and 905 and 930°C for Huckleberry Ridge rhyolites. The ilmenite-magnetite oxybarometer yields oxygen fugacity values to be about QFM, which is in a good agreement with previous data [2]. The water contents of the natural rhyolitic melts, which are below 2 wt%, were only roughly estimated by projecting glass shard compositions on the ternary Qz – Ab – Or diagram with eutectic and cotectic compositions experimentally determined at hydrous conditions in the range of 50MPa to 1000MPa.

Our temperature estimates obtained for younger centers together with previously determined relatively high temperatures for Bruneau Jarbidge eruptive center (~11Ma, 905 – 980°C, [1]) suggest the change of pre-eruptive temperatures in rhyolitic magma bodies along the track of Yellowstone hotspot.

The study of melt inclusions hosted in plagioclase and fayalite is still in progress and will be presented in addition to mineral thermometry data.

[1] Cathey & Nash (2004) *J. Petrology* **45**, 27-58. [2] Honjo & Bonnichsen (1992). *Bull. of Volcanology* **54**(3): 220-237

Numerical modelling for peridotite phase melting trends in the SiO_2-Al_2O_3-FeO-MgO-CaO system at 2 GPa

C. BONADIMAN AND M. COLTORTI

Department of Eath Sciences, University of Ferrara, Italy. (bdc@unife.it)

The partial melting is the mechanism that better explain the variability of the major refractory lithophile elements (RLE) of the upper mantle rocks through time and space. Several numerical and experimental models (e.g.: Hirshmann *et al*., 1998; Herzberg, 2004 Niu, 2004) are available to simulate major element depletion trends using whole rock but no particular attention has been devoted to the compositional evolution of the single minerals. On the basis of various primitive chemical composition of the mantle (PM) and using the experimental results of Herzberg (2004) at 2.0 GPa, various melting trends which constrain the composition of the four mineral phases in the peridotite system, are calculated. This accounts for the 98.59 wt% of the upper mantle composition (SiO_2-Al_2O_3-FeO-MgO-CaO) with spinel as the aluminium phase admitted for these bulk compositions. A mass balance calculation has been applied to find the theoretical compositions of ol, cpx, cpx and sp at various degrees of partial melting. The modelling was constrained by i) mineral compositions adjusted in order to account for the properly formula units and ii) the experimental and theoretical intermineral Fe/Mg and Al partition coefficients. An iterative calculation varying the modal contents of the peridotite phases where applied to minimize the differences between calculated and whole rock compositions experimentally determined at various melting degrees. The starting point for each phase depends on the chosen whole rock PM composition and on the modal percentage that minimize the residuum. The several melting trajectories may account for a multiplicity of mantle occurrences where bulk rock analyses are not available. this model provide a new tool for unravelling the melting processes occurring within the Earth's mantle.

[1] Niu, Y. 2004, *J. Petrol*. **45**, 2423-2458. [2] Herzberg, C. 2004, *J. Petrol*. **45**, 2507-2530. [3] Hirshmann *et al*., 1998, *GCA **62**, 883-902*.

Sorption of Hg(II) by nanocrystalline mackinawite (tetragonal FeS)

SHARON BONE[1]*, KIDEOK KWON[2], JOHN BARGAR[3] AND GARRISON SPOSITO[1]

[1]Environmental Science, Policy and Management, UC Berkeley (*correspondance: shbone@berkeley.edu) (gsposito@berkeley.edu)
[2]Earth Sciences Division, Lawrence Berkeley National Laboratory (kkwon@lbl.gov)
[3]Molecular Environmental & Interface Science, Stanford Synchrotron Radiation Light Source (bargar@slac.stanford.edu)

Mercury is transformed to the biomagnifying species monomethyl mercury by sulphate reducing bacteria in anoxic sediments. The iron sulphide mineral, mackinawite ($FeS_{(s)}$), can limit Hg(II) bioavailability by sequestering Hg in the solid phase or by reducing it to volatile Hg (0). We use a combination of extended X-ray absorption fine structure (EXAFS) spectroscopy, density functional theory (DFT) geometry optimization and X-ray diffraction (XRD) to examine the speciation of Hg sorbed by $FeS_{(s)}$ as a function of Hg concentration, pH, and reaction time. Analysis of the Hg L_{III}-edge EXAFS spectra indicates that Hg exists in multiple coordination environments upon sorption by $FeS_{(s)}$, including a metacinnabar ($HgS_{(s)}$)-like phase and a component that we have tentatively identified as surface bound Hg. We use DFT geometry optimization to clarify the coordination environment of the putative surface complex and our preliminary results indicate that Fe-bound Hg is energetically favoured relative to S- bound Hg, as we had previously hypothesized. Lastly, Hg L_{III}-edge EXAFS spectra indicate Hg (0) forms in the presence of $FeS_{(s)}$, while spectroscopic and diffraction analysis of $FeS_{(s)}$ leads us to hypothesize that Hg(II) reduction results in the formation of surface-bound Fe^{III}. This research demonstrates that Hg(II) interacts with $FeS_{(s)}$ through multiple mechanisms, leading to the production of both sorbed and volatile Hg species, which vary in their reactivity and bioavailability in Hg-polluted sulphidic waters.

Inhibited water diffusion and inhomogeneities in glassy atmospheric aerosol proxies

D.L. BONES[1], D.M. LIENHARD[1,2], U.K. KRIEGER[2] AND J.P. REID[1]

[1]School of Chemistry, University of Bristol, Bristol, BS8 1TS, United Kingdom
[2]Institute for Atmospheric and Climate Science, ETH Zürich, Zürich, Switzerland

Atmospheric aerosol particles are typically complex mixtures of organic and inorganic species with correspondingly complex behaviours in changing humidity regimes. We investigate the formation of glassy or highly viscous phases in aqueous sugar aerosols such as sucrose and levoglucosan and aerosols of mixtures of sugars and inorganic compounds. It has recently been recognised that many aerosols exist as highly viscous solutions or as amorphous glasses, rather than a crystalline state, over a wide range of relative humidities (Virtanen, *et al*. 2010).

We use optical tweezers to trap single aerosol particles, exploiting subtle changes in the Raman spectra to deduce the size changes due to water uptake and evaporation from aqueous particles exposed to varying RH. We compare the experimental data with a kinetic model of diffusional limited size change.

Changes in size are dramatically hindered at low RH, with time scales approaching 10000s, for both increasing and decreasing RH regimes. The shift in resonance modes suggests initial formation of a layer of water on the surface of the glassy particle and subsequent establishment of a steep concentration gradient within.

[1] Virtanen A. *et al*., (2010) *Nature*, **467**, 824– 827.

Tracing the geographical origin of beefs based on carbon and oxygen isotopes

Y.S. BONG, K.S. LEE* AND W.J. SHIN

Korea Basic Science Institute, Ochang Center, Chungbuk 363-883, Korea (*correspondence: kslee@kbsi.re.kr)

To distinguish the country of origin of beefs that are currently sold in Korean market, a comparative analysis was conducted to examine carbon and oxygen isotopic compositions of beefs imported (from the USA, Mexico, Australia and New Zealand) and domestically produced beef. The result of the carbon isotope analysis showed good distinction between Korean beef and beef imported from the USA, Mexico and New Zealand. Based on carbon isotope values, it was difficult to distinguish between beef produced in Korea and beef imported from Australia, but these origins were easily distinguishable from oxygen isotope values. The oxygen isotope values reflect differences in consumed waters of the animal [1,2], according to the latitude of the country in which the beef was produced [3]. Such a result can be utilized to identify the origin of beef samples.

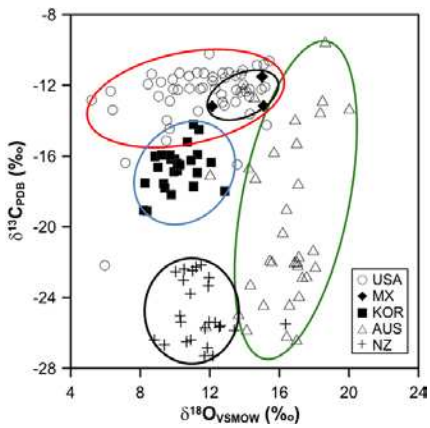

Figure 1: Cross plot of $\delta^{13}C$ and $\delta^{18}O$ values obtained from dry material from beefs produced in several countries.

[1] Franke *et al*. (2005) *Eur. Food Res. Technol*. **221**, 493-503.
[2] Kelly *et al*. (2005) *Trends food Sci. Technol*. **16**, 555-567.
[3] Nakashita *et al*. (2008) *Anal. Chim. Acta* **617**, 148- 152.

Rare earth elements fractionation as proxies of unconformity uranium deposit mineralized fluids

J. BONHOURE AND O. POURRET

HydrISE, LaSalle Beauvais, 60026 Beauvais cedex, France (jessica.bonhoure@lasalle-beauvais.fr)

To better understand the formation of uranium deposits, rare earth elements (REE) and particularly REE compositon of oxides is a powerful tool. Indeed, REE fractionation occurs in uranium oxide [1] by substitution with U and REEs are poorly affected by post-crystallization events [2]. In such a case, REE should provide information on the temperature and redox conditions during deposition, pH and complexing ion concentrations of mineralizing fluids.

We herein document the case of the Athabasca Basin unconformity type, for which REE patterns show a MREE enrichment during incorporation as free species in U oxide for a pH between 3 and 5 [3]. In order to understand the speciation of the mineralized fluid, REE speciation in three multi-ligand solutions (reduced seawater, groundwater and F-rich groundwater) was calculated using PHREEQ-C and Nagra/PSI data base [4], which was modified to include well-accepted infinite-dilution (from 25 to 200°C) of inorganic species. Results from 25 to 200 °C show that at $3<pH<5$ (i) in the reduced seawater lanthanides exists; (ii) in the groundwater, lanthanides occur as sulfate and fluoride complexes and free ionic species displaying a MREE enrichment; (iii) in the F-enriched groundwater, lanthanides occurs as free ionic species (HREE enriched) and complexed with fluoride (LREE enriched). Eventually, U oxides patterns are comparable with results of REE speciation in groundwater and LREE ratio indicates a deposition temperature between 125 and 150°C.

[1] Janeczek & Ewing, (1991) *J Nucl Mat* **185,** 66-77 [2] Fryer & Taylor, (1987) *Chem Geol* **63,** 101-108 [3] Kister *et al*. (2005) *Eur J Mineral* **17**, 325-342 [4] Hummel *et al*. (2002) Nagra/PSI Chemical Thermodynamic Data Base 01/01. Universal Publishers, Parkland.

Calibration and applications of the dolomite clumped isotope thermometer to high temperatures

MAGALI BONIFACIE[1]*, JOHN M. FERRY[2], JUSKE HORITA[3], CRISOGONO VASCONCELOS[4], BEN H. PASSEY[2] AND JOHN M. EILER[5]

[1]Institut de Physique du Globe de Paris, France (*correspondence: bonifaci@ipgp.fr)
[2]Johns Hopkins University, MD, USA
[3]Texas Tech University, Lubbock, TX, USA
[4]ETH, Zurich, Switzerland
[5]California Institute of Technology, Pasadena, CA, USA

Carbonate clumped isotope paleothermometry is based on the temperature-dependent formation of $^{13}C^{18}O^{16}O_2^{2-}$ ion groups within solid carbonate minerals. This thermometer has now been calibrated for various synthetic and natural biogenic and abiogenic minerals (calcite, aragonite and carbonate-apatites [e.g., 1, 2]) at temperatures below ~ 50°C. Here we extend the use of the carbonate clumped isotope thermometer to shallow crustal environments by determining the Δ_{47} values of CO_2 extracted from natural and synthetic dolomites grown at know temperatures from 25 to 350ºC. The experimental temperature dependance is not linear in the Δ_{47} vs T^{-2} plot and resembles the predicted theoretical temperature dependence, both in shape and absolute value [3]. These data for synthetic dolomites overlap the previous calibrations for inorganic calcite and some forms of biogenic carbonates between 25 and 50˚C, and are consistent with a single trend that also intersects data for synthetic calcite equilibrated at 1200˚C. These observations suggest that a single temperature dependant relationship reasonably approximates the calibration for both phases. Data from a variety of slowly-cooled (i.e., over geological timescales) natural marbles and rapid (i.e., laboratory timescales) heating experiments provide insights into the kinetics of solid-state ^{13}C-^{18}O bond reordering in carbonates and its closure temperature. More generally, our new calibration and constraints on high-temperature kinetics have implications for the application of this technique to burial and metamorphic processes. These issues will be illustrated through estimates of the thermal history and oxygen isotopic compositions and abundances of pore fluids for several suites of late Neoproterozoic carbonates [e.g., 4].

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Seasonal and tidal variations of dissolved thallium in coastal waters

P. BÖNING*, M. BECK, B. SCHNETGER AND H.-J. BRUMSACK

Institute for Chemistry and Biology of the Marine Environment, University of Oldenburg, Germany (*correspondence: p.boening@icbm.de)

Little is known on the distribution and behaviour of Thallium (Tl) in oceanic and coastal waters, perhaps due to its very low concentration level (8-20 ng L^{-1} or 40-90 pmol L^{-1}). Thallium is as highly toxic as Hg and Cd and is involved in redox reactions, which makes it an interesting candidate for the study of environmental processes.

Here we present a method for the rapid and reliable determination of dissolved Tl in sea water using sector field inductively coupled mass spectrometry (SF-ICPMS) without any preparation except 10 times dilution. Our method is suitable for the measurement of large time series of sea water samples [1]. Precision is 7 % RSD except for samples below the quantification limit (0.3 ng L^{-1}). Validation was done using the standards CASS-4 and NASS-5. For both CASS-4 and NASS-5 (salinity of 30.5) we calculated a concentration of about 11 ng L^{-1} assuming a Tl concentration of 14±2 ng L^{-1} at a salinity of 35±1. For CASS-4 we measured 10.6±0.7 ng L^{-1}, for NASS-5 10.3±0.8 ng L^{-1}[1], the latter of which is close to the value of 9.37±0.02 ng L^{-1} determined by isotope dilution-ICPMS by Nielsen *et al*. [2].

We applied our method to surface waters from the Jade Bay (an embayment of the Wadden Sea in NW Germany) [1]. Sampling was done hourly for 48 h during January, April, July and November 2010 at a fixed station located close to tidal flats, with a subsequent offshore transect. Pore waters were taken from sediments close to the fixed station.

In general, the results of all transect measurements (9-12 ng Tl L^{-1}) indicated conservative mixing since Tl varied with salinity. The time-series at the fixed station, however, yielded Tl concentrations of 6-11 ng L^{-1}, which only in part correspond to determined salinities. Hence, the distinct tidal variations in the concentration of dissolved Tl are rather explained by changes in the contribution of pore waters low in Tl (below the quantification limit).

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Vegetation and climate: The potential role of terpene emissions and aerosol particle formation on local climate conditions

BORIS BONN

WG Aerosol and Environmental Sciences, Institute for Atmospheric and Environmental Sciences, J.W. Goethe University, D-60438 Frankfurt/Main, Germany, (bonn@iau.uni-frankfurt.de)

Any ecosystem and its individual biogenic species survive at specific climate conditions such as temperature, water supply, nutrients and chemical stress factors. In order to take measures to buffering extremes several possible pathways have been suggested. One of these includes the emission of terpenes, their influence at ambient oxidant levels as well as in new aerosol particle formation. In this talk the role of individual mono- and sesquiterpenes will be discussed in a broader context emphasizing the ability of coniferous forests to compete with deciduous invaders in the context of changing climate conditions. The presentation is started with unraveling of new particle formation by induced organic volatile compounds conducted at three different scales, i.e. from gas-phase smog chamber studies via plant chamber to ecosystem smog chamber investigations. I will present a detailed understanding of the particle formation process taking into account the mixture of different mono- and sesquiterpenes emitted and their reactivity with ozone and OH. Both are essential for understanding since they limit the formation process at different steps via production of different large radicals. Since isoprene produces too small radicals any addition of isoprene by changing environmental conditions leads to serious consequences on feedback processes and climate cooling. In this context I discuss the effect of a) deciduous emissions such as isoprene and b) of anthropogenic emissions such as of NO on the intensity of new particle formation. My presentation is then finalized by drawing conclusions on potential radiation and climate effects.

Chromium isotopes as an indicator of redox conditions in the Cryogenian shallow oceans

P. BONNAND[1]*, I.J. PARKINSON[1], R.H. JAMES[2] AND I.J. FAIRCHILD[3]

[1]Dept. of Earth and Environmental Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK (*correspondence: p.bonnand@open.ac.uk)

[2]National Oceanography Centre, University of Southampton European way, Southampton SO14 3ZH, UK

[3]University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

Variations in atmospheric oxygen concentrations and the oxygenation level of the oceans during the geological past have been widely studied over the last 30 years [1]. A large increase in atmospheric O_2 during the Neoproterozoic has been postulated and is probably associated with a change in the redox condition of the oceans which enabled the explosion of life on Earth. Several models have been proposed, which have attempted to determine oceanic redox conditions during this Era [2]. The deeper oceans during the Neoproterozoic are generally believed to be anoxic until the end of the Ediacaran Period. However, little is known about redox conditions in the shallow oceans during the Neoproterozoic.

This study aims to determine the variation in redox conditions in the Cryogenian shallow oceans using REE chemistry and Cr isotopes in carbonate rocks. Chromium is a redox-sensitive element and its isotopes are fractionated during redox reactions [3]. Cryogenian carbonates from the Scottish Dalradian and the Greenland Eleanore Bay Supergroups are characterised by the lack of a Ce anomaly and positive δ^{53}Cr values. The lack of a Ce anomaly in ancient carbonates has been interpreted to reflect anoxic conditions [4]. However, these samples do record positive δ^{53}Cr values which are similar to modern and Phanerozoic carbonates [5]. These heavy δ^{53}Cr are interpreted to reflect oxidative weathering and the presence of sufficient O_2 to produce Cr(VI). These Cr isotopes data indicate that the shallow oceans during the Cryogenian was not anoxic and modelling suggests either dysoxic or suboxic conditions.

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Terrigenous input and microcharcoal changes in the Gulf of Papua during the last 60 kyrs

N. BONNET*, T. DE GARIDEL-THORON, G. MENOT, L. BEAUFORT, N. BUCHET AND E. BARD

CEREGE, Univ. Aix-Marseille, CNRS, IRD & College de France, Technopole de l'Arbois BP 80, 13545 Aix-en-Provence Cedex 04 (*correspondence: bonnet@cerege.fr)

The last glacial cycle is characterized by abrupt climate changes at high latitudes. Less documented at low latitudes, they seem to strongly impact the hydrological cycle, and therefore the amount of burnable vegetation. In Melanesia, though records of the aborigine's first migrations are scarce, it is established that human settlement occurred during the last glacial. To unravel the human impact on the fire regimes from the natural hydrological variability, we reconstruct microcharcoals and records of terrigenous inputs in a sediment core (MD97-2134) in the Gulf of Papua. We use MicroCharcoals Morphotypes (MCM) and BIT index, as respective indices of the types of burnt vegetation (woodland or grassland) and of terrigenous inputs. We assume that past terrigenous inputs in the Gulf of Papua respond to precipitations changes over the mainland which also control the frequency and intensity of fires.

The most striking feature of these records is the abrupt change in the MCM record at about 47 ka BP. Prior this change, from 60 ka BP to 47 ka BP, the BIT and MCM indexes are correlated, which suggests a direct forcing of droughts on the burnt vegetation. After 47 ka BP, each proxy shows a different dynamics: the elongation of microcharcoals decreases abruptly, whereas the BIT index still records high frequency oscillation until 31 ka BP. We interpret this abrupt decoupling of terrigenous and microcharcoal records as likely influenced by anthropogenic fires related to aboriginal practices consecutively of the first migration wave.

The MCM record further shows an increase during the early Holocene, indicating an increase in the proportion of bush/forest fires ratio. This increase might be due to the development of agriculture over Papua New Guinea, though the reduced frequency of El Niño Southern Oscillation events might have also contributed to this event.

Fungi accelerate mineral weathering via a synergy of mechanical and chemical attacks

S. BONNEVILLE[1,2]*, D.J. MORGAN[2], A.W. BRAY[2], A. BROWN[3], A. SCHMALENBERGER[4], S. BANWART[5] AND L.G. BENNING[2]

[1]Department of Earth Sciences and Environment, Free University of Brussels, BE (*s.bonneville@ulb.ac.be)
[2]School of Earth and Environment, University of Leeds, UK.
[3]Institut for Materials Research, University of Leeds, UK
[4]Department of Life Sciences, University of Limerick, IE
[5]Kroto Research Institute, University of Sheffield, UK

Rock weathering, through net transfer of atmospheric carbon into the Earth's crust, is the main climatic feedback over geological timescales. So far, the role of plant roots and, in particular, the ability of their symbiotic fungi (mycorrhiza) to accelerate mineral weathering remains debated. Mycorrhiza grow preferentially around, and on the surface of nutrient-rich minerals, making such mineral-fungi contact zones potential hot-spot of alteration in soils. However, because of their microscopic nature (only ~ 5 μm wide but up 1 mm long) and their tendency to strongly adhere to mineral substrates, an *in situ* quantification of the interfacial alteration rates by hypha on minerals has never been achieved.

Here, an ectomycorrhiza (*Paxillus involutus*) grown symbiotically with a pine tree (*Pinus sylvestris*) in the presence of freshly-cleaved biotite under humid, yet undersaturated, conditions typical of soils. A sequence of interfacial alteration cross-sections was sampled via FIB (Focussed Ion Beam) ion-milling along a single, surface-bound hypha. Elemental depth-profiles of Si, O, Fe, Al, Mg and K measured by high-resolution electron micro-spectroscopy (STEM-EDS) across these interfaces showed significant elemental transfer (for Fe, Mg, Al and K) from the mineral substrate into the hypha. A quantitative model based on solid-state diffusion was developed and hyphal interfacial alteration rates were derived from these profiles. When compared *consistently* with abiotic dissolution rates measured in batch and flow-through reactors (i.e., same substrate - biotite (001) basal plane-, pH and temperature), the results reveal that the surface bound-fungi were between 3.5 to 30 times faster to alter the basal plane of biotite. The remarkable capacity of surface-bound fungi to degrade biotite is not ascribed to hyphal acidification or organic acid exudation, but rather to the mechanical strain that these micro-organisms exert, simultaneously to chemical alteration, on the mineral substrate over which they grow [1].

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Palaeomag-dating of Kupferschiefer ore at Sangerhausen, Germany – An epigenetic, Late Jurassic age for stratabound Cu-mineralization

G. BORG[1]*, S. WALTHER[1], K. KAWASAKI[2] AND D. SYMONS[2]

[1]Petrology and Economic Geology Research Unit, Institute for Geosciences, Martin Luther University, Halle-Wittenberg (*correspondence gregor.borg@geo.uni-halle.de)

[2]Department of Earth and Environmental Sciences, University of Windsor, Windsor, Ontario, Canada, N9B3P4 (dsymons@uwindsor.ca)

Palaeomagnetic Dating of Mineralization

We have carried out paleomagnetic and rock magnetic measurements on 205 specimens from 15 underground sites from the abandoned Sangerhausen Mining District, Germany. Cu-mineralization is richest in Upper Permian (258±2 Ma) Kupferschiefer black marly shale (9 sites), extending into footwall sandstones (3 sites) and hanging wall carbonates (2 sites). ChRM directions were isolated for all sites using detailed alternating field and thermal step demag-netization. The site mean ChRM directions from the mine stratigraphic section yield a negative fold test that indicates that the ChRM post-dates Triassic to Jurassic fault block tilting of the strata.

Discussion of Results

The mean of all site mean directions gives a Late Jurassic paleopole at 149±3 Ma on the APWP for Europe [1]. This is significantly different (>>99% confidence) from a previous, hematite-alteration- derived paleopole [2] that initially gave an age of 254±6 Ma but cannot be maintained any longer. Our Late Jurassic, i.e. epigenetic, age for the ChRM in the black shale-hosted Kupferschiefer Cu-Pb-Zn ores at Sangerhausen correlates with crustal extension that formed the nearby North German Basin north of the Harz Mountains. This event reactivated major NW-SE striking faults and - arguably - major (ore)fluid pulses, associated with such fault movement. Spatial coincidence of major ore zones with intersections of NW-SE faults and fertile basement rocks additionally support our late, epigeneticlate metallogenetic model.

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$\delta^{13}C_{carbonate}$ chemostratigraphy of the Carrapateira Outlier (Lower Kimmeridgian), Southern Portugal

M. BORGES[1*,2], R. GOOGHUE[3], P. FERNANDES[1], Z. PEREIRA[2], V. MATOS[1] AND B. RODRIGUES[1]

[1]CIMA, University of Algarve, 8005-139 Faro, Portugal, (*correspondence: marisa.borges@lneg.pt)

[2]LNEG, 4466-901 S. Mamede de Infesta, Portugal, (zelia.pereira@lneg.pt)

[3]Department of Geology, Trinity College Dublin, Ireland (goodhuer@tcd.ie)

The Carrapateira Outlier (CO) located 20 km north of Sagres is formed by Upper Triassic to Kimmeridgian sediments. The studied section is located at Três Angras bay and consists of approximately 50 m of limestones interbedded with marls, assigned to the Early Kimmeridgian based on corals, foraminifera and dinoflagellate cysts. The uppermost limestone beds are rich in macrofossils with well-preserved corals in life position. To compile $\delta^{13}C$ chemostratigraphy for this section, sixty five bulk carbonate samples were studied.

The $\delta^{13}C$ values vary gradually throughout the succession showing a baseline with a general decreasing trend up section, ranging from 1,59‰ to -0.68‰. However, the $\delta^{13}C$ curve indicates two main negative $\delta^{13}C$ excursions, the first related to a coarse grained interval with a minimum value of -1.38‰ and a second excursion with a minimum value of -3,10‰, immediately below the bioclastic rich beds of the top of the section. In general, the decreasing baseline trend agrees with the global $\delta^{13}C$ curve for the Kimmeridgian in the Tethyan Realm, where the CO was located. The two negative excursions are tentatively related to regional perturbations in the carbon cycle. Hence, both are interpreted as a result of large input of ^{12}C to the basin as a result from regressive pulses as suggested by the sedimentological and palynofacies analysis studied.

Acknowledgments: This study was sponsored by FCT (PhD grant SFRH/BD/48534/2008).

Pyroxenites in peridotites from External Liguride ophiolites (Italy): Insights on small scale heterogeneities in MORB mantle

G. BORGHINI[1,2], E. RAMPONE[1], A. ZANETTI[3], C. CLASS[2], A. CIPRIANI[2], A.W. HOFMANN[2,4] AND S.L. GOLDSTEIN[2]

[1]DIPTERIS, Università di Genova, Corso Europa 26, 16132 Genova, Italy
[2]Lamont-Doherty Earth Observatory, Palisades NY 10964, USA
[3]CNR-Istituto di Geoscienze e Georisorse, Sezione di Pavia, via Ferrata 1, I-27100 Pavia, Italy
[4]Max Planck Institute for Chemistry, P.O. Box 3060, 55020 Mainz, Germany

The occurrence of mafic layers in peridotites constitutes an important compositional heterogeneity in the mantle, and their role in mantle melting and basalt generation is currently debated. We present field, chemical and isotopic data on pyroxenites and host peridotites from the western peridotite massifs of the External Liguride ophiolitic Units (Northern Apennines, Italy). Pyroxenites (mostly spinel-websterites) occur as cm-thick bands (up to 12 cm) parallel to the tectonite mantle foliation, and ,together with the peridotites, they are partially recrystallized at plagioclase-facies conditions. Whole-rock and mineral compositions are extremely heterogeneous, covering almost the entire compositional range of worldwide lithospheric pyroxenites (Mg# = 74-88, Al_2O_3 = 10-17 wt%, CaO = 7-20 wt%). The pyroxenite chemistry reflects high-pressure magma segregation of tholeiitic melts dominated by clinopyroxene crystallization. A multi-step, sequential leaching procedure on clinopyroxene separates enables us to remove partial contamination and provides reliable Sr isotope data. The Sr and Nd compositions of clinopyroxenes from pyroxenites and peridotites fall in the typical range of normal MORB ($^{87}Sr/^{86}Sr$ =0.7023-0.7029; $^{143}Nd/^{144}Nd$ =0.5134-0.5128). Internal Sm-Nd isochrons on plagioclase-clinopyroxene pairs from two pyroxenites yield ages of 183±14 Ma and 177±12 Ma for the low-P mantle exhumation. On a slightly larger spatial scale, chemical and isotopic profiles through the pyroxenite-peridotite boundaries indicate cm-scale modification of the wall-rock peridotite, presumably related to emplacement of the pyroxenites. This suggests that deep melt intrusion can locally modify the host peridotites and introduce small scale compositional heterogeneity in a MORB mantle.

Heating organoclays: Does it affect their potential to interact with organic compounds in aqueous environment?

M. BORISOVER[1]*, S. YARIV[2], N. BUKHANOVSKI[1] AND I. LAPIDES[2]

[1]The Institute of Soil, Water and Environmental Sciences,The Volcani Center, ARO, Bet Dagan, Israel (*correspondence: vwmichel@volcani.agri.gov.il)
[2]Institute of Chemistry, The Hebrew University of Jerusalem, Edmund Y. Safra Campus, Jerusalem, Israel

By replacing inorganic exchangeable cations in clay minerals with organic cations, hydrophilic mineral/water interfaces may be converted to organoclay interfaces of variable and controlled lipophilicity. This paper summarizes the data on aqueous sorption of a series of organic compounds on organoclays preheated at different temperatures [1]. Sorptive properties of thermally treated organoclays are of interest since: (1) they can shed light on mechanisms of organic compound - organoclay interactions; (2) the thermal treatment is considered as a tool to regenerate organoclays after their use in different environmental applications; (3) thermally treated organoclays can provide a model for examining such important environmental issue, as fire-affected soils. Thus, organoclays were (*i*) prepared from the Na-montmorillonite rich bentonite with a series of quaternary ammonium salts and freeze-dried, (*ii*) heated during two hours in air at different temperatures, from 150 ^{0}C to 420 ^{0}C, and (*iii*) characterized by C/N, FTIR, XRD, TG-DTG and surface area analyses. Mild preheating of organoclays at 150 ^{0}C was not associated with chemical changes in the sorbent structure but was able to enhance interactions with organic compounds present in water. The extent of this enhancement reflected the different abilities of organic sorbates to compete with water molecules for sorption sites on organoclays. This observation supported the earlier idea that the partial, incomplete hydration of preheated organoclays can be a reason of increased organic sorbate – organoclays interactions [2,3]. Yet, there is no clear understanding why this rehydration of preheated organoclays is partial. When organoclays were heated at higher temperatures, the significant changes in the organoclay chemistry did not result in the remarkable loss of the organoclay sorptive potential towards organic compounds present in aqueous solution.

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Uranium, thorium and REE in macrofungi from pristine and polluted sites

JAN BOROVIČKA[1,2]*, JAROSLAVA KUBROVÁ[3], JAN ROHOVEC[1] AND ZDENĚK ŘANDA[2]

[1]Institute of Geology, v.v.i., Academy of Sciences of the Czech Republic, Rozvojová 269, CZ-165 00 Prague 6 (*correspondence: borovicka@gli.cas.cz)

[2]Nuclear Physics Institute, v.v.i., Academy of Sciences of the Czech Republic, Řež 130, CZ-250 68 Řež near Prague

[3]Institute of Environmental Studies, Faculty of Science, Charles University, Benátská 2, CZ-128 01 Prague 2

In recent years, interest in the biogeochemical roles of fungi in the environment has increased rapidly. Part of this research involves studying the ability of macrofungi to accumulate trace elements in fruit-bodies. Available data on some elements are rather scant or even equivocal. Specifically, ambiguous data have been reported for U, Th and REE. Since recent studies highlighted the possible role of fungi in the environmental biogeochemistry of U (Fomina *et al*. 2007, Env. Microbiol. 9: 1696-1710), there is an obvious need for more knowledge of macrofungal ability to accumulate U.

We have determined concentrations of U, Th and REE (HR-ICP-MS) in a representative set of macrofungi from unpolluted sites with differing bedrock geochemistry. Analytical results are supported by use of certified reference materials and the reliability of the determination of U was verified by epithermal neutron activation analysis (ENAA).

It appears that some data recently published on these elements are erroneous, in part because of use of an inappropriate analytical method; and in part because of apparent contamination by soil particles resulting in elevated levels of Th and REE. Macrofungi from unpolluted areas, in general, did not accumulate high levels of the investigated metals. Concentrations of U and Th were generally below 30 and 125 ng g^{-1} (dry weight), respectively. Concentrations of REE in macrofungi did not exceed 360 ng g^{-1} and their distribution more or less followed the trend observed in post-Archean shales and loess.

Concentrations of U in macrofungi from mine tailings and U-polluted forest plantations in the former Příbram mining district (Central Bohemia, Czech Republic) were significantly elevated but rather low; the highest values were in lower units of μg g^{-1}.

This research was supported by the Grant Agency of Charles University (project 3010) and the Czech Science Foundation (project P504/11/0484).

The roentgenoluminescence of feldspars from granitoids of the Kolyvan'-Tomsk folded belt as a typomorphic character

N.N. BOROZNOVSKAYA, T.S. NEBERA, S.I. KONOVALENKO, A. BAYOVA AND O. ZHEREBETSKAYA

Tomsk State University, Tomsk, Russia

Basic luminogens within the earth's crust, 92 % of which is formed of silicates, are defects in silicon-aluminum-oxygen tetrahedron (O^-) and isomorphic admixtures instead of K, Na, Ca, Mg, Al, Si (Tl^+, Pb^{2+}, Mn^{2+}, Fe^{3+}, Cr^{3+} and rare earths). L of O^- defects may be regarded as background. Its intensity is often determined by presence of decay structures and cooling rate. L of impurity defects in the earth's crust minerals depends on formation conditions (depth, crystallization temperature and cooling rate). The study has been carried out on the roentgenoluminescence spectra in the wavelength optical range (250-900 nm) in common potash feldspars (CPFS) and plagioclases from granitoids of the Kolyvan'-Tomsk folded belt (KTFB). Feldspars (FS) from all rock diversities of the Kolyvanskiy, Barlakskiy, Obskoy and Novosibirskiy massifs situated in the western part of KTFB nearby the Novosibirsk Trough have been the object of the investigation. The cause and effect relationship has been ascertained between the composition, structural ordering, crystallochemical characteristics and luminescence of the feldspars under consideration. The RL spectra of the Barlakskiy, Obskoy and Kolyvanskiy feldspar massifs are of similar character and result from the slow cooling in the conditions between the average and hypabyssal depths. The peculiarities of the RL spectra of the FS granitoids of the Novosibirskiy massif suggest the quick cooling of these rocks in the conditions of shallow depths or of the tectonically active zone (in the zone of crush). The dominating and extremely intensive RL of Fe^{3+} in the rocks of all massifs is frequently indicative of the existence of the hyperalkaline silicate melt for all objects under consideration. The presence of the Tl^+ RL with the maximum of 285 nm is the distinctive property of leucogranites from the Kolyvanskiy and Barlakskiy massifs, suggests the presence of the rare metal mineralization and is applicable as a typomorphic character. *These researches have been supported by the Ministry of Education and Science of Russia*.

Putative Cryogenian ciliates from Mongolia

TANJA BOSAK[1], FRANCIS MACDONALD[2], DANIEL G. LAHR[3] AND EMILY D. MATYS[4]

[1]EAPS MIT, Cambridge MA 02139, tbosak@mit.edu
[2]EPS, Harvard University, MA 02138, fmacdon@fas.harvard.edu
[3]Graduate Program in Organismic and Evolutionary Biology, UMass Amherst, MA 01003, daniel.lahr@gmail.com
[4]EAPS MIT, Cambridge MA 02139, ematys@mit.edu

Major lineages of modern eukaryotes, represented primarily by microscopic taxa, are thought to have originated during the Neoproterozoic. However, microfossils older than 635 Ma rarely bear unambiguous relationships to modern microscopic eukaryotes.

Here we report exceptionally preserved 715-635 million year old eukaryotic tests in limestone strata of Mongolia. These structures are most abundantly preserved within rhythmite and ribbonite strata that record a large negative anomaly in $\delta^{13}C$ of both carbonate and organic matter.

The ~100 μm long organic-rich three-dimensional tests have flask-like shapes, constricted necks, distinct and often thickened collars. The test walls are flexible, composed of densely packed alveolar structures and stainable by dyes that react with polysaccharides. The combined morphological and ultrastructural properties of the Cryogenian tests are remarkably similar to the lorica of modern group of planktonic ciliates, tintinnids.

The presence of putative tintinnids in the pre-635 Ma strata places an upper bound on the divergence of ciliates, marks the increasing diversity of phagotrophic eukaryotes during this time and suggests a reorganization of Cryogenian foodwebs. The advent of planktonic organisms forming recalcitrant organic or mineral-rich tests may have increased export and burial fraction of organic carbon, driving an increase in atmospheric oxygen and the subsequent radiation of metazoans.

Origin and signficance of basic and ultrabasic outcrops from northeastern algeria (Edough massif)

D. BOSCH[1], D. HAMMOR[2], O. BRUGUIE[1], R. CABY[1], AND M. MECHATI[2]

[1]University Montpellier 2, Place Eugene Bataillon 34095, Cedex 05, France (bosch@gm.univ-montp2.fr)
[2]Université Badji-Mokhtar, BP12, El-Hadjar, Annaba 23 000, Algeria

The Maghrebian, Betics and Apenninic chains outcrop around the mediterranean basin and constitute dismembered fragments of the Alpine orogen. Conflicting geodynamic models have been proposed in order to explain the different paleogeographic settings from which these fragments derived. Crust-mantle interactions following subduction of Jurassic oceanic crust and collision-related tectonic events of Eocene age in relation to the northward motion of Africa have been demonstrated by numerous works. The incorporation of mafic/ultramafic rocks into the basement is evidenced in various peri-mediterranean areas, in particular at c. 22 Ma. This work is focused on the basic and ultrabasic rocks from the easternmost internal part of the Maghrebides. An extensive petrological and geochemical study has been performed on three distinct outcrops, i.e. Bou Maiza gabbros, amphibolites from La voile Noire and Sidi Mohamed peridotites. Peridotites display a primitive character (Mg number >85), but slightly enriched trace elements patterns (1 to 10 times CHUR) characterized by negative Nb anomalies and flat to slightly LREE-depleted patterns. Associated isotopic constraints suggest a possible continental contamination of the peridotites by the surrounding gneisses. These ultrabasic rocks are interpreted as parts of the lithospheric mantle incorporated into the continental crust during a late Burdigalian extensional event that opened the Algerian basin. The Bou Maiza gabbros and La Voile Noire amphibolites show complementary trace elements spectra suggesting derivation from a common MORB source reservoir, but without filiation with the Sidi Mohamed peridotites. Such affinities suggest they represent a fragment of the Neothetys lithosphere obducted onto the North African margin during Miocene times.

Natural analogue of CO_2 mineral sequestration: The Tuscan magnesite deposits

C. BOSCHI[1], L. DALLAI[1], A. DINI[1] AND G. RUGGIERI[2]

[1]Istituto di Geoscienze e Georisorse, CNR, Pisa, Italy
[2]Istituto di Geoscienze e Georisorse, CNR, Firenze, Italy

The magnesite deposit of Malentrata (Tuscany, Italy) was derived from silicification–carbonation of Ligurian serpentinites embedded in pelite-carbonate formations, and represents a natural analogue of *in situ* CO_2 mineral sequestration. Serpentinites were transformed to a brownish friable mineral assemblage of opal, chromian montmorillonite, Fe-rich magnesite and minor iron sulfides and oxides. The serpentinite alteration was accompanied by the formation of magnesite and dolomite veinlets, and large magnesite–dolomite veins along major tectonic structures. The major veins are characterized by the following crystallization sequence: i) early magnesite, ii) green and late pale-brown dolomite cementing the early brecciated magnesite vein infill, and iii) late quartz, chalcedony and opal. The observed mineral assemblage is indicative of low temperature hydrothermal alteration driven by Si- and CO_2-rich fluids under relatively low pH conditions. Geochemical data along transects from carbonated host rocks to carbonate-silica veins suggest a marked variation of fluid composition through the main stages of precipitation. Dolomites are more enriched in Cr, Sr, Y, U and REE with respect to magnesites. Magnesites are the most REE-depleted, whereas green dolomites show quite flat enriched patterns approaching the pattern of sedimentary formations. $\delta^{18}O$ of magnesites range from 23 to 32‰, and $\delta^{13}C$ from -2 to 0‰. Both dolomite types are depleted in $\delta^{18}O$ with respect to magnesite, especially late pale-brown dolomite. $\delta^{13}C$ of dolomites is similar to magnesite with slightly lower values in green dolomites. It seems to be conceivable that fluids first interacted with serpentinites precipitating magnesite. After the magnesite precipitation, fluids interacted with the sedimentary formations, becoming progressively enriched in calcium and REEs, and depleted in $\delta^{18}O$ due to the partial equilibration with the pelite portion. At this stage dolomite precipitation recorded geochemical variations of fluids. Malentrata deposit lies at the periphery of Larderello geothermal field and it highlights the near surface local interaction between low temperature fluids and serpentinite bodies in favourable tectonic conditions.

Deciphering arsenic sources in surface waters and the role of bacterial oxidation

A. BOSSY[1]*, C. GROSBOIS[2], C. JOULIAN[3], F. BATTAGLIA-BRUNET[3] AND A. COURTIN-NOMADE[1]

[1]EA GRESE, Limoges Univ., 87060 Limoges, France (*correspondence: angelique.bossy@etu-unilim.fr)
[2]UMR 6113 CNRS ISTO, Tours Univ., 37000 Tours, France
[3]Process and Environment Division, BRGM, 45060 Orléans, France

In a geochemical anomaly in As, different potential As contributions to stream waters, such as groundwaters, runoff and As-bearing phase weathering present within the soils were studied with a high sampling frequency. It allowed deciphering the contribution of each compartment to As contamination of surface waters. The role of indigenous bacteria in As oxidation state in ground- and surface waters was also studied in laboratory.

In the soil profile, total As concentrations indicated depletion (1500 to 385 $mg.kg^{-1}$) during pedogenesis relative to a mineralogical evolution of As-bearing phases upwards the soil profile: from arsenates (Ba-rich pharmacosiderite: 14-26 wt.% As) to Fe-oxyhydroxides (ferrihydrite-like: 4-16 wt.% As; ferrihydrite-type, hematite and goethite: <3 wt.% As). Conversely, an increase of dissolved As concentrations (15-52 $\mu g.L^{-1}$) was observed in soil solutions.

In stream waters, As concentrations (7.5 to 69.4 $\mu g.L^{-1}$) were attributed to several inputs: (i) runoff and soil solutions, (ii) waters from former adits (97-120 $\mu g.L^{-1}$ As), (iii) wetland and groundwaters (up to 169 and 215 $\mu g.L^{-1}$ As, respectively). The latter inputs were characterized by dissolved As(III) during low flow period which was rapidly oxidized, suggesting the contribution of bacterial oxidation.

Bacterial As oxidation tests showed a decrease of dissolved As(III) concentrations in stream and wetland waters (-17% and -41%, respectively). In groundwaters, a stronger decline for dissolved As(III) (-95% in 15 h) was observed, then followed by an As(III) release (+51%), suggesting the presence of As(V)-respiring bacteria. The study of the As(III)-oxidizing bacterial community (PCR-DGGE method on *aoxB* genes, a genetic marker of these bacteria), showed a divergence in the community structure between (i) surface and wetland waters, and (ii) groundwaters, probably due to variable As concentrations, redox conditions and bacteria number.

The effect of Cl on the solubilty of Au and Pd in andesitic melts

R.E. BOTCHARNIKOV[1]*, R.L. LINNEN[2], M. GUILLONG[3], F. HOLTZ[1] AND V.S. KAMENETSKY[3]

[1]Institut für Mineralogie, Leibniz Universität Hannover, Callinstr. 3, D-30167, Hannover, Germany (*r.botcharnikov@mineralogie.uni-hannover.de)
[2]Department of Earth Sciences, BGS 1000B University of Western Ontario, London, ON, N5A 5B7 Canada
[3]ARC Centre of Excellence in Ore Deposits, University of Tasmania, Hobart, Tasmania, 7001 Australia

Chlorine is considered as an important agent responsible for the mobilization and transport of metals in magmatic systems associated with porhyry ore mineralization and with late-stage metal-rich horizons of large igneous intrusions. In the former case, the considerable role of Cl is confirmed by the observation that fluid inclusions associated with porphyry ores are often composed of low-salinity aqueous vapor and high-salinity brines, whereas in the later case it is believed that the mobility of metals in different horizons of layered intrusions might have been controlled by the general process of chromatographic separation of metals during migration and evolution of Cl-enriched fluids. Since at given magmatic conditions the mobility and transport of metals by exsolving Cl-bearing fluid phase(s) is presumably dependent on chemical potential of metal components complexing with Cl in silicate melt, quantitative experimental data on metal solubility in melts and melt-fluid partitioning are required.

Here we report the results of experiments on the solubility of Au and Pd in andesitic melts equilibrated with $Au_{80}Pd_{20}$ capsule material at 1200°C, oxidizing conditions (FMQ+3) and pressures in the range from 50 to 500 MPa as a function of Cl content in the system. Due to non-ideality of mixing in Cl-bearing fluids, the investigated systems are characterized by coexistence of andesitic melts with vapor, vapor+brine, brine, or supercritical single-phase fluid, depending on the bulk Cl content and P. The obtained data show that an addition of Cl to the system increases significantly the solubility of both metals in the silicate melt at all investigated pressures, in particular in melts coexisting with brine or supercritical fluid. The concentration of Au increases from 1-2 upto 40-50 μg/g, whereas the concentration of Pd increases from 0.1 to 20 μg/g with increasing Cl content of the melt from 0 to 2.5 wt%. Since the calculated activity coefficients of Au and Pd in the $Au_{80}Pd_{20}$ capsule are both close to 0.7, the solubility values of pure metals should be slightly higher. The results clearly show that Cl can indeed control on the mobility of Au and Pd in natural magmas.

The transformation of ACC to vaterite; An *in situ* SAXS/WAXS study

P.BOTS[1]*, J.D. RODRIGUEZ-BLANCO[1], T. RONCAL-HERRERO[1,2], S. SHAW[1] AND L.G. BENNING[1]

[1]School of Earth and Environment, University of Leeds, LS2 9JT, United Kingdom (*eepbo@see.leeds.ac.uk)
[2]Department of Geosciences, University of Oslo, PB 1047, Blindern, Oslo, Norway.

Vaterite (μ-$CaCO_3$) is rarely observed in natural systems, as it is thermodynamically unstable with respect to calcite and aragonite [1]. However, some organisms produce and stabilize vaterite as biominerals [2]. At high supersaturation vaterite forms via a nanoparticulate, poorly-ordered and metastable precursor, amorphous calcium carbonate (ACC). In the pure system, ACC transforms to vaterite within minutes, and subsequently to calcite [3]. The detailed mechanisms of the ACC to vaterite transformation are however still lacking due to the fast kinetics of this first step of crystallization. In this study we demonstrate the use of *in situ* time-resolved synchrotron-based Small- and Wide-angle X-ray Scattering (SAXS/WAXS) combined with off-line characterization to quantify the kinetics and crystallization mechanisms of vaterite at fast time scales.

The SAXS/WAXS data collected at 1 second / frame for up to 32 minutes, revealed that the ACC to vaterite transformation occurs in 3 stages. The initial stage (0-2 min) was governed by ACC precipitation and growth (to Ø ~ 38 nm). During this stage ~70 % of the total vaterite (Ø ~ 10 nm) formed via spherulitic growth at the expence of the metastable ACC [4]. The end of the spherulitic growth (at 2 min) was concomitant with a drop in supersaturation below the limit for spherulitic growth of vaterite (SI≈1.4 [4]). During the 2nd stage (2-7 min), remnant ACC lead to a further increase of the amount of vaterite (~30 %) due to ACC dissolution and vaterite nanocrystal reprecipitation. During this stage the vaterite crystallite size increased from ~10 to ~35 nm. Finally during the 3rd stage (> 7 min), no *de nuovo* precipitation of vaterite occurred, however the vaterite crystallite size continued to increase reaching ~60 nm at the end of the experiment (32 min). This increase in crystallite size was solely governed by Ostwald Ripening.

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Understanding late accretion on the Earth, Moon, and Mars

W.F. BOTTKE[1], R.J. WALKER[2], J.M.D. DAY[3], D. NESVORNY[1] AND L. ELKINS-TANTON[4]

[1]Southwest Research Institute & NASA Lunar Science Institute, Boulder, CO, USA (bottke@boulder.swri.edu)
[2]Dept. of Geology, University of Maryland, College Park, MD 20742, USA
[3]Geosciences Research Division, Scripps Inst. Oceanography, La Jolla, CA 92093 USA
[4]MIT, Cambridge MA 02139 USA.

Highly siderophile elements (HSE) have low-pressure metal-silicate partition coefficients that are high [$>10^4$]. It is assumed the silicate portions of rocky planetary bodies with metallic cores are effectively stripped of HSE immediately following primary accretion and final core segregation. Accordingly, the 'giant impact' on Earth that formed the Moon should have cleansed HSE from the mantles of both worlds.

Curiously, the Earth and Moon (and Mars) have disparate, yet elevated HSE abundances. We argue late accretion may provide a solution, provided that ≥ 0.5% Earth masses of broadly chondritic planetesimals reaches Earth's mantle, and that ~10 and ~1,200 times less mass go to Mars and the Moon, respectively [1]. Our models show that leftover planetesimal populations dominated by massive projectiles can explain these additions, with our inferred size distribution matching those derived from the inner asteroid belt, ancient martian impact basins and planetary accretion models. The largest late terrestrial impactors, at 2,500-3,000 km in diameter, potentially modified Earth's obliquity by ~10°, while those for the Moon, at ~250-300 km, may have delivered water to its mantle.

To keep the iron core from such a large projectile sequestered in Earth's mantle, HSE delivery there may involve a "hit and almost run" collision. Here most of the projectile's core (and HSE) plows through the target mantle and emerges on the other side in a highly-fragmented state. The debris then evolves into a long spiral-arm-like structure that rains down across the target. These events may allow massive impactors to deliver large quantities of HSE, but in a manner akin to small body accretion that optimizes emulsification into the upper mantle. This potentially explains why mantle peridotites have similar HSE abundances and how the iron in the projectile's core became oxidized.

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Direct Injection Nebulization with MC-ICP-MS: Performances and prospects

J. BOUCHEZ*[1,2], P. LOUVAT[1], G. PARIS[2,3], J. GAILLARDET[2] AND J. MOUREAU[2]

[1]IPG Paris (UMR CNRS 7154), Université Paris Diderot, 1 rue Jussieu, 75252 Paris Cedex 05, France
[2]GFZ, Telegrafenberg, Potsdam, Germany (*correspondence: bouchez@gfz-potsdam.de)
[3]CalTech, Pasadena CA 91125, USA

The advent of MC-ICP-MS during the last decade has considerably improved isotope ratio measurements in terms of accuracy, precision, reproducibility and rate of sample throughput. Nevertheless, the search continues for more efficient, more stable, more sensitive and cleaner introduction systems. This is particularly true for (1) "sticky" elements displaying long washout times (2) volatile elements whose sensitivity cannot be improved by desolvation systems.

Boron belongs to both categories. Recent development of the d-DIHEN [1] (demountable Direct Injection High Efficiency Nebulizer) allows for faster and more precise determination of boron isotope ratio by MC-ICP-MS [2]. The principle of direct injection is to place a long quartz nebulizer in the plasma torch, spraying the sample directly into the plasma.

Using d-DIHEN along with Neptune MC-ICP-MS, sensitivity of 10 V/ppm (at an uptake rate of 30 μL/min) are obtained, with washout times of 2 to 3 minutes to reach background levels of less than 1 ‰ of the previous sample signal. Recent automation using a SC sampler and the FAST system (ESI) allows for systematic triplicate measurements of each sample, thereby improving the reproducibility to less than 0.2‰ (2 S.D.) in most cases. Performances obtained with the improved interface pumping capacity along with a Teflon spray chamber will also be presented for comparison.

Li isotope measurements with d-DIHEN yield reproducibilities similar to the ones obtained with the APEX desolvation system (ESI), despite a lower sensitivity and rounder peak shape, while allowing for faster measurements because of shorter washout times.

At this level of precision, drastic intensity matching between standards and samples appears to be highly critical, and has to be within 5%. Forthcoming improvements seem to lie in even more drastic chemical purification procedures.

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Experimental investigation of the stability of Fe-rich carbonates in the lower mantle

E. BOULARD[1], N. MENGUY[1], A.L. AUZENDE[1], K. BENZERARA[1], H. BUREAU[1], D. ANTONANGELI[1], A. CORGNE[1,2], G. MORARD[1], J. SIEBERT[1], J.P. PERRILLAT[3,4], F. GUYOT[1] AND G. FIQUET[1]

[1]Institut de Minéralogie et de Physique des Milieux Condensés, Paris, France
[2]Institut de Recherche en Astrophysique et Planétologie, Toulouse, France.
[3]European Synchrotron Radiation Facility, Grenoble, France
[4]Université de Lyon 1, Villeurbanne, France

Carbonates are the main C-bearing minerals that are transported deep in the Earth's mantle via subduction of the oceanic lithosphere [1]. The fate of carbonates at mantle conditions plays a key role in the deep carbon cycle. Decarbonation, melting or reduction of carbonates will affect the extent and the way carbon is recycled into the deep Earth.

High-pressure high-temperature experiments were carried out up to 105 GPa and 2850 K on oxide assemblages of (Mg,Fe)O + CO_2. The presence of $Fe^{(II)}$ in starting materials induces redox reactions from which $Fe^{(II)}$ is oxidized and a part of the carbon is reduced. This leads to an assemblage of magnetite, diamonds, and carbonates or, pressure depending, their newly discovered $Fe^{(III)}$-bearing high-pressure polymorphs based on a silicate-like chemistry with tetrahedrally coordinated carbon [2]. Our results show the possibility for carbon to be recycled in the lowermost mantle and provide evidence of a possible coexistence of reduced and oxidized carbon at lower mantle conditions.

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Advances in high precision Ca isotope ratio measurements using TIMS

CLAUDIA BOUMAN*, DIETMAR TUTTAS, MICHAEL DEERBERG AND JOHANNES SCHWIETERS

Thermo Fisher Scientific, Hanna-Kunath-Str. 11, 28199 Bremen, Germany.
(*correspondence: claudia.bouman@thermofisher.com)

Ca isotopes are used in various disciplines within Earth Sciences, e.g. paleoceanography, geochronology and biogeochemistry. Precise and reproducible measurements of Ca isotopes are among the most challenging measurements within TIMS. Most important factors influencing the precision and reproducibility are sample loading, choice of double spike, instrumental mass fractionation and mass spectrometer performance. Advances in mass spectrometry have been made with the introduction of the TRITON *Plus*.

The TRITON *Plus* has innovative features that enable high precision Ca isotope ratio measurements for all Ca isotope ratios. First of all, the TRITON *Plus* enables simultaneous collection of 40Ca up to 48Ca without zoom due to the extended mass dispersion. Also, the instrument can house different ohmic resistors (10^{10}, 10^{11} and 10^{12} Ohm). This is especially useful for isotope systems with a large dynamic range, such as Ca, where the abundance of the major isotope is almost 97%. If smaller samples are analysed, the low-noise 10^{12} Ohm amplifiers are advantageous, since they show up to a factor of 3 improvement in signal/noise ratio over the standard 10^{11} Ohm current amplifiers.

In this contribution, we present basic performance features for the TRITON *Plus* with regard to Ca isotope ratio measurements, as well as precision and reproducibility for different sample sizes.

Alteration of oil by gas: Experiments in fused silica capillary capsules

J. BOURDET[1]*, P.J. EADINGTON[1], R.C. BURRUSS[2] AND I.-M. CHOU[2]

[1]CSIRO, CESRE, 26 Dick Perry Ave., Kensington, 6151, WA, Australia (*julien.bourdet@csiro.au)
[2]US Geological Survey, 956 National Center, Reston, VA 20192, USA

Reservoir case studies showed that the fluorescence of oil inclusion assemblages of current or palaeo-gas zone has patterns that are not seen in zones that have only been invaded by oil [1, 2]. It is suspected that a fraction of the oil is retained in the pores when oil is drained by gas and that molecules from this residual oil partionned in gas.

To attempt to reproduce the alteration of oil by gas, or gas-washing, we sealed small amounts of crude oil (59º, 42º or 33º API) and excess pure gas (methane, ethane, propane or CO_2) in fused silica capillary capsules (FSCCs, [3]), with and without water. The UV-visible fluorescence spectra of oil phase(s) enclosed within the FSCCs were measured at temperatures of 20 to 100 ºC, and Raman and FT-IR spectra of the gas and oil phases were measured at 20ºC.

With ethane and propane, the 33°API oil formed a new immiscible fluorescent liquid phase with fluorescence that is more blue than the initial oil, which became more yellow or disappered, and formed semi-solid residues. Immiscible hydrocarbon liquid phases with solid residue formed in FSCCs with added water, but not in those without added water. Experiments with 59°and 42° API oil do not show immiscible hydrocarbon liquids. The fluorescence of those crude oils displays a similar yellow shift in presence of gas. Solid residues are minor.

We interpret (1) the decrease of fluorescence of the original oil at short wavelengths as due to partitioning of low molecular weight aromatic molecules into the new immiscible liquid phase and/or vapour phase; (2) the increase of fluorescence response at long wavelengths as due to loss of low molecular weight aromatic, including desorption of aromatics and resins from asphaltene. Water has effects on the precipitation of semi-solid residue and stability of oil phase in the lowest API gravity oil.

These results are consistent with the attributes of oil inclusions trapped in palaeo-oil zones that were displaced by gas and support the concept of gas-washing of residual oil.

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Conditions of metal-silicate segregration in the parent bodies of iron meteorites

BERNARD BOURDON

Laboratoire de Géologie de Lyon, CNRS, UMR 5276, Ecole Normale Supérieure de Lyon, France

While there has been extensive work on the conditions of core formation on Earth, little work has focused on the conditions of core formation in the parent bodies of iron meteorites. A major obstacle to addressing this question is that the bulk compositions of the parent bodies are unknown and the iron meteorites do not represent directly the metallic liquid that segregated from silicates. Rather the iron meteorite compositions reflect various degrees of crystallization and fractionation of metallic iron. In some cases, there can be more than one liquid making the modelling more difficult.

By making the assumption that the bulk composition of the parent bodies was chondritic for the refractory siderophile elements, one can obtain a rough estimate of the size of the core and then estimate the corresponding oxygen fugacity of the parent body. In addition, using experimental determinations of the partition coefficients between metal and silicate, one can reconstruct the temperature and pressure conditions of metal-silicate segregation for various parent bodies. Using this approach, one can also estimate the abundance of volatile siderophile elements in the parent bodies of magmatic iron meteorites.

Due to the large number of assumptions made in this modelling, one can only obtain estimates for the oxygen fugacities, pressures and temperatures during core formation of the iron meteorite meteoroids. In the case of the IIIAB meteorites, the oxygen fugacity is close to IW-1.1 while it is IW-0.8 for the IVA magmatic iron parent body, which confirms the more oxidized nature of these parent bodies compared with the Earth (IW-2). In the case of the IVA irons, the best match is obtained for a volatile depleted bulk composition and the conditions of metal segregation has to be less than 1 GPa with a temperature ranging between 1600 and 1800 K. The siderophile element abundance of IIIAB requires a slightly higher temperature range and similarly low pressure.

Molecular dynamics simulations of the electrical double layer on smectite clay surfaces

IAN C. BOURG AND GARRISON SPOSITO

Earth Sciences Division, Lawrence Berkeley National Lab, Berkeley, CA, USA (*correspondence: icbourg@lbl.gov)

We report new molecular dynamics (MD) simulation results elucidating the structure of the electrical double layer (EDL) on smectite surfaces contacting mixed NaCl-$CaCl_2$ electrolyte solutions in the range of concentrations relevant to pore waters in ocean sediments and in geologic repositories for CO_2 or high-level radioactive waste (0.34 to 1.83 mol_c dm^{-3}). Our simulations used methodologies known to correctly describe the structure and diffusion coefficients of water and solutes in smectite interlayer nanopores [1]. Our results confirm the existence of three distinct ion adsorption planes (0-, β-, and d-planes), often assumed in EDL models [2,3], but with two important qualifications: (1) the location of the β-, and d-planes are independent of ionic strength or ion type and (2) "indifferent electrolyte" ions can occupy all three planes. Charge inversion occurred in the diffuse ion swarm because of the affinity of the clay surface for $CaCl^+$ ion pairs. Therefore, at concentrations ≥ 0.34 mol_c dm^{-3}, properties arising from long-range electrostatics at interfaces (electrophoresis, electro-osmosis, co-ion exclusion, colloidal aggregation) will not be correctly predicted by most EDL models. Co-ion exclusion, typically neglected by surface speciation models, balanced a large part of the clay mineral structural charge in the more concentrated solutions. Water molecules and ions diffused relatively rapidly even in the first statistical water monolayer, contradicting reports of rigid "ice-like" structure for water on clay mineral surfaces.

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Quantifying weathering and erosion rates using cosmogenic nuclides.

D.L. BOURLES, R. BRAUCHER AND L. SIAME

CEREGE, UMR 6635 CNRS-Aix-Marseille Université, BP 80, 13545 Aix-en-Provence Cedex 4, France

Quantifying chemical weathering and physical erosion rates, whose sum corresponds to denudation rates, is of great importance across a wide range of environmental science disciplines Until recently, this has nevertheless been difficult over millenial timescales. Accumulating within mineral grains exposed to cosmic ray secondary particles in the uppermost few meters of the Earth's surface, *in situ*-produced cosmogenic have provided opportunities to quantify on such timescales not only the mineral grains exposure duration near the surface, but also the rates of the processes bringing them to the surface and removing them from above it.

Corresponding to their build-up in the suitable mineral over thousands of years, the cosmogenic nulide concentrations measured in rocks, sediments or soils are relatively insensitive to short-term fluctuations and thus allow quantifying natural, long-term weathering and erosion rates. More, they permit to evidence landscapes that are not at natural steady state because affected by natural hazards (landslides) or by anthropogenic activities. Cosmogenic nuclides thus provide reliable methods to measure long-term average denudation rates in a wide range of settings and to point out any perturbations that may have disturbed them.

Through the presentation of pertinent case studies from notably Brasil, Taïwan and Africa, the following general types of denudation-related problems will be addressed: (i) denudation rates from rock surface samples; (ii) denudation rates from vertically mixed continental sediments; (iii) spatially averaged denudation rates.

Magma recharge and eruption processes at Volcán Llaima (Andean Southern Volcanic Zone, 38.7°S)

C. BOUVET DE MAISONNEUVE[1]*, M.A. DUNGAN[1], O. BACHMANN[2] AND F. COSTA[3]

[1]Earth Science Section, University of Geneva, 1205 Geneva, Switzerland (*correspondence: caroline.bouvet@unige.ch)
[2]Earth and Space Sciences, University of Washington, Seattle, WA 98195-1310
[3]Earth Observatory of Singapore, Nanyang Technological University, Singapore 639798

Volcán Llaima (38.7°S) is one of the most active volcanoes in Chile with over 50 eruptions since 1640. Periods of eruptive activity are generally characterized by a combination of violent Strombolian explosions and voluminous lava flows. A previous study based on whole-rock, mineral, and olivine-hosted melt inclusion compositions of basaltic-andesitic magma erupted during three different episodes revealed shallow magma storage (2-3 km depth) as mush (>50 vol% crystals) in multiple dike-like reservoirs. Further characterization of the olivine compositions and comparison of the lava and tephra yield information on magma recharge time scales and eruption triggering. Multi-element zoning patterns (Fe, Mg, Mn, Ca, Ni, Cr, Ti, Co, Sc, V, Y, Al, P) were measured by LA-ICP-MS in olivine crystals from tephra. Coherence in the zoning patterns between various traverses and crystals from the same eruption allow us to reliably identify multiple magma replenishment events and the time scales at which they occur. Most elements record the latest recharge event, which took place between 100 and 600 days before eruption, while others (e.g. V, Ti, and Sc) also preserve compositional oscillations in the crystal core which we interpret as older recharge events. Comparison of the lava and tephra reveal higher crystallinities (~50 vol% vs. ~30 vol%) and a greater fraction of more evolved (mush-derived) crystals in the lava than in the tephra. This suggests that shifts in eruptive style at Volcán Llaima are strongly affected by the ratio of volatile-rich magma recharge to resident mush. When this ratio is low, the crystallinity of the erupted magma is high, which implies that (1) the resistance to flow is large, and (2) a permeable volatile network is achieved early, thereby promoting volatile-loss and diminishing the magma buoyancy. When the fraction of recharge magma is large, the crystallinity of erupted magma is lower and bubbles will tend to couple with the magma, entraining it rapidly toward the surface and producing a Strombolian eruption.

The first 10 million years of the Solar System

A. BOUVIER

Arizona State University, School of Earth and Space Exploration, Tempe, AZ 85287, USA (correspondence: audrey.bouvier@asu.edu)

The initial conditions of the solar nebula and subsequent formation and evolution of the protoplanetary disk can be constrained using chronological and isotopic studies of meteorites and samples returned from space missions. Chronology of early Solar System processes at a sub-My resolution is based on the long-lived U-Pb and short-lived (e.g., ^{26}Al-^{26}Mg) radiogenic systems. The precision of isotopic dating has dramatically increased over the last decade with the development of new mass spectrometry techniques. The accuracy, nevertheless, relies on knowledge of the initial composition, the distribution of the isotope pairs throughout the nebula, possible late additions, and disturbances during planetary processes. The degree of heterogeneity of the solar nebula can be evaluated from isotopic variations found for some elements (e.g., Nd, Ni) in chondritic and differentiated meteorites. Recently, U isotopic variations measured in CAIs [1] revealed the presence of ^{247}Cm in the early Solar System and consequently required the adjustment of previous U-Pb dates. For example, the U-Pb and Al-Mg chronologies of the formation of CAIs relative to chondrules are important constraints for the lifetime of the protoplanetary disk but are discordant [e.g., 2,3]. This brings into question the use of some meteoritic samples as reference materials, and reinforces the need for high-precision U-Pb isotopic studies of planetary materials.

The presence of short-lived radionuclides (SLR) has implications for the astrophysical environment of the Solar System. It is essential to determine the initial abundances and distribution of SLR in the Solar System to understand their origin and transfer within the nebula and possibly the protoplanetary disk. In particular, the source(s) of ^{26}Al and ^{60}Fe in the Solar System need to be constrained more tightly. As the major initial radiogenic heat sources, these two isotopes played a crucial role in the formation and evolution of habitable planetary worlds. I will discuss the most recent advances in the chronology of primitive and differentiated meteoritic objects using the U-Pb and extinct radioactivities and how they affect our models for Solar System formation and planetary evolution.

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The formation of the angritic crust

A. BOUVIER*, G.A. BRENNECKA, M.E. SANBORN AND M. WADHWA

Arizona State University, School of Earth and Space Exploration, Tempe, AZ, 87287-1404, USA. (*correspondence: audrey.bouvier@asu.edu)

Angrites are a small group of basaltic meteorites which record the early stages of planetary formation and differentiation [1]. They are comprised of two main textural subgroups reflecting different cooling and metamorphic histories: fine-grained 'quenched' angrites (e.g., D'Orbigny), and coarse-grained 'plutonic' angrites (e.g., Angra dos Reis) [1]. The recently recovered angrite Northwest Africa (NWA) 6291 is suggested to be paired with NWA 2999; both have larger modal abundances of metal and spinel compared to other angrites [2, 3]. NWA 6291 contains fine- (FG) and coarser-grained (CG) lithologies comprised of pyroxene, anorthite, olivine, and spinel.

We measured trace element abundances and the $^{238}U/^{235}U$ ratio in a whole-rock (WR) sample of NWA 6291 (WR1, washed in 0.05M HCl). We processed 7 acid-washed WR powders prepared from the FG and CG lithologies and 3 pyroxene separates from the CG lithology of NWA 6291 for Pb isotopic analysis. The weak leachates (L_{1-3}) and all Pb column matrices of subsequent leachates (L_{4-8}) and residues (R) were recombined respectively for U separation and isotopic analysis. Analytical details are provided in [4,5]. The REE pattern is LREE-depleted (La/Yb_N=0.6), with HREE abundances at ~4×CI. The Th/U is ~3.5. The $^{238}U/^{235}U$ =137.754 for WR1, =137.785 for the recombined L_{1-3}, and =137.744 for the recombined L_{4-8} and R (±0.026, 2SD); these values are similar to those for other angrites [6].

The Pb-Pb internal isochron age of NWA 6291 (calculated using its measured $^{238}U/^{235}U$) is 4560.1 ±1.1 Ma (MSWD=2), identical to that of NWA 2999 [7] using $^{238}U/^{235}U$ =137.75. The incompatible element depletion in both these angrites relative to other quenched and plutonic angrites is attributed to lack of phosphate. Their similarities confirm their pairing and suggest a new angritic subgroup, while their ages indicate that crust formation on the angrite parent body began ~5 Ma after CAI formation, and continued for a period of ~6 Ma thereafter [4,7,8].

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Interaction of small organic molecules with the calcite surface

N. BOVET*, M. YANG, M.P. ANDERSSON AND S.L.S. STIPP

Nano-Science Center, Department of Chemistry, University of Copenhagen, Denmark (*correspondence: bovet@nano.ku.dk)

Calcite ($CaCO_3$) is one of the most abundant salts in the Earth's crust. Its surface behaviour in the presence of liquids and gases controls its dissolution, precipitation, adsorption and desorption. To help understand these complicated phenomena, a fundamental understanding of surface/gas interaction is required.

In this work, we investigated the molecular interaction of small organic molecules with the {10.4} surface of calcite. X-ray photoelectron spectroscopy (XPS), a surface sensitive technique that allows quantitative and qualitative investigation of surfaces, and simulations using molecular dynamics (MD) and density functional theory (DFT) were applied to determine the geometry, coverage and bond strength of ethane, ethanol, t-butanol, carbon dioxide, acetic acid and glucose molecules on calcite.

A series of pristine calcite {10.4} surfaces, prepared by cleavage in vacuum, were examined with XPS while gases were leaked into the experimental chamber. We used the high resolution carbon 1s signal, which has significant energy shifts, to observe coverage of the organic molecules. We also measured the temperature of desorption for each species to estimate its bonding strength.

The results show that CO_2 molecules form the weakest bond with calcite, with a desorption temperature of –130 °C. Glucose forms the strongest bond among the molecules studied and does not desorb even at 560 °C. We also observed that all the molecules formed a compact layer on the surface, except ethane, which does not adsorb at all in our experimental conditions, exhibiting no affinity with calcite. The MD and DFT calculations parallel the experimental results, indicating that CO_2, alcohols and acetic acid form a well ordered monolayer on calcite.

We are using the information about the bonding of simple molecules on calcite to interpret interaction of more complex organic molecules, such as those that play a role in biomineralisation, adsorbing from solution and inhibiting calcite growth and recrystallisation.

Mineralogy and geochemistry of a potential CO_2 sequestration reservoir and seal system, Illinois Basin, USA

B.B. BOWEN[1]*, T. LOVELL[1], R. NEUFELDER[1], J. RUPP[2], J. BROPHY[3] AND R. LAHANN[2]

[1]Department of Earth and Atmospheric Sciences, Purdue University, West Lafayette, IN 47907 (*correspondence: bbowen@purdue.edu)
[2]Indiana Geological Survey, Bloomington, IN 47405
[3]Department of Geological Sciences, Indiana University, Bloomington, IN 47405

Increasing atmospheric CO_2 concentrations have resulted in numerous studies into methodolgies for sequestering antropogenic CO_2 in the subsurface. Demonstrations of geologic CO_2 sequestration in the Illinois Basin are targeted at the basal Cambrian Mount Simon Sandstone as the potenital reservoir and the overlying Eau Claire Formation as the primary seal. Characterizing the mineralogy and geochemistry of these formations is an essential step towards predicting how these units will perform as a storage reservoir and seal respectively. Ongoing investigations are focused on characterizing the mineralogical and geochemical composition of these formations utilizing core analysis, microscopy, x-ray diffraction, reflectance spectroscopy, stable isotope geochemsitry and major and trace element whole rock geochemical analysis. Minerals identified in the Mount Simon Sandstone include monocyrstalline and polycrystalline quartz, k-feldspar, illite, kaolinite, goethite, hematite, and calcite with minor zircon, muscovite, and biotite. The amount and spatial context of the mineral phases vary with depth and across the basin. Some of the minerals, such as k-feldspar and the iron oxides, occur as overgrowths and grain coatings, putting them directly in contact with pore-fluids. Principle mineral phases identified in the Eau Claire Formation include: quartz, k-feldspar, plagioclase feldspar, illite, glauconite, dolomite, ankerite, calcite, chlorite, pyrite, goethite, and hematite. The suite of minerals identified in both of these units includes both detrital grains and multiple generations of authigenic precipitates that suggest a burial history that has included multiple episodes of fluid-rock interactions. Detailed analysis of the geochemistry of specific mineral phases (e.g., stable isotopes, trace elements, etc.) can be used to determine the nature of the fluids that have interacted with these rocks in the past. These analyses help to constrain the role of fluids in the evolution of these formations, the current reactivity of the minerals present, and the potential changes that could occur with the introduction of CO_2 into the pore fluids.

Impacts and feedbacks: Are the PETM and Eocene hyperthermals relevant to future global change?

GABRIEL J. BOWEN

Purdue University, West Lafayette, IN 47907, USA (*correspondence: gabe@purdue.edu)

After more than two decades of study, significant uncertainty remains regarding the causes and mechanisms underlying Early Paleogene transient "hyperthermal" climate events such as the Paleocene-Eocene thermal maximum and Eocene Thermal Maximum-2. Despite a lack of consensus on key details such as the trigger for these events and sources of carbon to the ocean and atmosphere, these events are frequently invoked as being among the paleoclimate case studies most relevant to understanding our climate future. Given all the uncertainty, it's fair to ask whether our current level of understanding of these events really has relevance to the study of the anthropogenic climate era.

I will make the case that by focusing on the impacts and feedbacks associated with Eocene hyperthermal events researchers have been able to demonstrate several key patterns that are of relevance to informing and testing models of future anthropogenic climate change. The foundation for this inference is the unequivocal result, supported most strongly by records of widespread deep-sea carbonate dissolution, that the PETM and other hyperthermals are distinguished first and foremost by the massive addition of CO_2 to the exogenic carbon cycle. Despite uncertainties regarding the source and amount of this CO_2, we can view the subsequent sequence of events for any hyperthermal as a realization of CO_2-driven global change.

Important impacts and feedbacks associated with hyperthermals have been identified in at least four different systems. First, observations have largely supported existing models for the centennial-to-millennial-scale dynamics of the carbon cycle in response to massive CO_2 release. Second, estimates of pCO_2 change have been used to suggest high equilibrium climate sensitivity relative to most IPCC models. Third, there is increasing evidence for continental-scale water cycle change that is broadly consistent with the predictions of global climate models. Fourth, to the degree it has been studied these events have been demonstrated to have widespread, if not always deleterious, impacts on the biota. Although many details remain to be resolved, our current state of knowledge of Early Paleogene hyperthermals enables tests, and should support refinement, of models for anthropogenic global change.

IsoMAP: A web-GIS workspace for modeling isotope ratios in the environment

GABRIEL J. BOWEN[1], JASON B. WEST[2], LAN ZHAO[1], CHRIS C. MILLER[1], TONGLIN ZHANG[1], ZHONGFANG LIU[1], HYOJEONG LEE[1], AND AJAY B. KALANGI[1]

[1]Purdue University, West Lafayette, IN 47907, USA (*correspondence: gabe@purdue.edu)
[2]Texas A&M University, College Station, TX 77843, USA

Researchers have amassed a vast quantity of data on the stable H and O isotope ratios of environmental waters during the past 6 decades, and these data have supported the development of numerous paleoenvironmental, paleoecological, and paleoclimatic proxies. As new analytical instrumentation supports the gathering of water isotope data at increasing rates, these measurements promise to spawn new approaches to studying our contemporary environment. A key element in the development and interpretation of H and O isotope-based applications is the development of models for water isotope data to describe and predict relationships between these parameters and environmental variables.

In order to support widespread access to large water isotope databases and facilitate modeling of water isotopes and their propagation into hydrological and biological systems we have developed a web-GIS workspace called IsoMAP (Isoscape Modeling, Analysis and Prediction; http://isomap.org). IsoMAP consists of a set of Graphical User Interface that runs within the user's internet browser, server-side databases that host and serve isotopic and climatic monitoring data and GIS layers, and codes supporting the development and use of statistical and process-based models for environmental isotope ratio variation. Working through the GUI, users can select data and specify model parameterizations, submit and manage jobs, and visualize, download, or publish output including statistical descriptions of models and map predictions of the geographic variation in environmental isotope ratios.

Potential and demonstrated applications of the current version of IsoMAP include quantification of water isotope/climate relationships for different regions and time periods, evaluation of the stability or difference in isotope/climate relationships among regions and times, calibration of H- and O-isotope based proxies, and interpretation of H and O isotope data from biological and geological materials as a geographic source tracer. Future updates will provide additional functionality such as forward-modeling of H and O isotopes in plant leaf water and biological compounds.

Tracking the evolution of phase changes in ilmenites in microbial fossilization experiments: Understanding the role of microbes in diagenesis

D.M. BOWER[1], A. KYONO[2] AND A. STEELE[1]

[1]Geophysical Laboratory, Carnegie Institution of Washington,Washington, D.C., 20015, (dbower@ciw.edu.asteele@ciw.edu)
[2]Division of Earth Evolution Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8572, Japan, (kyono@geol.tsukuba.ac.jp)

Ilmenite and related Fe-,Ti-oxides are ubiquitous components of beach sands and sedimentary rocks [1]. In many ancient sedimentary rocks, "fossil" microstructures that are used as biosignatures often contain mineral assemblages dominated by these metal oxides, and in some cases, are preserved along with trace amounts of graphitic carbon [2,3]. Passive microbial biomineralization occurs in a wide range of natural environments, and can dictate the types of minerals that precipitate [4]. Furthermore, complicated histories and atmospheric inputs also influence much of the mineralic makeup of the rocks present today. Thus, the assemblages in these rocks may not be the same as what was originally formed in the newly lithified sediments billions of years ago. To constrain the effects of microbial processes on diagenesis, phase changes in natural ilmenites (Fe_3TiO_4) were observed in the presence of microbes amd compared to those without microbes under laboratory controlled conditions of increasing temperatures. To identify the mineral phases in these samples, micro Raman spectroscopy, SEM, and XRD were used. Collectively, the results show a correlation bewteen Fe- and Ti-oxide phase changes and the presence of microbes under early diagenetic conditions ($T<70^oC$), where the precipitation of maghemite (γFe_2O_3) and magnetite (Fe_3O_4) starts to occur on the ilmenite surface. The preliminary results presented here are part of an ongoing collaborative study to understand the role of biological processes in diagenesis. In the process, mineralic biosignatures can be established as we continue to perfect analytical instrument techniques for future planetary life exploration missions.

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Alkali metal and H_2O dynamics at clay-water interfaces: Lessons from NMR

GEOFFREY M. BOWERS*,[1] JARED WESLEY SINGER[2] AND R. JAMES KIRKPATRICK[3]

[1]Departments of Chemistry and Materials Engineering, Alfred University, 1 Saxon Drive, Alfred, NY, 14802. (*correspondence: bowers@alfred.edu)
[2]Department of Materials Engineering, Alfred University, 1 Saxon Drive, Alfred, NY, 14802. (jws4@alfred.edu)
[3]College of Natural Science, Michigan State University, East Lansing, MI, 48824. (rjkirk@msu.edu)

Many geochemical processes are highly dependent on the fundamental molecular-scale structure and dynamics of ions and H_2O at solid-water interfaces. We present here a detailed description of the behavior of alkali metal cations and H_2O in the interlayers and on external surfaces of smectite/H_2O pastes based on variable temperature nuclear magnetic resonance (VT NMR) spectroscopy.

Our new and previously published data show that alkali metal cations occupy multiple distinct binding environments in natural hectorite and that dynamic averaging of these sites is intimately linked to the dynamics of free and confined H_2O from -80°C to 50°C. For hectorite, K^+ and Cs^+ occupy two cation sites (likely 12-coordinate and 9-coordinate interlayer environments) that undergo rapid exchange above -20°C and -50°C, respectively [1, 2]. Companion ^2H NMR shows that exchange between K^+ environments is linked to the onset of diffusional exchange among confined and free H_2O populations [1]. Recent variable temperature ^{23}Na NMR data at 9.4 T and 21.1 T reveal two Na^+ sites in hectorite with distinct quadrupolar couplings. These two sites experience distinct dynamic behaviors (and no evidence of direct two-site exchange) that appear more strongly linked with the dynamics of specifically free H_2O. The dynamics of confined H_2O in the Na- and K-hectorites appear to be quite similar at temperatures < -20°C and reflect a combination of fast C2 symmetry jumps and exchange among positions in the ion hydration shell. Above -20°C there is diffusional exchange between confined and free H_2O populations for the Na- and K-hectorites. Differences in the residual ^2H quadrupolar splitting at these temperatures are likely due to differences in cation hydration energies and whether the cations prefer inner- or outer-sphere interactions with the clay surface.

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Isotopically-zoned zircons: Records of fluid/melt flow in the lower crust, Kapuskasing Uplift

J.R. BOWMAN[1]*, D.E. MOSER [2], J.W. VALLEY[3], J.L. WOODEN[4], N.T. KITA[3] AND F.K. MAZDAB[5]

[1]Dept. of Geology and Geophysics, Univ. of Utah, Salt Lake City, UT, 84112, USA (*corr: john.bowman@utah.edu)
[2]Dept. of Earth Sciences, Univ. of Western Ontario, London, Ontario, CAN N6A 5B7, (desmond.moser@uwo.ca)
[3]WiscSIMS, Dept. of Geoscience, Univ. of Wisconsin, Madison, WI, 53706, USA
[4]U.S.G.S.-Stanford Ion Probe Laboratory, Stanford, CA, 94305, USA
[5]Dept. of Geosciences, Univ. of Arizona, Tucson, AZ 85721, USA

Ion microprobe (SHRIMP and CAMECA 1280) analyses document primary isotopic (Pb, O) and trace element zoning in zircon from lower crustal paragneiss in the granulite zone of the Kapuskasing Uplift, Archean Superior Province. Older and low-$\delta^{18}O$ (5.1 to 7.1‰) igneous cores are overgrown by metamorphic zircon rims (2.66±0.01 to 2.58±0.01 Ga in age) which have significantly higher but variable $\delta^{18}O$ values (8.4 to 10.4‰). Several individual rims are zoned, with $\delta^{18}O$ decreasing outward from >10‰ to values as low as 8.4‰ at rim edges. Rims fall into two geochemically distinct groups: Type 1 rims have lower $\delta^{18}O$ (8.4 to 9.4‰), higher Th/U (0.1 ave.) and lower U/Yb (6.9 ave.). Type 2 rims have higher $\delta^{18}O$ (9.4 to 10.4‰), lower Th/U (0.025 ave) and higher U/Yb (20 ave.). Garnets separated from leucosome and melanosome in this paragneiss have significantly different $\delta^{18}O$ values of 9.2 and 9.9‰ (laser fluorination), respectively. These $\delta^{18}O$ values are similar to the average $\delta^{18}O$ values of the type 1 and 2 zircon rims; this similarity suggests that type 1 and type 2 rims are equilibrated with the leucosome and melanosome domains, respectively. The $\delta^{18}O$ data indicate that the leucosome domain is not in isotopic equilibrium with the rock matrix, which supports leucosome formation by infiltration of lower $\delta^{18}O$ fluid/melt rather than by *in situ* partial melting.

In mafic gneiss adjacent to this paragneiss, metamorphic zircons (2.67±0.01 to 2.56±0.01 Ga) have variable $\delta^{18}O$ values from 7.6 to 11.3‰. A number of zircon rims are markedly zoned, with $\delta^{18}O$ values ranging from 11.1‰ down to values as low as 7.6‰ at rim edges. These variations in $\delta^{18}O$(Zrc), coupled with some cases of disquilibium fractionation between zircon and garnet (up to 1.1‰), record multiple fluid/melt infiltration events involved in the geochemical evolution of this section of the deep crust.

Uranium dynamics in biostimulated field-site sediments: Spatial distribution and formation of non-uraninite U(IV) phases

MAXIM I. BOYANOV[1]*, EDWARD J. O'LOUGHLIN[1], KELLY SKINNER[1], BHOOPESH MISHRA[1], SHELLY D. KELLY[2], WEI-MIN WU[3], CRAIG CRIDDLE[3], MARCELLA MUELLER[4], TONIA MELHORN[4], DAVID WATSON[4], SCOTT BROOKS[4] AND KENNETH M. KEMNER[1]

[1]Molecular Environmental Science Group, Biosciences Division, Argonne National Laboratory, Argonne, IL 60439, USA (*email: mboyanov@anl.gov)
[2]EXAFS analysis, 719 Crestview Dr., Bolingbrook, IL 60440
[3]Department of Civil and Environmental Engineering, Stanford University, Stanford, CA 94305-4020
[4]Oak Ridge National Laboratory, Oak Ridge, TN 37831

The fate of U released in the environment is determined by a complex array of complexation, adsorption, redox, and precipitation reactions. Reduction of soluble U^{VI} species to U^{IV} by direct or indirect bacterial activity often results in the precipitation of $U^{IV}O_2$ (uraninite) and has been explored as an immobilization strategy for subsurface U plumes. We will present results from a three year experiment in which the biogeochemical conditions in U-contaminated groundwater and sediments from a field site at Oak Ridge National Laboratory (U.S.A.) were allowed to evolve in diffusion limited reactors under iron- and sulfate-reducing conditions. The reactors were amended with ethanol at the water-sediment interface, mimicking the injection of electron donor during *in situ* subsurface remediation by biostimulation. Synchrotron x-ray absorption spectroscopy (XANES and EXAFS) was used to track *in situ* the spatial distribution, valence state, and speciation of U and Fe in the reduction zone propagating into the sediment, in parallel with measurements of solution phase [SO_4], [U], [ethanol], and pH. Results show rapid initial reduction of Fe^{III} and U^{VI} in the sediment near the interface, as well as redistribution of U^{VI} in the areas ahead of the reduction front. Sulfate removal from the solution phase and U^{VI} reduction throughout the sediment continued for two years. EXAFS spectroscopy demonstrated that U^{IV} in the reduced sediment was present as a non-uraninite U^{IV} species, similar to the non-uraninite U^{IV} species detected in sediment samples collected from the injection wells during field-scale biostimulation campaings at Oak Ridge National Laboratory. The immobilization of U^{IV} as a non-uraninite species in natural settings has important implications for the post-remediation stability of U plumes.

Sulfur speciation in lunar apatite

J.W. BOYCE[1,2]*, C. MA[1], J.M. EILER[1], Y. LIU[3], E. STOLPER[1] AND L.A. TAYLOR[3]

[1]Division of Geological & Planetary Sciences, Caltech, Pasadena, CA 91125 (*jwboyce@alum.mit.edu)
[2]Department of Earth & Space Sci., UCLA
[3]Department of Earth & Planetary Sci., Univ. of Tennessee

Apatite incorporates several volatile elements (including S, as SO_4^{2-}) and can provide a record of magmatic volatile evolution. Recent measurements of volatiles in apatite from Apollo sample 14053.241 revealed 300-450 ppm S. Although many lunar melts have sufficient S for sulfide saturation, the observed S content of lunar apatite is surprising because lunar samples (especially 14053) are highly reduced (≤ IW) and are thus expected to contain little SO_4^{2-}. One possibility is that there are micro-environments in late-stage lunar melts that are more oxidized than one would infer from conditions recorded by other components of these rocks. Alternatively, it may be that S^{2-} substitutes for F+Cl+OH in lunar apatite: S^{2-}bearing apatite has been synthesized, but to our knowledge has not been observed in nature.

The Kα X-ray wavelength can be used to determine the relative amounts of S^{2-} and SO_4^{2-} in lunar apatite. Analyses were conducted at Caltech (JEOL 8200 with a 15 kV, 300nA, 15μm defocused beam, at 30 s/step, using PET crystals), referenced to FeS_2, $CaSO_4$, and SO_4^{2-}-rich Durango apatite.

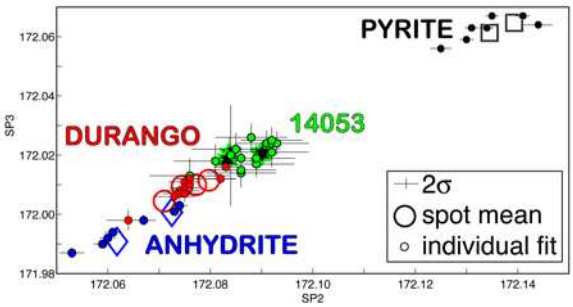

Figure 1: S Kα peak position (L-value) for two spectrometers.

The Kα peak of S in 14053 apatite is consistently shifted toward sulfide relative to both anhydrite (Δ = 29-44%) and Durango apatite (Δ = 19-24%; presumably containing all sulfur as sulfate) standards. This may indicate the first observation of a sulfide component in natural apatite. However, large uncertainties and apparent matrix effects (offset between anhydrite and Durango apatite) demand more data. Nevertheless, taking these data at face value indicates that lunar apatite includes both a S^{2-} and SO_4^{2-} component, in sub-equal proportions. The apparent SO_4^{2-} component in lunar apatite may indicate the presence of SO_4^{2-} in the late-stage lunar melt from which this apatite crystallized.

Lead and lead isotopes in the Atlantic and Indian Ocean: GEOTRACES data

E. BOYLE[1], Y. ECHEGOYEN-SANZ[1], K. FORNACE[1], J.-M. LEE[1], T. GAMO[2], H. OBATA[2] AND K. NORISUYE[3]

[1]Massachusetts Institute of Technology, Earth, Atm. & Planet. Sci., (eaboyle@mit.edu)
[2]University of Tokyo, Atm. & Ocean Research Institute, (gamo@aori.u-tokyo.ac.jp, obata@aori.u-tokyo.ac.jp)
[3]Kyoto University, Insitute for Chemical Research, (knorisue@inter3.kuicr.kyoto-u.ac.jp)

We will present data on the evolving anthropogenic Pb penetration into the Atlantic and Indian Oceans. In the North Atlantic Ocean, a few sites have multidecadal (Bermuda) and decadal data that show lead decreasing in the upper ocean in response to the phaseout of leaded gasoline; the decrease at depth depends on the ventilation time as shown by anthropogenic transient tracers (although Pb has been entering the deep Atlantic for at least the past 2 centuries, much longer than bomb nuclides and fluoro-compounds). The Atlantic Pb isotopic composition evolves as U.S. dominance is displaced by European Pb gas dominance; the southern Atlantic shows a distinct surface isotope composition. We will show a 10-station section in the Atlantic western boundary from 32degN to 25degS that shows N. Hemisphere Pb penetrating the S. Hemisphere dominantly with the Labrador Sea Water with some from the lower NADW. We will also show the Pb isotopic composition of these waters, including for the first time data on the scarce isotope Pb-204. We will also show a section of 8 stations from Lisbon to the Cape Verde Islands collected on the first US GEOTRACES North Atlantic Transect (2010). In the subtropics, the temporal Pb decrease due to Pb gas phaseout is reflected in this new data as compared to data from 1989 and 1999. In the tropical North Atlantic, thermocline Pb is low (<35 pmol/kg) reflecting the limited ventilation of this "shadow zone", but shows a maximum at about 700m depth. We have data from 11 stations from the Japanese Indian Ocean GEOTRACES cruise, from the Bay of Bengal and Arabian Sea into the Antarctic (18degN to 65degS). In response to later industrialization and a two-decade lag of Pb gas phaseout (and limited convection), anthropogenic Pb is higher in the surface waters of the Indian Ocean (40-80 pmol/kg) than in the present-day North Atlantic and North Pacific (20-30 pmol/kg), although Pb has not penetrated as deeply in the Indian Ocean (with little occurring below about 2000m, and some of the deep waters having extremely low Pb (~3 pmol/kg).

Modelling of hydrogeochemical processes in groundwaters of the North German Basin (NGB)

ELKE BOZAU AND WOLFGANG VAN BERK

TU Clausthal, Hydrogeologie, Leibnizstraße 10, D-38678 Clausthal-Zellerfeld (elke.bozau@tu-clausthal.de)

Modelling and forecasting quantitative hydrogeochemical changes in highly mineralised groundwaters is still a challenge. The extraction of deep groundwater for geothermal energy production from the NGB is affected by the precipitation of certain minerals, e.g. sulphates (Ba, Ca, Sr), carbonates (Ca, Fe), and silicate phases (SiO_2). These scalings often disturb the continuous production of geothermal energy and should be avoided in the technical sytems.

Groundwaters in deep aquifers of the NGB are dominated by Na^+ and Cl^-, or Na^+, Ca^{2+}, and Cl^-. The amount of total dissolved solids ranges from 100 to 300 g/l and increases with depth and temperature. Compared to surface groundwaters the deep groundwaters are enriched in a broad range of elements, including trace elements such as Ba, Pb, Sr, and Zn, and contain high amounts of dissolved gases (N_2, CO_2, H_2S, and CH_4).

An extended hydrogeochemical thermodynamic database for the well known and commonly used software PHREEQC has been developed to predict possible mineral precipitations during the use of highly mineralised groundwaters for geothermal energy production. Temperature (up to 200°C) and pressure (up to 500 bar) adaptations of the equilibrium constants were necessary. Pitzer parameters for the calculation of activity coefficients in waters of high ionic strength and solubility equilibria among gaseous and aqueous species of N_2, CH_4, and H_2S had to be implemented into the database.

In order to validate the implemented parameters the modelled mineral solubilities have been compared to experimental data gathered from the literature. First modelling results confirm the experimental data for the solubility of the minerals quartz, barite, anhydrite and calcite. However, there are problems with the solubility of several minerals at higher temperatures. Hence, evaluation and improvement of the thermodynamic database will be an ongoing process.

Acknowledgements. The presented data are results of the project "gebo" (Geothermal energy and high performance drilling research) financed by the Ministry of Science and Culture of the State of Lower Saxony and the company Baker Hughes.

An attempt to set the relation between chemical composition and microbiological activity in AMD reservoirs in the Łęknica region (the Muskau Arch, western Poland)

P. BOŻĘCKI AND G. RZEPA

Dept. of Mineralogy, Petrography and Geochemistry, Faculty of Geology, Geophysics and Environmental Protection, AGH - University of Science and Technology, Krakow, Poland (pbozecki@geol.agh.edu.pl)

The Muskau Arc is a large horseshoe-shaped glaciotectonic belt formed mainly during the Mid Polish Glaciation. Lignite deposits containing pyrite were excavated there to the early seventies. The abandoned mining areas were filled with acidic water, forming so-called "anthropogenic lakeland".

The aim of this study is to assess the impact of weather conditions and biological activity of selected microorganisms on the variability of chemical composition of acid mine drainage reservoirs. Water was sampled over one year period (from July 2009 to September 2010) from 11 selected locations. Water and ambient temperature, pH, Eh, EC, color, turbidity were determined in the field and samples were taken for major cations, anions and trace elements. In addition, 5 locations for microbiological research have been selected. These part consisted of qualitative determination of bacterial and fungal microflora in the waters with particular attention to microorganisms involved in the processes of iron transformation.

The results of the study show that most of the measured parameters have not only time but also spatial variability. The time variability results from seasonal changes in ambient condition as well as extreme weather events such as spring thaw and summer floods. One of the reasons for spatial variability is the variability in sources of water for distinct reservoirs. The results also show a positive correlation between :

- population size of *Acidithiobacillus ferrooxidans* bacteria and the concentration of such components as Fe and SO_4^{2-}.
- concentration of such components as Ca^{2+} and SO_4^{2-}, which may indicate that concentration level of these ions is closely linked with precipitation and dissolution of gypsum processes

This work was supported by MNiSW (project No. 0700/B/P01/2009/37) and AGH-UST (research project no. 11.11.140.158).

Sulfur isotope composition of the Bagirkacdere lead-zinc deposit, Biga Peninsula, Turkey

G. BOZKAYA

Cumhuriyet University, Department of Geological Engineering TR58140 Sivas, Turkey (gbozkaya@cumhuriyet.edu.tr)

Bagirkacdere lead-zinc deposit is one of the important deposits which are being mined on the Biga Peninsula. The vein type deposits are hosted by Triassic metamorphic rocks (Nilufer Unit of Karakaya Complex; [1]). The vein zones were emplaced within the meta-sedimentary rocks (phyllite, schist and marble) and are mainly concordant and partly discordant to foliation and/or schistosity planes. The mineralized zones contain galena, sphalerite, chalcopyrite, pyrite, marcasite, covellite, and specular hematite as ore minerals, with quartz and calcite as gangue minerals.

The $\delta^{34}S_{VCDT}$ values of galena range from -2.2 to 0.6 (average -1.07) ‰. The $\delta^{34}S_{VCDT}$ values of H_2S in equilibrium with sulphide minerals were estimated to be in the range of 2.4 to 0.14 ‰ (average 1.05‰) by evaluating the minimum and maximum $\delta^{34}S$ values of galena. For the calculation of $\delta^{34}S_{VCDT}$ values of H_2S, the average temperature of the hydrothermal fluids during the sulphide mineralization episode was assumed as 250 °C, which is obtained from the homogenization temperature measurements during fluid-inclusion studies, and the equations suggested by Li & Liu [3] was used. The $\delta^{34}S$ values of both sulphide and H_2S, which are close to 0‰, suggest a sulphur reservoir dominated by magmatic origin.

Additionally, $\delta^{18}O$ and the δD data of the fluids, trapped quartz crystals, indicate that the hydrothermal fluids were completely originated from meteoric water [2], in contrary to mineralizing fluids of sulphide minerals. Regarding to the combined fluid inclusion and stable isotope data indicate that the sulfur concentrated was leached by the heated meteoric water throughout the magmatic basement.

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Demir Kapija ophiolite: A snapshot of subduction initiation within a back-arc

M. BOŽOVIĆ[1], D. PRELEVIĆ[1], R.L. ROMER[2] AND M. BARTH[1]

[1]Uni Mainz, Mainz, Germany (bozovic@uni-mainz.de, prelevic@uni-mainz, barthm@uni-mainz.de)
[2]GFZ, Potsdam, Germany (romer@gfz-potsdam.de)

The Demir Kapija ophiolitic complex (Macedonia-FYROM) includes a mafic volcanic sequence (pillow lavas, diabases, and gabbros) that was intruded by intermediate to felsic and adakite-like rocks in an island arc setting.

The mafic volcanic sequence of the ophiolite complex formed in intra-oceanic back-arc setting. They are characterized by slightly increased LILE/HFSE, flat REE patterns, and radiogenic $^{143}Nd/^{144}Nd$ (up to 0.51272) and high TiO_2 contents, which reflect Pl+Ol+Cpx fractionation. The fractionation pattern between TiO_2 and MgO indicates that Ti saturation was reached and Ti-magnetite fractionated.

The intermediate to felsic and adakite-like intrusions are spatially and temporally closely related. The adakite-like volcanics show most of the features of typical adakites, i.e., low HREE, high Sr/Y, high LILE and LREE of whole-rock samples, as well as clinopyroxene major and trace element composition that are typical for adakite. The very high Th/La, Th/Yb and Ba/Yb ratios and the reduced $^{143}Nd/^{144}Nd$ values (around 0.51245) reflect contributions of sedimentary material to the mantle source of these melts. In analogy to adakites, these rocks are thought to be the product of slab melting in an unusually hot subduction zone. The intermediate to felsic volcanics show a broad range of SiO_2 content (51-75%) and more radiogenic Nd isotopic compositions than the adakite-like rocks. Their genesis is related to magma mixing of two different components; one is mantle derived, while the other one is a product of melting of an arc crust. The geochemistry of these rocks indicates that the melting of sedimentary rocks contributed to a variable extent to the source of these magmas.

During the Mid-Jurassic, opening of the short-lived Demir Kapija back-arc basin was initiated by slab roll back of the Western Vardar Ocean. Intra-oceanic subduction began within the collapsing ridge. As the subduced oceanic crust was young and hot, the thermal regime was favourable for slab melting and the formation of adakite-like rocks. Thus, the adakite-like rocks and the intermediate to felsic intrusions are related to the switch from an extensional to a compressional regime.

Testing crustal deformation and erosion-tectonic feedback models in the easternmost Himalaya using palaeo-Brahmaputra deposits

L. BRACCIALI[1,2,*], R.R. PARRISH[1], Y. NAJMAN[2] AND M.S.A. HORSTWOOD[1]

[1]NERC Isotope Geosciences Laboratory, British Geological Survey, Keyworth , Nottingham NG12 5GG, UK (*correspondence: laur@bgs.ac.uk)
[2]Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, UK

Strain, uplift and exhumation of the Earth's surface impact on, and are impacted by, fluvial drainage evolution. An investigation of the latter therefore provides a key to understanding crustal deformation processes and erosion-tectonic-climate interactions. In the Himalaya, the unusual fluvial drainage configuration of the eastern syntaxial region has been interpreted either as distorted drainage resulting from crustal shortening (due to India-Asia convergence) and lateral extrusion of crustal material, or as the result of river capture events tectonically-induced by surface uplift. Determining if and when the Brahmaputra river captured the Yarlung Tsangpo is crucial to testing these models of crustal deformation. In addition, rapid fluvial incision potentially resulted in sufficient erosion by focused weakening of the crust, that deep seated ductile rocks were induced to flow upwards and be rapidly exhumed in the syntaxial region, providing a viable example of erosion-tectonic coupling. The first arrival of detritus carried by the Yarlung Tsangpo (draining the Jurassic-Paleogene Trans-Himalayan arc of the Asian plate) in the Neogene deposits of the palaeo-Brahmputra river in Bangladesh (that prior to capture would have drained the southern Himalayan slopes composed only of Precambrian-Palaeozoic Indian crust) should date the capture event, while input from the eastern syntaxis can be identified by the appearance of very young (<10 Ma) and rapidly exhumed mineral grains.

To address the river capture and the erosion-tectonic coupling hypotheses, U-Pb LA-MC-ICP-MS dating of detrital zircon grains (from palaeo-Brahmputra sediments as well as sands from modern rivers draining the Trans-Himalaya and Himalayan southern slopes) is integrated with microtextural analysis in a revised approach to the use of detrital zircon data as applied to provenance studies. In this ongoing multi-technique study, zircon data are complemented by the novel application of U-Pb dating to rutile detrital grains as well as by Ar-Ar dating of detrital white mica and zircon fission-track thermochronology.

Molecular tools for understanding biomarker compounds

ALEXANDER S. BRADLEY[1]* ANN PEARSON [2] AND CHRISTOPHER J. MARX [1]

[1]Department of Organismic and Evolutionary Biology, Harvard Univeristy, Cambridge MA 02138 USA (*correspondence: bradley@fas.harvard.edu)
[2]Department of Earth and Planetary Sciences, Harvard University, Cambridge MA 02138 USA

Hopanoids are pentacyclic triterpenoids found in some bacteria and widely used as organic geochemical proxies. A confident interpretation of this record requires an understanding of the function and distribution of these compounds among bacterial taxa. Recent analytical developments allowing the rapid identification of hopanoid structures [1] have made large strides towards this end. We complement this approach by performing three types of experiments: i) genetic experiments in a model organism (*Methylobacterium*) to identify genes involved in the synthesis of hopanoid side chains; ii) physiological experiments to understand the function of hopanoids, iii) replicate experimental evolution in the laboratory to understand how an organism might acquire adaptations to compensate for the absence of hopanoids.

Our studies have yielded results that have consquences for geochemical interpretation. By constructing genetic mutants, we have found that adenosylhopane is an intermediate in the synthesis of composite hopanoids in *Methylobacterium*, and this likely holds in all hopanoid-producing bacteria. This compound has previously been interpreted as a marker of terrestrial input to marine sediments [2], and this can be evaluated in light of our new understanding.

We have also found that the disruption of genes involved in hopanoid biosynthesis in *Methylobacterium* causes growth defects. The growth defect is particularly severe in a strain of *Methylobacterium* in which we disrupted hopanoid synthesis Experimental evolution of this strain in the laboratory has allowed this strain to overcome some of this defect. Other mutants, which can make hopanoid backbones but lack the ability to make either composite hopanoids or A-ring methylated hopanoids, have less-severe but still detectable growth defects. Examination of these phenotypes may cast light on the function of these molecules, which can be used to interpret the geochemical record.

[1] Talbot, Rohmer & Farrimond (2007), *Rapid Comm. Mass. Spec.* **21**: 1-13. [2] Cooke, Talbot & Wagner (2008), *Org. Geochem.* **39**:965-971

Effect of different vegetation cover on throughfall chemistry

M. BRADOVÁ[1]*, V. TEJNECKÝ[1], L. BORŮVKA[1], K. NĚMEČEK[1], J. ZENÁHLÍKOVÁ[2] AND O. DRÁBEK[1]

[1]Department of Soil Science and Soil Protection, Faculty of Agrobiology, Food and Natural Resources, Czech University of Life Sciences in Prague, CZ-165 21 Prague 6 – Suchdol, Czech Republic (*correspondence: bradova@af.czu.cz)
[2]Department of Silviculture, Faculty of Forestry and Wood Sciences; Czech University of Life Sciences in Prague, CZ-165 21 Prague 6 – Suchdol, Czech Republic (zenahlikova@fld.czu.cz)

The monitoring of throughfall at the forest ground is a widely accepted approach for the estimation of trace-substance input in different forest types and in different regions [1, 2]. This study is focused on the evaluation of quantity of materials incoming into forest soil affected by acidification process under spruce forest (*Picea abies (L.) Karst)* and under beech forest (*Fagus sylvatica L.),* and describing the fluctuation of elements in precipitation within the monitoring period. Precipitation samples were collected at monthly intervals from April to October during the years 2008 - 2010 in the Jizera Mountains. Precipitation samples were quantified and analyzed for selected components (NO_3^-, SO_4^{2-}, Cl^-, F^-) and total amount of Na, Ca, K, and Mg. pH and conductivity of precipitation were measured. Statistical analyses like simple and multiple regression and correlation and multifactorial analysis of variance were used. Results of this work showed the elements, which flow into the soil under beech forest and under spruce forest, their preference transport way and amount of them.

[1] Likens & Bormann (1995) *Biogeochemistry of a forest ecosystem*. 159 p. 2nd ed. Springer-Verlag, New York. [2] Puhe & Ulrich (2001) *Global Climate Change and Human Impacts on Forest Ecosystems*. Springer-Verlag, Berlin.

Using opal and organic carbon as proxies for migration of the North African monsoon

L.I. BRADTMILLER[1]*, M.B. AWALT[1], D. MCGEE[2] AND P.E. DEMENOCAL[2]

[1]Macalester College, Saint Paul, MN, 55406, USA (*correspondence: lbradtmi@macalester.edu)
[2]Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY, 10964, USA

Marine and terrestrial records from northern Africa have greatly enhanced our understanding of both the causes and effects of climate change in the geologic past. Specifically, proxy records of changes in paleoproductivity yield information about upwelling strength, and therefore trade wind strength along the North African margin. Changes in wind strength, in turn, have been shown to correlate with changes in the relative aridity of the Sahel: periods of increased precipitation in the past were periods of weaker trade winds and decreased upwelling, and vice verse.

Records of opal flux over the past 18kyr illustrate the inverse relationship between precipitation and marine productivity, as periods of greater opal flux (increased wind-driven upwelling) correspond to periods of increased terrigenous flux (increased wind-borne dust flux). Paleoceanographic records have identified the African Humid Period (AHP; ~11 – 5.5 kyr) as a period of low dust flux and decreased opal flux consistent with a northerly shift in the ITCZ, increased precipitation and reduced upwelling. However, our current understanding of the causes and effects of the AHP is limited by the lack of upwelling/productivity data along a north-south transect of the African margin, as well as by a general lack of high-resolution data.

Here we present opal and organic carbon (C_{org}) records from a north-south transect of marine sediment cores on the northwest African margin. We observe decreased fluxes of opal and C_{org} in all cores at the onset of the AHP, although the magnitude of this response varies greatly from core to core. At the end of the AHP, opal and C_{org} fluxes increase, albeit not to pre-AHP levels. During both transitions the magnitude of flux change is greatest in the southernmost cores, which are closest to the region of maximum upwelling in the modern ocean. Current age models suggest that decreased fluxes of opal and C_{org} occur first in the southernmost core at the onset of the AHP, consistent with the hypothesis that these changes represent a northward shift in the ITCZ.

Chemical evolution of MORB: New insights from old crust

P.A. BRANDL*, M. REGELOUS AND K.M. HAASE

GeoZentrum Nordbayern, Universität Erlangen-Nürnberg, Schlossgarten 5, 91054 Erlangen, Germany (*correspondence: philipp.brandl@gzn.uni-erlangen.de)

The chemistry of mid-ocean ridge basalt (MORB) is studied almost exclusively using samples dredged from active spreading ridges. However, flows erupted at the ridge axis itself eventually make up the lowermost part of the extrusive section, and may not be representative of the entire oceanic crust. In contrast, samples drilled from old oceanic crust will include flows erupted both on- and off-axis, and also can be used to determine whether changes in MORB composition occur over the lifetime of an ocean basin. Despite this, few detailed studies of ancient MORB have been carried out.

We have analysed major element compositions of more than 400 fresh volcanic glasses from 35 DSDP-ODP drillsites in the Atlantic and Pacific, which range in age from 10 to 170 Ma. Trace element analyses of the same samples using LA-ICPMS are in progress.

In contrast to some previous studies, we find no significant difference in fractionation-corrected major element composition of Mesozoic and zero-age MORB in either the Pacific or the Atlantic. There is no indication that EMORB are concentrated in the upper parts of the oceanic crust, as would be expected if they were preferentially erupted off-axis. Instead, the youngest lavas (upper 100m) at a given drillsite tend to have relatively homogenous compositions, which could be explained if larger-volume flows flow further from the axis. If this is the case, then sampling MORB only from active spreading ridge axes may not give an entirely accurate picture of the average composition of the oceanic crust. It also means that direct comparison of lavas from slow- and fast-spreading ridges, which differ in axial topography and average flow volumes, will not be straightforward.

Quantifying rates and mechanisms of shale weathering across a continental-scale climosequence

SUSAN L. BRANTLEY, ASHLEE DERE AND TIMOTHY WHITE

The Pennsylvania State University, University Park, PA 16802; (*correspondence: sxb7@psu.edu)

Both ecosystems and humans are dependent on soil for nutrient and water cycling as well as food, making the loss of soil a major issue facing humanity. However, the rate at which soil forms has not been well quantified. To investigate rates of soil formation as a function of climate, a latitudinal climosequence of forested sites has been established in North America and Wales. The climosequence is bounded by a cold/wet end member in Wales and a warm/wet end member in Puerto Rico. In between, temperature and rainfall increase as sites extend south through New York, Pennsylvania, Virginia, Tennessee and Alabama. All sites, except Puerto Rico, are underlain by an organic-poor, iron-rich (Silurian-age) shale, providing a constant parent material from which soil is forming. Puerto Rico is located on chemically similar, but younger, shale. Soil sampling and geochemical analyses were completed similarly at all sites to allow direct comparisons and modelling of shale weathering. Independent Be^{10} estimates of erosion rates for a few locations along the transect are used to estimate residence times. Initial results show soil depth increases as a function of temperature, with shallow (~30 cm) profiles in Wales and Pennsylvania varying up to 630 cm deep in Puerto Rico. Depletion profiles of Na, a proxy for feldspar dissolution, are less than 20 % depleted at the surface in Wales and Pennsylvania, 50-60% depleted in Virginia and Tennessee, and 100% depleted at the surface in Puerto Rico. Using estimated soil residence times, apparent activation energies for Na depletion were calculated using different assumptions to range from 15-19 kcal mol^{-1}, values that are slightly higher than those reported for Na plagioclase dissolution in the laboratory. Overall, data collected from soils across the transect will promote a better understanding of how climate changes can impact soil formation rates.

CAPRAM mechanism development: Evaluation of prediction methods for aqueous phase rate constants and model results

P. BRÄUER[1]*, C. MOUCHEL-VALLON[2], A. TILGNER[1], B. AUMONT[2] AND H. HERRMANN[1]

[1] Leibniz-Institut für Troposphärenforschung, Permoserstr. 15, D-04318 Leipzig, Germany. (*correspondence: braeuer@tropos.de)

[2]LISA, UMR CNRS 7583, Universités Paris Est Créteil et Diderot, IPSL, 61 Av. du Gal de Gaulle, 94010 Créteil cedex, France. (bernard.aumont@lisa.u-pec.fr)

Organic compounds are ubiquitos in the tropospheric multiphase system. With either large biogenic and athropogenic sources they play an important role and have thus become a major research topic within the last decades.

Modelling can provide a useful tool to explore the chemical and microphysical processes in the troposphere. However, detailed oxidation mechanisms exist mainly in the gas phase while they are very limited in the aqueous phase. Current studies aim to expand the aqueous phase mechanism CAPRAM 3.0i, which is the currently most comprehensive chemistry mechanism with 777 reactions and 380 species. However, the oxidation scheme is still incomplete for C3 and C4 organic chemistry and higher organics are missing at all.

The huge amount of organic species relevant in the troposphere makes it impossible to determine all the needed kinetic data experimentally. Therefore, estimation methods become necessary. Besides the construction of an up-to-date database of about 600 experimentally determined reaction rate constants of OH and NO_3 radicals with organics, estimation methods for the prediction of missing data have been evaluated. The evaluation led to a new oxidation schemes for C3 organic compounds added to the existing CAPRAM 3.0i mechanism. Furthermore, branching ratios were introduced for already prescribed OH reactions with organics. Model runs have been performed with the multiphase mechanism MCMv3.1 and the extended CAPRAM version for a meteorological scenario with non-permanent clouds under remote and urban conditions.

The addition of new C3 organic compounds led to the modified concentration profiles of many organic and inorganic species. For example, acid production is enhanced although contrations are still lower than measured in the field due to the missing implementation of the oxidation of higher organics. The introduction of branched OH attack to organics let to further refined results.

Bioavailability and toxicity of metals in an estuary contaminated by acid mine drainage

C.B. BRAUNGARDT[1]*, C. MONEY[2] AND E.P. ACHTERBERG[3]

[1]University of Plymouth, SoGEES, PL4 8AA, UK (*correspondence: cbraungardt@plymouth.ac.uk)
[2]AstraZeneca, Brixham TQ5 8BA, UK
[3]University of Southampton, NOC, SO14 3ZH, UK

Motivated by the need for a better understanding of the human impact on ecosystems (Water Framework Directive), we combined a bioassay (*Crassostrea gigas* larva) with high temporal resolution *in situ* metal speciation measurements to assess the temporal variability, biological availability and toxicity of dissolved metals in an estuary affected by historic (tin streaming) and contemporary (acid mine drainage) metal sources. Voltammetric *in situ* Profilers were deployed in the estuary for a tidal cycle to determine Cd and Cu species ('dynamic') in a size range (<4 nm) highly relevant for uptake by organisms [1]. Oyster larvae were exposed to discrete samples taken at regular intervals during the survey.

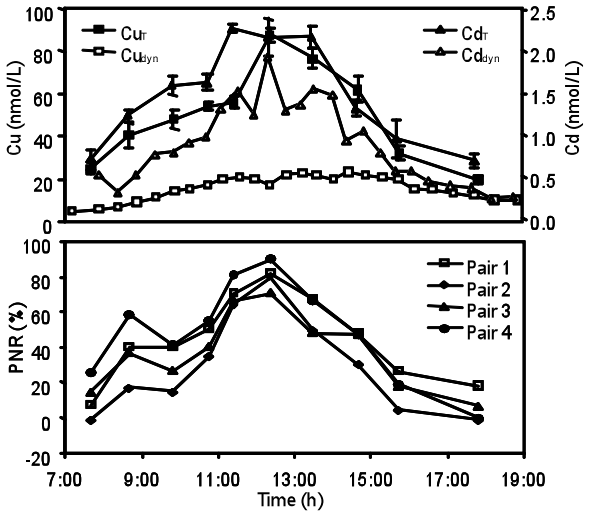

Figure 1: Dynamic (Cu_{dyn}, Cd_{dyn}) and total (Cu_T, Cd_T) metal concentrations and percent net response (PNR) of oyster larva.

Oyster larva responded to the highest dynamic Cu and Cd concentrations with maximum abnormal development (71-90% (Fig.1). Synergistic toxicity and model calculations suggest that bioavailable metal concentrations in this estuary are likely to severely compromise the ecosystem structure [2].

[1] Buffle, Tercier-Waeber (2005) TRAC **24**, 172-191. [2] Rivera-Duarte *et al*. (2005) ES&T **39**, 1542-1546.

Biotite dissolution: The effect of organic ligands and pH

A.W. BRAY[1]*, S. BONNEVILLE[1,2], D. WOLFF-BOENISCH[3] AND L.G. BENNING[1]

[1]School of Earth and Environment, University of Leeds, Leeds, UK (*correspondence: a.bray@leeds.ac.uk)
[2]Département des Sciences de la Terre, Université Libre de Bruxelles, Brussels, Belgium
[3]Institute of Earth Sciences, University of Iceland, Reykjavik, Iceland

Traditionally mineral weathering studies are based on abiotic and, more recently, dissolution in the presence of living organisms. However, for biotite, a key nutrient bearing mineral (i.e., K), the piece of the puzzle linking abiotic [1] and biotic [2] dissolution rates - the effect of organic ligands - is still missing. Here we fill this gap via biotite dissolution experiments conducted with various organic ligands typical in soils or groundwaters to better quantify the full range of processes affecting rock weathing and soil formation.

Batch (pH = 2, 4, 6, 12 hrs) and flow-through (pH = 3.3 and 6, 96 hrs) experiments were carried out at 25°C with biotite with and without oxalic and citric acids and desferrioxamine-b (DFO-B) or a mixture of these. Aqueous Si, Al, Mg, K and Fe concentrations, analysed by UV-VIS, AAS, or ICP-MS, BET surface area and EMPA compositional analyses, were used to derive rate constants.

Our results show that the presence of organic ligands can enhance the dissolution rate of biotite by up to 2 orders of magnitude (Fig. 1). The degree of enhancement of the ligand promoted dissolution, compared to the abiotic dissolution, increases with increasing pH due primarily to the speciation and extent of surface complexation of the organic ligands.

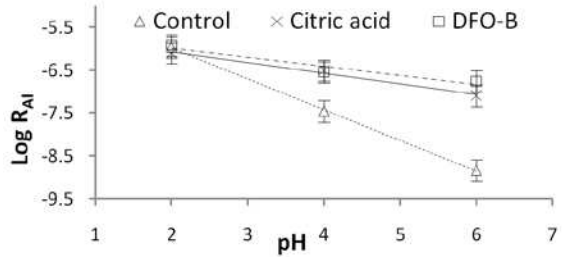

Figure 1. Log R_{Al}($mol_{(biotite)}$ m^{-2} h^{-1}) vs pH from the batch dissolution experiments (control = no organics). Rates were calculated from elemental release data (here Al) and normalised to the EMPA derived biotite stoichiometry.

[1] Malmström and Banwart (1997) *GCA* **61**, 2779-2799 [2] Bonneville *et al*. (2009) *Geology* **37,** 615-618

Toward calibrating the paleosol carbonate CO_2 barometer for paleoVertisols

D.O. BREECKER[1], L.A. MICHEL[2], J. YOON[1], J.S. MINTZ[2], S.G. DRIESE[2] AND L.C. NORDT[2]

[1]Department of Geological Sciences, The University of Texas at Austin, 1 University Station C1100, Austin, TX 78712
[2]Department of Geology, Baylor University, One Bear Place 397354, Waco, TX 76798 USA
*Correspondance: breecker@jsg.utexas.edu

The concentration of CO_2 ($[CO_2]$) in soils during soil calcite formation must be known in order to accurately calculate ancient atmospheric $[CO_2]$ using the paleosol carbonate CO_2 barometer [1]. The average *S(z)* value ($S(z) = [CO_2]_{soil} - [CO_2]_{atmosphere}$) appropriate in the barometer has recently been estimated at 0.25% [2]. In the present study, we measured soil $[CO_2]$ in modern Vertisols (high shrink/swell clay content soils) in order to test the value of 0.25% and help calibrate the barometer for paleoVertisols which are commonly used to reconstruct ancient atmospheric $[CO_2]$.

We installed 7 soil gas wells in the Bkss horizon of modern Vertisols in a C_4 grassland at the USDA Riesel Watershed in Riesel, TX, USA. Soil $[CO_2]$ was measured in soil gas samples withdrawn from the wells on a monthly basis. The resulting time series currently extends from January 2010 through March 2011. Soil $[CO_2]$ varied seasonally and interannually during the period of study, reaching a maximum of 9.3% in June 2010 and a minimum of 0.13% in February 2011. Soil $[CO_2]$ was above 1% at every site during the winter of 2009/2010 when the soil was water-saturated and was below 1% at every site during the winter of 2010/2011 when the soil was dry and cracked. Soil $[CO_2]$ decreased rapidly from maximum values (~3-9%) in June 2010 to values as low as 0.2% in August 2010 as the soil warmed, dried and cracked. Without indpendent evidence for the timing of calcite formation, we cannot yet confidently quantify *S(z)* values appropriate for the barometer. However, the decrease of *S(z)* values below 0.25% during the summer when soil calcite is thought to form is consistent with the conclusions drawn by [2]. Our data suggest that soil $[CO_2]$ is strongly decoupled from temperature in Vertisols and is controlled by soil moisture and the opening and closing of soil cracks which act as gas transport conduits. Preservation of foraminifera skeletons from parent material in this soil suggest that calcite dissolution/reprecipitation is limited, even under seasonal changes in soil pCO_2 that span orders of magnitude.

[1] Cerling (1991), *American Journal of Science* **291**, 377-400. [2] Breecker, Sharp & McFadden (2010) *PNAS* **107**, 576-580.

Hydraulic-hydrochemical modelling of a geothermal reservoir in Indonesia

MAREN BREHME*, SIMONA REGENSPURG AND GÜNTER ZIMMERMANN

Helmholtz-Centre Potsdam, German Research Centre for Geosciences (GFZ), International Centre for Geothermal Research, Telegrafenberg, 14473 Potsdam, Germany (*correspondence: brehme@gfz-potsdam.de; regens@gfz-potsdam.de; zimm@gfz-potsdam.de)

The purpose of this study is to explain the hydraulic and hydrochemical connection between different surface and subsurface reservoirs at a geothermal site in Indonesia. By using an integrated model to determine hydraulic pathways through porous media as well as fault structures and connecting it to a chemical transport model, the effect of geology on the hydrochemical characteristics should be explained. The numerical simulator OpenGeoSys is used for modelling the thermo-hydraulic situation. Results will eventually be combined with hydrochemical PHREEQC calculations.

In November 2010 a geothermal plant has been visited and available hydraulic, geological, and hydrochemical properties were reviewed. Additionally, water samples from production wells, hot springs, and a lake have been taken and analysed. Physicochemical parameters were measured *in situ*.

At the investigated site three different fluid containing reservoirs have been identified at various depths with temperatures between 250 and 350 °C, which show each different hydrochemical characteristics: The deepest reservoir (2300 m) with a moderate pH of 5 is marked by Silicium (Si) concentrations up to 350 mg/L and high chloride (Cl) concentrations of 430 mg/L The fluid in the most shallow (1000 m) reservoir above is highly acidic (pH 1). Still higher Cl (1550 mg/L), Si (1600 mg/L), and sulphate concentrations (460 mg/L) appear in this reservoir. Acid water (pH 2.6) was also observed in a nearby lake indicating a hydraulic connection to that reservoir. PHREEQC-calculations show an oversaturation of several minerals such as alunite, silicates e.g. kaolinite, Ca-montmorillonite, and quartz at temperatures between 25 and 45°C. Therefore silicate mineral precipitation upon fluid cooling can be expected to occur in the wells, pipes or the reservoir, which would harm the plant components or even damage the reservoir in the long term.

Apparently three aspects are challenging for the model build-up: (I) a three level-reservoir with the connected acidic lake; (II) the oversaturation of silicates upon cooling; (III) the change in composition over time.

How small-volume basaltic magmatic systems develop: A case study from Jeju, Korea

MARCO BRENNA[1]*, SHANE J. CRONIN[1], IAN E. M. SMITH[2], ROLAND MAAS[3] AND YOUNG KWAN SOHN[4]

[1]Volcanic Risk Solutions, Massey University, Palmerston North, New Zealand, (*correspondance: m.brenna@massey.ac.nz)
[2]School of Environment, University of Auckland, Auckland, New Zealand
[3]School of Earth Sciences, The University of Melbourne, Parkville, Australia
[4]Dep. of Earth and Environmental Sciences, Gyeongsang National University, Jinju, Republic of Korea

Jeju is a volcanic field active since c. 1.8 Ma ago. Eruptive activity began with dispersed, basaltic, monogenetic, volcanism. Continuing monogenetic volcanism was later joined by more voluminous, alkali and sub-alkalic, evolved lava effusion events building a central composite edifice. Samples from older (>0.7 Ma) and younger (<0.2 Ma) monogenetic centres were analysed for whole-rock major elements, trace elements and Sr-Nd-Pb isotopic compositions. Early monogenetic centres are depleted in MgO, Cr and Ni reflecting considerable olivine fractionation. By contrast, younger monogenetic magmas fractionated clinopyroxene + olivine at deeper levels. Isotopes show little variation across the suite, but the younger monogenetic centres have generally lower $^{87}Sr/^{86}Sr$ and $^{208}Pb/^{204}Pb$ and higher $^{143}Nd/^{144}Nd$ than the older centres and sub-alkali lavas. Major and trace element and isotope data suggest a common, shallower source for older monogenetic magmas and sub-alkali lavas, in contrast to a deeper source for younger monogenetic magmas. We propose that mantle melting was initiated near the garnet to spinel transition at a depth of near 2.5 GPa, followed by extension of the melting zone to 3-3.5 GPa, with a concomitant increase in the volume of melt derived from the shallower part of the system to produce sub-alkali magmas, possibly related to accelerated heat transfer resulting from deepening of the melting zone, and/or increased mantle upwelling. A classical mantle plume model for Jeju is not viable due to physical constraints; however decompression melting is still responsible for magmatic activity in the area. Uplift of mantle blocks under Jeju occurred due to lubrication by shear zones created during the opening of the Sea of Japan/East Sea c. 15 Ma ago, and reactivated during rotation of the direction of subduction of the Philippine Sea plate c. 2 Ma ago. This is the first attempt to directly link subduction processes and intraplate volcanism on Jeju.

Volume control on magmatic evolution and eruption style transition, Jeju, Korea

MARCO BRENNA[1]*, SHANE J. CRONIN[1], IAN E. M. SMITH[2] AND YOUNG KWAN SOHN[3]

[1]Volcanic Risk Solutions, Massey University, Palmerston North, New Zealand, (*correspondance: m.brenna@massey.ac.nz)
[2]School of Environment, University of Auckland, Auckland, New Zealand
[3]Dep. of Earth and Environmental Sciences, Gyeongsang National University, Jinju, Republic of Korea

Jeju is a volcanic field active over the last c. 1.8 Ma. Eruptive activity began with dispersed, basaltic, monogenetic, volcanism. Continuing monogenetic volcanism was later joined by more voluminous, alkali and sub-alkali lava effusion events building a central composite edifice. From three deep cores (400-500 m) through the main edifice flanks, lava samples were analysed for major, trace-element and Sr-Nd-Pb isotope compositions. The low-volume monogenetic volcanoes erupted mainly primitive alkali basalts, whereas the larger-volume lavas have chemical variability spanning alkali basalt to trachyte compositions. The oldest erupted lavas form part of a high-Al alkali suite and evolved to Sanbangsan trachytes (SiO_2 c. 62 wt%). The topmost lavas show less Al_2O_3 enrichment and MgO depletion and hence form a low-Al alkali suite, which evolved to the Hallasan trachytes (SiO_2 c. 66 wt%). The similarities in the chemical evolution trends between low- and large volume magmas suggests similar magma sources and analogous crystal fractionation processes. This implies that the volume and proportions of parent melt was the dominating factor in determining the eventual course of magmatic activity. Based on the chemical trends, the proportions of partial melts must have increased in the middle and later stages of Jeju Island's formation. This may relate to increased uplift of mantle domains (or increased mantle convection) beneath the island, leading to accelerated decompression melting, compared to the early stages of activity. This resulted in the construction of the central composite edifice. Mantle upwelling was greater in the core of the system, resulting in the larger volume lava outpourings, compared the lower supply in distal parts of the field, resulting in low-volume monogenetic activity. These results have implications for hazard forecasting in monogenetic volcanic fields, with a first conclusion being that eruptions situated in the centre of the field may give rise to larger volume lava outpourings compared to those at the outer margins.

$^{238}U/^{235}U$ ratios of angrites: Adjusting absolute ages of anchors

G.A. BRENNECKA* AND M. WADHWA

School of Earth & Space Exploration, Arizona State Uni., Tempe, AZ (*correspondence: brennecka@asu.edu)

The use of short-lived chronometers is critical to our understanding of the high-resolution time sequence of events in the early Solar System. To map relative ages from short-lived systems onto the absolute time scale, they are "anchored" to the Pb-Pb ages of appropriate meteoritic materials. Previously reported high precision Pb-Pb dates of the basaltic angrite meteorites, some of which have been used extensively as anchors [1-2], have assumed a $^{238}U/^{235}U$ ratio (=137.88). However, the $^{238}U/^{235}U$ ratio has recently been shown to be variable in Solar System materials [3-6], requiring the reevaluation of these previously reported Pb-Pb ages. An adjustment to the Pb-Pb age of an anchor would consequently require a corresponding correction to the calculated "model" ages for any other meteoritic materials dated using that anchor and an extinct chronometer, such as the ^{26}Al-^{26}Mg, ^{53}Mn-^{53}Cr, or ^{182}Hf-^{182}W chronometers.

Here we report U isotope compositions of several angrites. Specifically, $^{238}U/^{235}U$ ratios were measured in whole-rock (WR) samples of the D'Orbigny, NWA 4801, NWA 4590, and NWA 6291 angrites. Additionally, phosphate separates from Angra dos Reis, pyroxene separates from D'Orbigny, and the leachate and residue from a separate acid-washed WR fraction of NWA 6291 were also measured. For D'Orbigny, two WR fractions and the pyroxene mineral separate yield identical (within 2SD errors) U isotope compositions. From these measurements, a $^{238}U/^{235}U$ ratio of 137.776±0.026 is determined, corresponding to a corrected Pb-Pb age of 4563.34±0.30 Ma (using the age previously reported by [2]). Furthermore, the $^{238}U/^{235}U$ ratios determined for WR samples of the angrites NWA 4590 (137.757±0.026), NWA 4801 (137.763±0.026), NWA 6291 (137.754±0.026), as well as for the phosphate separates of Angra dos Reis (137.791±0.042) are also identical (within 2SD errors) to those determined for D'Orbigny. Therefore, there is no detectable variation in the $^{238}U/^{235}U$ ratios measured in the angrite WR samples and mineral separates. This indicates that the angrite parent body was homogenous (at our current level of precision) in terms of its $^{238}U/^{235}U$ composition.

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Simultaneous analysis of dissolved noble gases, SF_6 and CFCs in water

M.S. BRENNWALD[1]*, M. HOFER[1], AND R. KIPFER[1,2]

[1]Eawag, Swiss Federal Institute of Aquatic Science and Technology, Dübendorf, Switzerland (*correspondence: matthias.brennwald@eawag.ch)
[2]Institute of Geochemistry and Petrology, Swiss Federal Institute of Technology (ETH), Zurich, Switzerland

Dissolved atmospheric noble gases, sulfur hexafluoride (SF_6) and chlorofluorocarbons (CFCs) are widely used as (transient) environmental tracers in water bodies. The concentrations of these trace gases in the water are determined by their partial pressure in the air, the gas equilibration at the water surface, the (partial) dissolution of air bubbles entrapped in the water ("excess air"), and the mixing within the water body.

In contrast to the noble gases, the partial pressures of SF_6 and CFCs in the atmosphere have increased strongly during the recent decades, e.g. due to release from industrial appliances. The SF_6 and CFC concentrations therefore contain direct information on the time when the water was last in contact with the atmosphere (water age), which is highly useful to study the mixing and deep-water formation in surface waters, the transport and mixing dynamics in groundwaters, and the geochemical origin and fate of other solutes and gases in aquatic environments (e.g. oxygen, methane, nutrients or contaminants).

For reliable water dating with SF_6 and CFCs, the relative gas contributions from air/water equilibration at the water surface and the formation of excess air to the total SF_6 and CFC concentrations in the water need to be quantified. However, the information required to disentangle these two components from each other is usually poorly constrained from the data available from the conventional analytical techniques.

A way forward to address this issue is to derive the required information from the noble-gas concentrations in the water. However, the analysis of SF_6, CFCs and noble gases in water usually involves the use of separate instruments and techniques in different and highly specialized laboratories. We therefore developed a new method and apparatus for the simultaneous analysis of He, Ne, Ar, Kr, Xe, SF_6, CFC-11, CFC-12, CFC-113, N_2 and O_2 in a single water sample. The apparatus is constructed using only standard and commercially available components. The method is based on vacuum extraction of the dissolved gases from the water. The sample gases are then separated into three fractions. He and Ne is quantified by static mass spectrometry, the remaining gases are quantified by gas chromatography.

U-Th-Ba elemental fractionation during partial melting of crustal xenoliths and its implications for U-series disequilibria in continental arc rocks

RAUL BRENS JR.*[1] AND ROSEMARY HICKEY-VARGAS[2]

[1]Earth & Environment, Florida International University, Miami, FL, USA. (*correspondence: RaulJr00@hotmail.com)
[2]Earth & Environment, Florida International University, Miami, FL, USA. (hickey@fiu.edu)

Understanding U-series isotopic disequilibria of partially melted crust is integral for determining the effect crustal assimilation has on the U-series signature of magmas. The U-series isotopes are too low in abundance to determine by any microbeam technique. Therefore, in this work, U, Th and Ba (as a proxy for Ra) elemental abundances were gathered on the quenched glass in partially melted crustal xenoliths of granitic composition using microbeam techniques. The crustal xenoliths, which are from basaltic volcano Mirador in Chile, are old (Miocene), and can be assumed to be at secular equilibrium, whereas melting occurred during eruption of Mirador in 1979. Any recent fractionation of U from Th or Th from Ra (Ba) by partial melting will result in isotopic disequilibrium. A comparison of the ratios Ba/Th and U/Th in the partial melts with those of the whole rock reveal how much fractionation has occurred during partial melting.

An EPMA was used to locate and analyze glass pockets in the samples, through BSE images. Laser ablation ICP-MS was used to analyze U, Th and Ba in the quenched partial melts and solution ICP-MS was used for the whole rocks.

The SiO_2 content in measured glass samples was between 54% and 75%, Al_2O_3 (13% - 27%), K_2O (0.2% to 7%). Measured Ba/Th (glass/whole rock) are between 0.2 to 51 and Th/U (glass/whole rock) range from 0.3 to 7, with the majority Ba/Th between 1 to 51 and Th/U 0.3 to 1. Different ratios of U, Th and Ba compared to the whole rock substantiate fractionation via partial melting. Thus, assimilation of partial melts of crust can play a role on U-series isotopic disequilibria, which is commonly observed in continental arc magmas. Accessory minerals show variable effects as 'restite', with allanite having a large Th excess and zircon having U excess, these are foremost accessory minerals responsible for the fractionation. Potential U-series disequilibria impacts on magma through melt extraction from country rock or incomplete homogenization during assimilation is discussed.

Mineralizing fluids of the barite-fluorite mineralization at the S edge of the Thuringian Basin, Germany

M. BREY[1], J. MAJZLAN[1], R.J. BAKKER[2] AND W. PROCHASKA[2]

[1]Friedrich-Schiller Universität, Institut für Geowissenschaften, Burgweg 11, D-07749, Jena, Germany (maria.brey@uni-jena.de)
[2] Department Applied Geosciences and Geophysics, Montanuniversity, 8700 Leoben, Austria

Numerous small deposits and occurrences of barite-fluorite mineralization are developed along the southern edge of Thuringian sedimentary basin. It is a series of Upper Permian and Triassic strata (Zechstein, followed by Buntsandstein, Muschelkalk, and Keuper). The Tertiary tectonic activity uplifted the marginal portions of the today's basin where the pre-Permian rock complexes are exposed. The studied mineralization consists mostly of barite, calcite, dolomite, and locally quartz for Kamsdorf and mostly of barite and fluorite in Trusetal and Gehren. The primary fluid inclusions in barite from Kamsdorf show a wide range of salinities between 8-22 wt% $CaCl_2$ eq, the primary inclusions in fluorite from Gehren and Trusetal have about 24 to 27 eq wt% $CaCl_2$ eq. Th measurements range between 85°C to 160°C in barite and between 80°C to 130°C in fluorite. Chemical analysis of fluids extracted from fluid inclusions in fluorite and barite show compositions dominated by Na and Ca. The Cl/Br ratio in the fluorite samples is 260-340 and in barite between 150-240, always lower than in seawater (650). Raman analyses of the vapor phase inside an inclusion suggest traces of N_2 in fluorite and CH_4 in barite. Fluorite samples were analysed for rare-earth elements and two types of REE distribution patterns were found. Type 1 is characterized by high amount of light REE without any Ce anomaly and a steep decrease towards Lu. Type 2 has significantly lesser amount of LREE, a weak Tb/Dy anomaly, and a depletion in HREE. The most fluorite samples belong to the type 2.

The paragenesis of the primary minerals and the physical-chemical properties of the fluids can be explained by large-scale fluid circulation and mixing at the edge of the Thuringian basin and the adjacent Variscan crystalline basement, mostly likely during the late Mesozoic.

This work is a part of INFLUINS, a research project funded by the German Federal Ministry of Education and Research (BMBF) whose financial assistance is gratefully acknowledged.

Integrating multi-scale experiments and modeling to couple biotic weathering at nano and global scales

JONATHAN W. BRIDGE*[1], LYLA L. TAYLOR[2], STEVEN A. BANWART[1] AND THE WEATHERING SCIENCE CONSORTIUM TEAM[1]

[1]Kroto Research Institute, The University of Sheffield, Sheffield, UK
(*correspondence: j.bridge@sheffield.ac.uk)
[2]Department of Animal and Plant Sciences, The University of Sheffield, UK.

Soil mycorrhizal fungi act through chemical interactions at nanometer scale to dissolve minerals and transport weathering products to plant symbionts through metre scale mycelial networks [1]. Soil development occurs at regional scale over millenia (ka) and coupling between ecological, geological and atmospheric systems is apparent over evolutionary (Ma) timescales [2]. We hypothesise that biologically-driven weathering reactions at molecular scale persist through scale transitions to exert strong controls on soil formation and atmospheric CO_2 evolution that occur over much larger temporal and spatial scales.

To test this we have applied an integrated suite of observations at scales from nanometre to decimetre using common minerals, fungi and physical and chemical conditions. Our experiment results demonstrate that fungal hyphae-grain contact leads directly to mass loss from mineral grains over time [3]. Cell exudates and nanoscale cell-mineral interaction forces progressively modify mineral surfaces and alter the pore microenvironment, conditioning subsequent biotic and abiotic weathering mechanisms. Crucially, these processes are directed by mycorrhiza towards minerals which yield the best nutrient supply for plants [1].

Here, we describe the development of numerical models for key nano-scale weathering processes coupled to stochastic, agent-based simulations of hyphal growth at the micron to cm scales which permit quantitative analysis of the dynamic interactions between plant carbon energy supply and soil mineral weathering rates, mediated by mycorrhizal fungi. These profile-scale data are aggregated in a continental scale process-based model [2,4] and tested for representation of the global carbon cycle at evolutionary timescales by comparing with proxy data for paleoenvironmental conditions [5].

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Strontium incorporation into carbonate granules secreted by earthworms

LOREDANA BRINZA[1]*, J. FRED W. MOSSELMANS[1], PAUL F. SCHOFIELD[2], PAUL D. QUINN[1] AND MARK E. HODSON[3]

[1]Diamond Light Source, UK, (Loredana.Brinza@diamond.ac.uk)
[2]Natural History Museum, London, UK, (pfs@nhm.ac.uk)
[3]University of Reading, Reading, UK, (m.e.hodson@reading.ac.uk)

Earthworms secrete significant quantities of calcium carbonate in the form of granules (0.5mg $CaCO_3$/g worm/day), which can also contain other metals depending on the soil content (Pb, Mn, Mg). This may affect metal bio-availability and impact upon element bio-geo-cycling. We have examined Sr incorporation into the granules produced by earthworm *Lumbricus terrestris* cultivated in Sr containing soil. These granules contained up to 3.5% Sr with a positive correlation between Sr concentration in pore water and Sr in the granules. Sr-μXRF maps of the granules show Sr enrichment within the outer region of the granules. These both suggest that the mechanism of Sr incorporation is either adsorption onto or co-precipitation during granule growth.

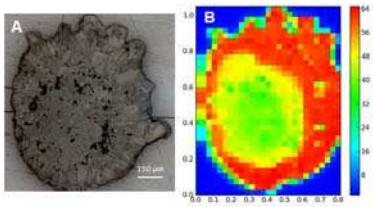

Figure 1. Slice of a calcium carbonate granule produced by ***Lumbricus terrestris*** incorporating 1.2% strontium: (A) Zeiss microscope image; (B) Sr-μXRF map: axis are in mm and the colour bar indicates: blue - low Sr and red - high Sr.

Analysis of Ca-μXANES and Sr-μEXAFS suggests that most Sr substitutes for Ca in the rhombohedral calcite structure rather than producing the orthorhombic carbonates. The results significantly improve our understanding of Sr sequestration within bio-synthesized carbonate granules in the context of its biogeochemical cycle. In terms of earthworm tolerance to Sr, earthworms showed significant mortality at soil bulk concentrations above 1000ppm.

Evaluation of surface complexation parameters for Eu^{3+} on muscovite and orthoclase

S.M. BRITZ[1]*, U. NOSECK[1], V. BRENDLER[2] AND M. STOCKMANN[2]

[1]GRS Braunschweig, D-38122 Braunschweig, Germany (*correspondence: susan.britz@grs.de)

[2]Helmholtz-Zentrum Dresden-Rossendorf, D-01328 Dresden, Germany

Sorption on mineral surfaces of sediments is an important retardation process for radionuclides to be considered in safety assessments for radioactive waste repositories.

This study deals with sediments of the overburden at Gorleben site that are mainly composed of tertiary and quaternary sands and clays [1]. A bottom-up approach is chosen to describe the sorption of Eu^{3+} (as homologue for trivalent actinides) on each single mineral phase of a representative sediment. Orthoclase and muscovite are important constituents of the sediment significantly contributing to the overall distribution coefficient.

The scope of the study is the assessment of surface complexation parameters by applying the geochemical speciation model PhreeqC, Version 2.17 which is coupled with the parameter-estimation code UCODE_2005. Since relevant data were missing for the sediment constituents orthoclase and muscovite batch experiments are performed for the parameter estimation. Establishing solid/liquid ratios of 1/20 and 1/80 the minerals are suspended in 0.01 M $NaClO_4$. Subsequently pH values ranging between 6 and 9 are employed in the suspensions over a period of several weeks. Eu^{3+} concentrations of 10^{-5} M, 10^{-6} M, 10^{-7} M, and 10^{-8} M are applied, whereat a chemical equilibrium between Eu^{3+} and the mineral is reached within 24 h.

PhreeqC and UCODE are used to acquire protolysis constants via a diffuse double layer model as well as the cation exchange capacity from measured titration curves. In the second step the basic required parameters, i.e. logK-values for selected surface reactions, the surface site density, and the specific surface area are iteratively determined by fitting the experimental data.

It is now intended to apply the derived surface complexation model to simulate Eu-sorption on a sediment representative for the Gorleben overburden composed of 10% muscovite, and orthoclase, respectively, and 80% quartz.

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Molecular fossils and the late rise of eukaryotes and oxygenic photosynthesis

JOCHEN J. BROCKS

Research School of Earth Sciences, The Australian National University, Canberra ACT 0200, Australia.

Hydrocarbon biomarkers are the molecular fossils of natural products such as lipids and pigments. They can yield a wealth of information about early microbial ecosystems and are particularly valuable when preserved in > 1 billion-year-old (Ga) sedimentary rocks where conventional fossils are often lacking. Therefore, in 1999, the detection of traces of biomarkers in 2.5 to 2.7 Ga shales from Western Australia [1, 2] was celebrated as a breakthrough. The discovery, which was later confirmed by several independent studies, led to far-reaching conclusions about the early evolution of oxygenic photosynthesis [2] and ancestral eukaryotes [1]. However, here we present new data based on the carbon isotopic composition of solidified hydrocarbons [3] and the spatial distribution of liquid hydrocarbons within the original 2.5 and 2.7 Ga shales [4] that demonstrate that the molecules must have entered the rocks much later in Earth's history and therefore provide no information about the Archean (>2.5 Ga) biosphere or environment.

The elimination of the Archean biomarker data has immense implications for our understanding of Earth's early biosphere. 2α-methylhopanes have been interpreted as evidence for the existence of cyanobacteria at 2.7 Ga, about ~300 million years before the atmosphere became mildly oxygenated in the Great Oxidation Event (GOE; between 2.45 and 2.32 Ga). Now, the oldest direct fossil evidence for cyanobacteria reverts back to 2.15 Ga, and the most ancient robust sign for oxygenic photosynthesis becomes the GOE itself. Moreover, the presence of steranes has been interpreted as evidence for the existence of ancestral eukaryotes at 2.7 Ga. However, without the steranes, the oldest fossil evidence for the domain falls into the range ~1.78-1.68 Ga. Recognition that the biomarkers from Archean rocks are not of Archean age renders permissive hypotheses about a late evolution of oxygenic photosynthesis, and an anoxygenic phototrophic origin of the vast deposits of Archean banded iron formation.

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Palaeoclimate record from groundwater of the Great Artesian Basin, Australia

LISA BRÖDER[1]*, ROLAND PURTSCHERT[2], ANDREW LOVE[3], SIMON FULTON[4], DANIEL WOHLING[5] AND WERNER AESCHBACH-HERTIG[1]

[1]Institute of Environmental Physics, Heidelberg University, Heidelberg, Germany (*correspondence: Lisa.Broeder@iup.uni-heidelberg.de)
[2]Climate and Environmental Physics, Physics Institute, University of Bern, Bern, Switzerland
[3]Flinders University and NCGRT, Adelaide, Australia
[4]NRETAS, Northern Territory, Australia
[5]DFW, South Australian Government, Australia

The Great Artesian Basin (GAB) is one of the largest artesian groundwater basins in the world, underlying more than one-fifth of the Australian continent. The water is stored in a multi-layered confined aquifer system. Earlier studies using different dating methods showed a wide range of water ages up to more than 400 000 years [1,2]. As the GAB aquifers constitute the major water source in this semi-arid to arid region their careful management is of great importance.

Study area of this project is the western margin of the GAB as part of the project "Allocating water and maintaining springs in the Great Artesian Basin" of the Australian National Water Commission. We aim to obtain a full record of palaeoclimate data over the last 30 kyr by analysing groundwater samples for dissolved noble gases and stable isotopes. Noble gas studies have proven to be a valuable tool for determining palaeotemperatures all over the world [3]. By examining the excess air component estimations of palaeohumidity can be made [4].

^{3}He, ^{4}He, Ne, Ar, Kr and Xe concentrations are measured using mass spectrometry. For dating mainly ^{14}C and ^{4}He, in some cases other radioisotopes, will be used. Radiogenic ^{4}He concentrations increase with distance along presumed flow lines. First results for noble gas temperatures of recent groundwaters correspond well to the mean annual air temperature in the study area (21.7°C).

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The rapid emplacement of the Val Fredda Complex, Adamello batholith, N. Italy

C.A. BRODERICK[1]*, U. SCHALTEGGER[1], D. GÜNTHER[2] AND P. BRACK[3]

[1]University of Geneva, Earth Sciences, Switzerland (*corresponence: Cindy.Broderick@unige.ch)
[2]ETH Zürich, D-CHAB, Lab of Inorg Chem, Switzerland
[3]ETH Zürich, Earth Sciences, Switzerland

Recent advances in U-Pb zircon geochronology have revealed the complexities of pluton construction, by multiple injections on 10-100 ka to Ma timescales [1, 2]. Using high precision U-Pb dating we are potentially able to determine timescales of magma generation, crystallization and emplacement within the crust. The potential exists to better understand magma forming processes with detailed high precision U-Pb dating and trace element analyses of zircon and titanite, combined with Hf isotope analysis of zircon.

The focus of this study is on the Val Fredda Complex (VFC) in the southern tip of the Adamello batholith, N. Italy. The VFC shows complex relationships among mafic melts that were injected into solidifying felsic magmas. Single zircon crystals, from the VFC, have been dated using CA-ID-TIMS, employing the ET2535 tracer solution for maximum precision and accuracy. The mafic units have apparent autocrystic zircons that indicate growth over a duration of 100 ka, with the majority of zircons crystallizing near the solidus, as indicated by ^{206}Pb/^{238}U zircon and titanite dates, both with permil uncertainties. Data from the VFC felsic units show more complex zircon populations, including xenocrystic, antecrystic and autocrystic zircons. Trace element ratios such as Y/Hf aide in our distinctions between autocrystic and antecrystic zircons. These felsic units have apparent autocrystic zircon growth over 100 to 200 ka, with zircons crystallizing near the solidus during the last 20 to 50 ka as indicated by titanite dates. Our data suggest that the oldest autocrystic zircon could be used to approximate the injection of the respective magma pulses into the host rock, whereas the youngest zircon and titanite could be used to approximate (final?) solidification. It appears that the five units from the VFC were injected into the crust between 42.58 Ma and 42.52 Ma and achieved the final solid state between 42.48 Ma and 42.42 Ma.

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Overcoming the Barker effect

W.S. BROECKER*

Lamont-Doherty Earth Observatory of Columbia University, 61 Route 9W / P.O. Box 1000, Palisades, NY 10964-8000, USA (*correspondence: broecker@ldeo.columbia.edu)

Dissolution leading to shell breakup complicates the use of benthic - planktic ^{14}C age differences as indicators of changes in deep ocean ventilation rates. Specifically, the age difference between benthics (dissolution resistant) and *G. sacculifera* (dissolution prone) often leads to serious overestimates of isolation times. In recognition of the one who first put his finger on this, it is referred to as "the Barker effect."

Sr isotope ratios determination by LA-MC-ICPMS in Rb rich samples: Online separation of Rb by electrothermal aerosol heating

R. BROGIOLI, L. DORTA, B. HATTENDORF AND D. GÜNTHER

Laboratory of Inorganic Chemistry, ETH Zurich, Wolfgang-Paulistrasse 10, 8093, Zürich, Switzerland

Rb/Sr geochronology using LA-ICPMS has successfully been demonstrated for solid samples where the Rb/Sr concentration ratio is lower than 0.02 [1] and 0.14 [2]. For samples with higher Rb content, the determination of Sr isotope ratios remains challenging because mathematical correction of the isobaric interference from ^{87}Rb leads to increased uncertainties in the results. Using electrothermal vaporization (ETV)-ICPMS, a method has been conceived by Rowland *et al*. [3] in order to selectively pre-vaporize Rb from a reference potassium feldspar sample (NIST SRM607) making the measurement of Sr isotope ratios possible for samples where the Rb/Sr ratio can be as high as 8.

In an earlier study we could demostrate that heating laser generated aerosols from a silicate glass reference material (NIST SRM610, Rb/Sr ~1) with a commercially available ETV unit (Perkin Elmer, HGA 600MS) to about 2000 °C, enables the reduction of the signal intensity of Rb by 99%, while the signal intensities for Sr remain practically unaffected [4]. The approach has now been used for Sr isotope ratios measuerments in NIST SRM 610 (Rb/Sr = 1), USGS BCR2G (Rb/Sr = 0.14) and $Li_2B_4O_7$ fused disks of NIST SRM607 (Rb/Sr = 8) using multicollector ICPMS coupled to the LA-ETV setup. The combination of electrothermal vaporization for interferences suppression and laser ablation for spatially resolved sampling of solids is expected to broaden the range of applications for Rb/Sr –geochonology since both, isotope ratios and elemental concentrations, can principally be determined under highly similar conditions when using either sequential LA-ICPMS approaches or a split-flow prior to ETV configuration with MC-ICPMS and single collector ICPMS operating in parallel [5].

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Bioreduction of biotite and chlorite: Effects on mineral reactivity

D.R. BROOKSHAW*, R.A.D. PATTRICK, J.R. LLOYD AND D.J. VAUGHAN

School of Earth, Atmospheric and Environmental Sciences, and Williamson Research Centre for Molecular Environmental Science, University of Manchester, Manchester, M13 9PL, UK (*correspondence: diana.brookshaw@postgrad.manchester.ac.uk)

Interactions with mineral phases can dictate the mobility of contaminants in the subsurface. Electron transfer processes in particular have the potential to reduce redox-sensitive metals (including radionuclides) so as to form much less soluble and less mobile phases. This work concerns investigating the role that microorganisms can play in such electron-transfer processes, examining interactions involving two key phyllosilicates found in the sub-surface.

Biotite and chlorite are sheet silicate minerals containing both ferric and ferrous iron in their octahedral layers. The redox reactivity of these minerals when fresh, and after undergoing bioreduction, was studied. The model Fe(III)-reducing microorganism *Shewanella oneidensis* MR-1 was used in anaerobic batch experiments where reduction of structural iron was stimulated by addition of an electron donor. The bioreduced mineral was collected and washed before use in redox reactivity experiments.

Ferrous iron assays using the ferrozine method show that *S. oneidensis* MR-1 is able to reduce the bioavailable Fe(III) in both minerals, both in the presence and absence of an artificial electron shuttle and humic analogue (AQDS). Chromate (Cr(VI)) was used as a redox probe to explore mineral reactivity. Unaltered biotite and chlorite reduced up to ~15% of 1mM Cr(VI), compared to 82.8% for the bioreduced biotite, and 91.6% for the bioreduced chlorite. This demonstrates the importance of bioreduction in metal cycling, with the mineral surfaces conditioned to reduce the metals in solution. The amount of reduction suggests that the processes involve more than just the available Fe(II) surface atoms. Surface analysis (XPS) combined with XAS are being used to detemine the biologically induced mineralogical changes that are driving the reduction process.

The work is being extended to radionuclides, and the reduction of technetium (^{99}Tc). It is anticipated that the amount of reduction will be similar to that of Cr(VI) as Tc reduction is also a three-electron transformation (Tc(VII) to Tc(IV)).

Geochemistry and tectonic setting of Una-Una volcano, Sulawesi, Indonesia

S. BROOM-FENDLEY*, M.F. THIRLWALL, M.A. COTTAM AND R. HALL

SE Asia Research Group, Department of Earth Sciences, Royal Holloway University of London, Egham, Surrey TW20 OEX, UK (*correspondence: s.broom.fendley@gmail.com)

Una-Una is an isolated volcano in Gorontalo Bay, North Sulawesi situated in a complex tectonic setting. Previously, Una-Una has been linked to southward subduction of the Celebes Sea under the North Arm of Sulawesi or northward subduction linked to collision in East Sulawesi. These hypotheses have problems with the apparent depth to the Benioff zone and amount of continental underthrusting.

We present new geochemical and Sr, Nd & Pb isotope analyses of volcanic rocks from Una-Una (<~100 Ka) and the nearby Togian islands (~2 Ma). These are both alkaline or high-K calc-alkaline trachytes with elevated Sr, Pb and LILE and depleted HREE, Nb and Ta. Sr and Nd isotopes plot in the enriched quadrant on a Sr-Nd diagram and ^{207}Pb/^{204}Pb show a steep trajectory extending from Indian Ocean MORB. The isotopic trends and similar geochemistry indicate that the rocks are genetically related and have similar continental derived components. The elevated isotopic values require an ancient continental contribution to the source. Mixing trends between Sr and Nd isotopes show that contamination is not likely to have come from Celebes Sea sediment compositions and Indian Ocean pelagic sediment is more likely. Contamination could have occurred during Eocene-Early Miocene subduction of Indian Ocean lithosphere. Una-Una is not above a subducted slab, and is at least 200 km above any projected subduction zone. The age of volcanic rocks from the Togian Islands rule out subduction at the North Sulawesi trench as the slab would not have been deep enough.

We propose that Una-Una and the Togian Islands are the product of young extension of Gorontalo Bay due to slab roll-back. This provides a mechanism for upwelling of a pre-metasomatised mantle.

Assessing calcium isotopes as a dietary proxy for terrestrial vertebrates

J. BROSKA[1], T. TÜTKEN[2]*, S.J.G. GALER[3], P. HELD[1] AND K.W. ALT[1]

[1]Institut für Anthropologie, Johannes Gutenberg-Universität Mainz, 5099 Mainz, Germany
[2]Steinmann-Institut, Rheinische Friedrich-Wilhelms-Universität Bonn, Poppelsdorfer Schloß, 53115 Bonn, Germany (*correspondence: tuetken@uni-bonn.de)
[3]Max-Planck-Institut für Chemie, Abteilung Biogeochemie, Postfach 3060, 55020 Mainz, Germany

Vertebrates ingest calcium along with their diet, and during biomineralization the light calcium isotopes are preferentially enriched in the bioapatite of bones and teeth. Therefore, $\delta^{44/42}$Ca should decrease systematically along a food chain, and display a trophic level effect (TLE). Since calcium isotope signatures of bones and teeth seem robust against strong diagenetic alteration, $\delta^{44/42}$Ca is a promising proxy for reconstructing both past diets of extinct vertebrates and fossil food webs.

However, in order to be able to use $\delta^{44/42}$Ca to elucidate the diet of extinct animals, a better understanding of $\delta^{44/42}$Ca and TLE in modern ecosystems is paramount. With this in mind, we analysed $\delta^{44/42}$Ca in more than 40 bones of 19 extant mammals with a broad range of well-characterized diets from savannah ecosystems in Africa. The Ca isotope data were obtained by TIMS using a ^{43}Ca-^{46}Ca double spike at MPI. Additional, established proxies for diet and trophic level such as δ^{13}C and δ^{15}N of collagen were also analyzed on the same specimens for comparison and to assess dietary differences and trophic level relationships.

A large variability in $\delta^{44/42}$Ca was observed within each trophic level. Browsers and grazers, and some of the frugivores, had similar $\delta^{44/42}$Ca values. A significant TLE difference in $\delta^{44/42}$Ca of –0.36 was found to exist between herbivores (–0.53 ± 0.32‰) and carnivores (–0.89 ± 0.18‰). This TLE difference is smaller than the –0.65 that has been reported thus far, but appears to vary between different areas and geological substrates.

Carnivores with high amounts of bone consumption, such as leopards and hyenas, display the lowest $\delta^{44/42}$Ca, down to –1.2‰ (hyenas). In contrast, ant-eating insectivores, such as the aardvark and aardwolf, have the highest bone $\delta^{44/42}$Ca (+0.03±0.27‰) observed for extant vertebrates thus far, being significantly higher than found for both herbivores and carnivores. Thus, $\delta^{44/42}$Ca may potentially be a useful indicator of insectivory in fossil vertebrates.

Combining $\delta^{44/42}$Ca with δ^{13}C and δ^{15}N allows us to refine our interpretation of diet of foodwebs significantly in extant and extinct vertebrates.

Effect of differentiation on Fe oxidation in arc basalts

MARYJO BROUNCE[1, 2], KATHERINE A. KELLEY[1] AND ELIZABETH COTTRELL[2]

[1]Graduate School of Oceanography, University of Rhode Island, 215 S. Ferry Road Narragansett, RI 02882 USA
[2]National Museum of Natural History, Smithsonian Institution, Washington DC 20560, USA

The role of crustal differentiation processes in creating or modifying the relatively oxidized condition of arc basalts relative to mid ocean ridge basalts (MORB) is not well constrained. We present the first combined data set for major elements, dissolved volatile concentrations and $Fe^{3+}/\Sigma Fe$ ratios (determined by μ-XANES) in olivine-hosted basaltic glass inclusions from four Mariana arc volcanoes in order to examine how Fe oxidation varies with extent of fractional crystallization, degassing and contributions from the slab to the arc mantle source.

Glass inclusions span a variety of compositions and are consistent with multi-phase crystallization and degassing. A strong trend in Fe reduction accompanies magmatic degassing and inclusions with the highest MgO (>6.5 wt%) are consistently the most oxidized ($Fe^{3+}/\Sigma Fe$>0.235). The reduction trend suggests that redox exchange may occur during SO_2 degassing that redistributes e^- in the residual magma ($S^{2-}_{melt} \rightarrow S^{4+}_{vapor} + 6e^-$). We show that the high $Fe^{3+}/\Sigma Fe$ observed here cannot be created through extensive multi-phase fractionation (olv ± cpx ± plag) of a MORB-like primary melt ($Fe^{3+}/\Sigma Fe$=0.16 [1]). These observations support the hypothesis that the elevated $Fe^{3+}/\Sigma Fe$ of arc and back-arc basalts are due to differences in the source mantle. Primary melt compositions were reconstructed by restoring the most mafic inclusion compositions to equilibrium with Fo_{90}. A strong positive correlation exists between $Fe^{3+}/\Sigma Fe_{Fo90}$ and H_2O_{Fo90}, suggesting that slab derived fluids may contain an oxidized signature that contributes significantly to the oxidation state of basalts erupted at the Mariana arc.

[1] Cottrell and Kelley, *EPSL*, (2011).

Simultaneous reaction and creep in the KCl-KBr-H_2O system

J. BROUWER* AND A. PUTNIS

Institut für Mineralogie, Westf. Wilhelms Univ. Münster
Corrensstr. 24, 48149 Münster , Germany
(* correspondence: J.Brouwer@uni-muenster.de)

As early as 1983 [1] it has been suggested that dissolution-precipitation creep rates may be affected by chemical reaction. However, for a long time research has focused mainly on creep of single phase mineral aggregates in order to understand the physics of stress-driven dissolution-precipitation creep [2,3,4]. More recent research has shown that background ions in solution may significantly effect surface kinetics and solubility both negatively and positively [5]. We present experiments on simultaneous reaction and dissolution precipitation creep in the system KBr, KCl, K(Br,Cl), H_2O.

When KBr and KCl are reacted in the presence of an aqueous fluid at room temperature a solid solution $K(Br_x, Cl_{1-x})$ will form. Creep rates of KBr and KCl in their respective aqueous solutions are compared with those of KBr and KCl in the solution of the other endmember, and with creep rates of mixtures of KBr and KCl in an aqueous solution that is in equilibrium with the solid solution that will form when reaction has gone to completion. These results provide in insight the complex combination of effects that reaction has on deformation, including changes in solid volume due to solubility differences between parent and product phases, changes in grain size and material properties, and changes in kinetics.

[1] Rutter (1983) *J. Geol. Soc.* **140**, 725-740. [2] Raj (1982) *JGR* **87**, 4731-4739. [3] Spiers and Schutjens (1990) in *Deformation Processes in Minerals, Ceramics and Rocks*, ed. Barber and Meredith, London, 334-353. [4] Gratier *et al.* (2009) *JGR – Solid Earth* **114**, B03403. [5] Zhang *et al.* (2011) *Geofluids* **11**, 108-122.

Redox reactions on mineral surfaces: Spectroscopic and imaging studies at the molecular level

GORDON E. BROWN, JR.[1,2,3]*, GUILLAUME MORIN[4], GEORGES ONA-NGUEMA[4], FARID JUILLOT[4], YUHENG WANG[4], DIK FANDEUR[4], KARIM BENZERARA[4], GEORGES CALAS[4], YINGGE WANG[1], JU YOUNG HA[1], SARP KAYA[2], TOM KENDELEWICZ[1], ALFRED M. SPORMANN[3], AND ANDERS NILSSON[2]

[1]Dept. of Geological & Environmental Sciences, Stanford University, Stanford, CA 94305-2115, USA (*gordon.brown@stanford.edu)
[2]Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA, USA.
[3]Dept. of Chemical Engineering, Stanford University, Stanford, CA, USA.
[4]Institut de Minéralogie et de Physique des Milieux Condensés (IMPMC), UPMC; Université Paris 7; CNRS; 4, Place Jussieu, 75252 Paris Cedex 05, France.

Electron transfer at mineral-water and mineral-microbe interfaces is a major biogeochemical process that can result in transformation of redox-sensitive minerals and adsorbed pollutant ions, capture (through adsorption and precipitation reactions) or release (through reductive transformation of the sorbent and desorption of surface complexes) of pollutant species, and major controls on element cycling. Over the past decade, a growing number of spectroscopic and imaging studies of the products of electron transfer reactions in model mineral-water systems have advanced our understanding of these reactions and their kinetics in the laboratory. Here, we will review a number of these studies, including abiotic reduction of As(V), Cr(VI), and Se(VI) on metal oxide surfaces, photocatalyzed As(III) oxidation on kaolinite and anatase surfaces, the role of reactive oxygen species and Fe^{2+} on the oxidation kinetics of As(III) on iron oxides, microbially mediated redox reactions of arsenic at iron oxide-water interfaces, and the role of exopolysaccharides in the reduction of nanoparticulate hematite by *Shewanella oneidensis* MR-1, and microbially mediated oxidation of metal sulfides. We will also present the results of several studies of complex environmental samples that illustrate the effects of electron transfer reactions in natural settings, including chromium reduction by magnetite, the effect of electrically insulating coatings on the Cr(VI) to Cr(III) reduction at the magnetite-water interface, Cr(III) oxidation by Mn-oxides, and arsenic redox reactions, including As(III,V) biomineral formation in an acid mine drainage environment.

Interfacial area measurements for robust models of multiphase flow in porous media

KENDRA I. BROWN[1], DORTHE WILDENSCHILD[1], WILLIAM G. GRAY[2] AND CASS T. MILLER[2]

[1]School of Chem/Bio/Env Eng, Oregon State University, Corvallis, OR 97331; (brownke@engr.orst.edu, dorthe@engr.oregonstate.edu)

[2]Dept of Env Science and Engineering, University of North Carolina, Chapel Hill, NC; (graywg@unc.edu, casey_miller@unc.edu)

Understanding the physics of natural flow systems that include *three* immiscible fluid phases in porous media is important to applications such as remediation of NAPL from the vadose zone, oil and gas recovery, and CO_2 sequestration.

Flow and transport in such systems are strongly influenced by the presence of fluid-fluid interfaces. Theoretical work based on conservation laws and the second law of thermodynamics has demonstrated the advantage of a different approach to modeling multiphase flow, accounting not only for traditional variables such as saturation and porosity, but that also incorporate specific interfacial areas, specific common curve lengths, and average curvatures, that are measures of the morphology and topology of the phase distributions.

This research expands previous work on two-fluid-phase systems to three-fluid-phase systems, and the particular focus is the generation of a pore-scale experimental data set that expresses the dependency of capillary pressures in the system on two saturations, as well as interfacial areas per volume. Synchrotron-based X-ray computed microtomography (CMT) is used to generate high-resolution images during drainage and imbibition, which are analyzed to measure the saturations and interfacial areas, and to calculate capillary pressures via meniscus curvature.

Magnetic properties of ilmenite-hematite containing magnetite nano-crystals

SARAH J. BROWNLEE*[1], JOSHUA M. FEINBERG[2], TAKESHI KASAMA[3] RICHARD J. HARRISON[4], GARY R. SCOTT[5] AND PAUL R. RENNE[5]

[1]Earth Research Institute, University of California, Santa Barbara, 6832 Ellison Hall, Santa Barbara, CA 93106-3060

[2]Institute for Rock Magnetism, University of Minnesota, 310 Pillsbury Drive SE, Minneapolis, MN 55455

[3]Center for Electron Nanoscopy, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark

[4]University of Cambridge, Department of Earth Sciences, Downing Street, Cambridge, CB2 3EQ

[5]Berkeley Geochronology Center, 2455 Ridge Road, Berkeley, CA 94709

This study investigates changes in the rock magnetic properties of single crystals of ilmenite-hematite from the Ecstall pluton containing nm-sized magnetite crystals that formed as a result of reheating by the adjacent Quottoon plutonic complex. Measurements of hysteresis properties, low temperature remanence, room temperature IRM acquisition, and observations from magnetic force microscopy (MFM) and off-axis electron holography show that samples fall into 3 groups, which are defined by the presence of mineral microstructures documented in *Brownlee et al*. [2010], which are in turn related to distance from the Quottoon plutonic complex. Ilmenite-hematite grains from the two groups closest to the Quottoon plutonic complex contain nm-sized magnetite crystals within hematite and ilmenite lamellae. Reheating of the Ecstall pluton led to an increase in coercivity and overall magnetic intensity, as well as the development of mixed phase hysteresis. Though the potential for lamellar magnetism exists in all of these samples, off-axis electron holography results indicate that the magnetic signal is dominated by magnetite precipitates at intermediate distances from the Quottoon plutonic complex. Increased single grain coercivity may reflect further development of exsolution lamellae at very close distances to the Quottoon plutonic complex. These results indicate that reheating had a profound affect on the overall magnetic properties of the Ecstall pluton through the growth and modification of Fe-Ti oxide microstructures.

Fate of an Eocene HT metamorphic complex in a forearc location

E. BRUAND[1]*, D. GASSER[2] AND K. STUEWE[3]

[1]SEES, University of Portsmouth, Portsmouth PO1 3QL, UK (*correspondence: emilie.bruand@port.ac.uk)
[2]Department of Geosciences, University of Oslo, 0316 Oslo, Norway (deta.gasser@geo.uio.no)
[3]Department of Earth Sciences, Karl-Franzens Universität, 8010 Graz, Austria (kurt.stuewe@uni-graz.at)

The Chugach and St Elias mountains in southern Alaska are a peculiar and interesting region from many geological aspects. For example, this area encloses a high temperature Eocene complex (CMC) developed in a Late Cretaceous accretionary prism: such a high-thermal regime is uncommon in a subduction setting during the Phanerozoic. In addition, this investigated area is also currently the focus of intense research related to the coupling of surface processes (glacial erosion) and tectonics, since fast Neogene exhumation rates have been observed in areas of intense glaciation [1]. Therefore, in order to understand links between crustal thermal evolution, metamorphism, deformation and erosion in this area, it is crucial to obtain a detailed description of its PTdt-evolution through time. For this purpose, aspects of metamorphic petrology, geochemistry, structural geology and geochronology are combined and presented in this contribution to develop a crustal scale geodynamic model of this region.

The CMC is more than 300 km long, made up of metasediments associated with an amphibolite layer in its southern part. Detailed petrological work across several parts of this complex permits to discuss the uncommon presence of such a HT complex in a forearc location. Results highlight a pressure gradient from north to south and an interesting behaviour of the southern amphibolite belt that make up the suture between the CMC and the outboard accreted terrane. In addition, our dataset including detailed structural geology and geochronology suggests that fast burial and exhumation rates in this region do not only occur in the Neogene but also during the Eocene. Our new results assess that exhumation from depths of >20 km in parts of the complex were accompanied by erosion at the surface. Our data set documents a complex deformational and thermal history including accretion of sediments, subsequent vertical flattening leading to compressed isotherms, followed by dextral transpression, exhumation and erosion within a short time period of ca. 10-15 Ma.

[1] Enkelmann *et al*. (2009) *Nature Geoscience* **5**, 360-363

Experimental quantification of plagioclase CSD during decompression of hydrous rhyodacite

C. BRUGGER-SCHORR AND J. HAMMER*

Dept. GG, Univ. Hawaii, 1680 East-West Rd., Honolulu, HI, 96822, USA (*correspondence jhammer@hawaii.edu)

Few experimental studies [1,2] constrain the link between crystal size distributions (CSDs) and known chemical, thermal, or barometric histories. We determine CSDs of plagioclase forming during decompression experiments on hydrous rhyodacite magma. Samples were annealed at 130 MPa, subjected to continuous decompression at either 2 MPa hr^{-1} or 0.5 MPa hr^{-1}, and then quenched at ~20 MPa intervals to provide snapshots of the system along the decompression path [3]. Crystal nucleation and growth rates derived from CSDs using standard assumptions are compared with values obtained using 2D measurements of the largest crystals (L_{max} methods) as well as bulk crystal populations (batch methods). The characteristic growth rate in the rapidly decompressed series is approximately five times faster than the growth rate in the slowly decompressed series. Because crystal growth rate depends on decompression rate, CSDs are incapable of revealing decompression timescales or magma ascent rates without independent knowledge of crystal growth rate.

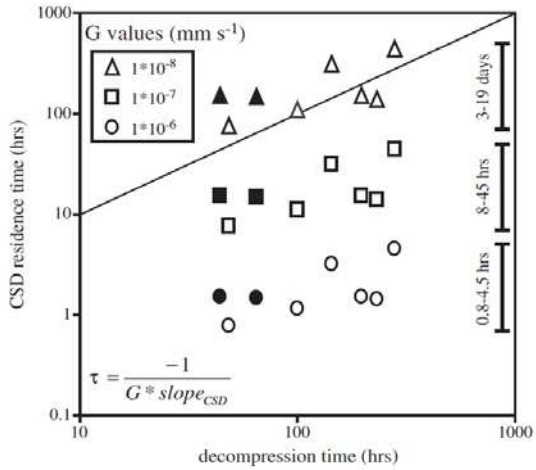

Figure 1: Residence time is computed using three published values of plagioclase growth rate. Only independent knowledge of G permits recovery of actual crystallization interval (1:1 line).

[1] Zieg and Lofgren (2006), *J Volcanol Geotherm Res* **154**, 74-88. [2] Pupier *et al*. (2008) *Contrib Mineral Petrol* **155**, 555-570. [3] Brugger and Hammer (2010) *J Petrol* **51**, 1941-1965.

Composition of Hippopotamid enamel: Paleoenvironmental reconstruction and enamel formation

G.E. BRÜGMANN,[1]*, J. KRAUSE[2], T.C. BRACHERT[3], O. KULLMER[4], I. SSEMMANDA[5] AND D.F. MERTZ [1]

[1]Institut für Geowissenschaften, Johannes Gutenberg-Universität Mainz, 55099 Mainz, Germany (*correspondence: bruegmag@uni-mainz.de)
[2]Max-Planck-Institut für Chemie, Joh.-Joachim-Becher-Weg 27, 55128 Mainz, Germany
[3]Institut für Geophysik und Geologie, Talstraße 35, Universität Leipzig, 04103 Leipzig, Germany
[4]Forschungsinstitut und Naturmuseum Senckenberg, Senckenberganlage 25, 60325 Frankfurt, Germany
[5]Geology Department, Makerere University, P.O. Box 7062, Uganda

Bioapatite in mammalian teeth is readily preserved in continental sediments and represents an important archive for environmental reconstructions. Here we present electron microprobe data for fossil and modern molar enamel of Hippopotamids from different ecosystems in Eastern Africa, representing modern and fossil lacustrine (Lake Kikorongo, Lake Albert, and Lake Malawi) and modern fluvial environments of the Nile River system.

Fossil enamel from the saline Lake Kikorongo has a much higher MgO/Na_2O ratio (~1.11) than from the Neogene fossils of Lake Albert (MgO/Na_2O~0.4), which was a large fresh water lake. Similarly, the MgO/Na_2O ratio in modern enamel from the White Nile River (~0.36), which passes through several saline zones, is higher than that from the Blue Nile River (MgO/Na_2O~0.22). Thus, MgO/Na_2O is suggested be a fingerprint for environments where river and lake water have suffered strong evaporation.

Linear regression analysis reveals very tight physiological control on the MgO, Na_2O and Cl variations (R^2: 0.6-0.84) despite large concentration variations (40% to 300%) along sections perpendicular to the enamel-dentin junction (EDJ). MgO and Na_2O decrease from the EDJ towards the outer enamel rim, whereas Cl displays the opposite variation. Nevertheless, there are co-linear relationships among these elements which can be interpreted as binary mixing lines. Enamel crystallites precipitating during amelogenesis equilibrate with a continuously evolving fluid. During this process Na_2O and MgO behave incompatibly whereas Cl is incompatible to hydroxyapatite. This results in the formation of MgO, and Na_2O-rich, but Cl-poor bioapatite near the EDJ and MgO- and Na_2O-poor, but Cl-rich bioapatite at the outer enamel rim.

The relationship between $\Delta^{14}C$ and $\delta^{13}C$ of DIC in the LGM Ocean

S.P. BRYAN[1]*, S.J. LEHMAN[2] AND T.M. MARCHITTO[2]

[1]Dept. of Marine Chemistry & Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA (*correspondance: sbryan@whoi.edu)
[2]Dept. of Geological Sciences & INSTAAR, University of Colorado, Boulder, CO 80303, USA (scott.lehman@colorado.edu, tom.marchitto@colorado.edu)

Reconstructed atmospheric radiocarbon activities ($\Delta^{14}C$) during the last glacial period were higher than can be explained by ^{14}C production rates, seemingly requiring reduced ventiliation of the glacial deep ocean relative to the preindustrial ocean. Estimates of glacial deep ocean $\Delta^{14}C$ generally support this prediction; though large uncertainites exist in deep ocean paleo-$\Delta^{14}C$ reconstructions due to the paucity of records, generally low sedimentation rates in the deep ocean, bioturbative mixing of foraminifera of differing ages, and uncertain surface reservoir ages. Due to these uncertainties there is currently no consensus regarding the spatial extent or the degree of ^{14}C depletion in the glacial deep ocean. The lack of a strong decrease in $\delta^{13}C$ in the glacial deep Pacific Ocean has been used as an argument against the existance of a large ^{14}C-depleted water mass. However, the distributions of ^{14}C and ^{13}C of dissolved inorganic carbon are not strictly analogous. For example, in the modern ocean, differences in the depths of organic carbon remineralization vs water mass aging cause the slope of the relationship between $\delta^{13}C$ and $\Delta^{14}C$ to increase with water depth.

We explore the relationship between $\delta^{13}C$ and $\Delta^{14}C$ during the Last Glacial Maximum (~19-23 kyr BP) using a global compilation of published measurements. Despite the uncertainties listed above, there is credible evidence that deep waters in the North Atlantic, Southern Ocean and Eastern Equatorial Pacific were depleted in ^{14}C during the LGM. The decrease in deep Pacific $\Delta^{14}C$ with little associated change in $\delta^{13}C$ is equivalent to a steepening of the $\delta^{13}C$ - $\Delta^{14}C$ relationship. We suggest that this steepening may be explained by reduced organic carbon remineralization rates in the glacial deep Pacific and/or changes in preformed $\delta^{13}C$ and $\Delta^{14}C$ values. We discuss the evidence for such changes and the implications for reconstruction of the glacial ocean carbon cyle.

Rollback-enhanced decompression melting of a volatile-rich mantle: The ancient lavas of Mt. Etna

J.G. BRYCE[1]*, D. GRAHAM[2], J. BLICHERT-TOFT[3], B.B. HANAN[4], S. MILLER[1], J. BARKMAN[1], F.J. SPERA[5] AND G.R. TILTON[5]

[1]UNH Earth Sciences, Durham NH, USA (*julie.bryce@unh.edu, correspondence)
[2]COAS, Oregon State University, Corvallis, OR, USA
[3]Ecole Normale Supérieure de Lyon, Lyon, France
[4]SDSU Geological Sciences, San Diego, CA, USA
[5]UCSB Earth Sciences, Santa Barbara, CA, USA

Mount Etna, Europe's largest and most active volcano, sits above a complicated tectonic setting near the intersection of the Tyrhennian, African and Ionian plates. Geophysical evidence suggests that the large volumes of mafic lavas at Etna and the neighboring Hyblean plateau are due to enhanced melting caused by perturbations in mantle convection associated with the oversteepened Ionian slab. Here, we present new Sr-Nd-Hf-Pb data on ancient Etna basalts. We use these data, together with new major/trace element and literature data, to constrain the source lithologies responsible for early Etnean magmatism. Our sample suite includes basal tholeiites followed (at ~ 200 ka) by lavas of dominantly transitional and alkaline compositions. Major and trace element trends within the tholeiitic and alkaline series can separately be modeled by fractional crystallization, but processing through crustal magma bodies cannot satisfactorily explain the links between these two compositional series. Isotopic data are distinctive between the two groups, with the tholeiitic lavas bearing less radiogenic Sr ($^{87}Sr/^{86}Sr < 0.7032$) and Pb ($^{206}Pb/^{204}Pb < \sim 19.6$, $^{208}Pb/^{204}Pb < \sim 39.3$) when compared to the alkaline lavas ($^{206}Pb/^{204}Pb \sim 20$, $^{208}Pb/^{204}Pb > \sim 39.5$). Nd and Hf isotopic signatures define narrower ranges, with shifts of < 2 ε units across this compositional boundary and markedly more radiogenic compositions than modern Etna lavas. We interpret the isotopic data to signify mixtures of MORB mantle and enriched mantle (defined as where MORB and OIB mantle compositions generally intersect). Major element modeling using compositions of the most magnesian basalts from early Etna lavas, as well as those from the associated Hyblean plateau, indicates that these lavas represent melting from relatively fusible lithologies (volatile-rich peridotites and pyroxenites) with lower solidi than ambient asthenospheric mantle. The prevalence of fusible lithologies coupled with enhanced convection due to the unique tectonic setting, gives rise to the voluminous volcanism in the Etna /Hyblean region.

Thermodynamics of long-term metastable magnesium (chloro) hydroxo carbonates at 25°C

C. BUBE, M. ALTMAIER, V. METZ, D. SCHILD, B. KIENZLER AND V. NECK

Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology, Herrmann-von-Helmholtz-Platz, 76344 Eggenstein-Leopoldshafen (bube@kit.edu, marcus.altmaier@kit.edu, volker.metz@kit.edu, dieter.schild@kit.edu, bernhard.kienzler@kit.edu)

The thermodynamics of magnesium (chloro) hydroxo carbonate phases is important to assess the geochemical conditions in carbonate-containing magnesium chloride-rich solutions for nuclear waste disposal scenarios in rock salt. Though Magnesite ($MgCO_3$) is known to be the thermodynamically stable solid in the Mg-Cl-HCO_3-CO_3-H-OH-H_2O system at room temperature, long-term metastable carbonates are observed to control the solution chemistry (Hydromagnesite ($Mg_5(CO_3)_4(OH)_2{:}4H_2O$) and Chlorartinite ($Mg_2CO_3OHCl{:}3H_2O$)). In the present study we focus on determining the phase transition between Hydromagnesite and Chlorartinite in order to estimate the equilibrium constant for Chlorartinite, which has not been reported so far.

Batch experiments with $MgCl_2$ solutions (0.25 to 4.5 M $MgCl_2$) and 0.05 M Na_2CO_3 are conducted over >3 years in Ar glove boxes. The pH_c ($-\log(m_{H+})$) is monitored with time and the respective precipitates are analysed with different methods (Raman, XRD, SEM-EDS, XPS). The equilibrium constant for Chlorartinite is calculated based on the equilibrium at the Hydromagnesite and Chlorartinite phase transition $Mg_5(OH)_2(CO_3)_4{:}4H_2O(s) + 3Mg^{2+} + 4Cl^- + 10H_2O(l) \Leftrightarrow 4Mg_2(OH)CO_3Cl{:}3H_2O(s) + 2H^+$. Calculations are done using the known $MgCl_2$-concentration, the measured pH_c and published solubility constants of Hydromagnesite. Under the given conditions, stability of Hydromagnesite is observed in solutions of less than 2.5 M $MgCl_2$, while Chlorartinite is found to exist in solutions with $MgCl_2$ concentrations higher than 3.2 M $MgCl_2$. In the intermediate solution of 2.8 M $MgCl_2$, both solid phases are detected with the analytical methods. Assuming a phase transition between 2.5 M and 3.2 M $MgCl_2$, the equilibrium constant for Chlorartinite is calculated as $\log K_{CA} = 13.15 \pm 0.36$ for reaction $Mg_2(OH)CO_3Cl{:}3H_2O(s) + 2\,H^+ \Leftrightarrow 2\,Mg^{2+} + HCO_3^- + Cl^- + 4\,H_2O(l)$, using the Pitzer approach for activity corrections. This equilibrium constant together with literature data allows for a comprehensive thermodynamic description of the system Mg-Cl-HCO_3-CO_3-H-OH-H_2O at room temperature.

Fluids in the upper continental crust

KURT BUCHER

Mineralogy Geochemistry, University of Freiburg, Germany (bucher@uni-freiburg.de)

The brittle upper continental crust consists predominantly of granite and gneiss. Fractures form an interconnected network of water conducting structures with an appreciable permeability also providing substantial fluid saturated fracture porosity.

The chemical composition of fluids in the fracture porosity of granite and gneiss changes with depth. Near the surface Ca-Na-HCO_3 waters dominate. With increasing depth water contains increasing amounts of alkalis and sulphate and grade into chloride-rich waters at greater depth. Total dissolved solids (TDS) of 10^5 mg L^{-1} are common at 5 km depth in most basement rocks. All reported deep fluids from the upper crust contain predominantly NaCl and $CaCl_2$. The brines vary from NaCl-rich in granites to $CaCl_2$-rich in mafic reservoir rocks such as amphibolites and gabbros.

In regions of the crust with strong topography, fluid flow is important and recharge water may have flushed the basement efficiently thereby removing old brine components from the granites.

Water samples from the new Gotthard Rail Base Tunnel of the Alps, from Norwegian road tunnels, from Korean granites and other localities represent this type of basement fluid. Analyzed fluids from up to 2.5 km depth differ from basement fluids from areas with less extreme topography in the following ways. Such waters have relatively low TDS of some 100 mg L^{-1} and are typically of the Na_2CO_3-Na_2SO_4 type. pH tends to be high and varies from 9 to more than 10. Low Ca and ultra-low Mg of such waters result from efficient deposition of secondary Ca-Mg-minerals as coatings on fracture walls. Reduction of CO_2 to amorphous carbon or further to CH_4 provides the oxidation capacity for sulphate production from primary rock sulphides. Ferrous iron silicate minerals (e.g. biotite) are oxidized to ferric oxides and hydroxides (e.g. hematite). Evidence for this mechanism is the presence carbon in sheared, water conducting granite and measurable quantities of methane in fracture water. Extreme local variations of redox conditions are reflected by the presence of pyrrhotite and other sulphides in a fracture system and anhydrite in nearby fractures of the same granite.

Geochemical signature of rocks of the neo-archean ultramafite-mafite mass in the Dzhugdzhur-Stanovoy Superterrane (the South-Eastern rim of the North-Asian craton)

I.V. BUCHKO[1]* AND S.D. VELIKOSLAVINSKY[2]

[1]Institute of Geology and Nature Management, Blagoveshchensk, Relochny, 1, Russia, (*correspondence: inna@ascnet.ru)

[2]Institute of Precambrian Geology and Geochronology, St.Petersburg, Russia

The first geochemical and geochronological data were obtained for the Neoarchean rhythmically stratified ultramafite-mafite massif in the Dzhugdzhur-Stanovoy superterrane of the south-eastern rim of the North-Asian craton.

The main petrochemical peculiarities of ultramafites and pyroxenites of the mass are the moderate increase in TiO_2 and FeO* contents at practically constant Al_2O_3, at a decrease of magnesia content from the earliest occurrences to the later ones. At the same time an increase in SiO_2, Al_2O_3 is typical for gabbro-anorthosites in the process of crystallization at a decrease of Mg# which is characteristic of high aluminiferous basalts. The duality of the petrochemical trends and the results of modeling suggest that crystallization of the rhythmically stratified ultramafites and gabbro-anorthosites occurred from two different melts corresponding in composition to pyrites and high aluminiferous basalts, respectively.

The conformity of spectra of REE and minor elements distribution are present. This lets us to conclude that the fusion of the both melts occurred from a single source that was close to Al non-depleted pycritoid in the intermediate magmatic chamber. It may be assumed that this ultramafite-mafite massif is an example of Arcean pycritoid magmatism.

The age of this massif is preliminary estimated as ~2.6 Ma (LA-ICP-MS method).

This study was supported by FEB RAS (Gr.No 09-II-SB-08-007).

Age relations, mineral-chemical and isotopic investigations on basaltic gem stone zircons from Eastern Germany

JÖRG BÜCHNER [1]*, OLAF TIETZ [1], WOLFGANG SEIFERT[2], AXEL GERDES[3] AND ULF LINNEMANN[4]

[1]Senckenberg Museum für Naturkunde Görlitz, D-02806 Görlitz, Germany
(*correspondence: joerg.buechner@senckenberg.de)
[2]GFZ Potsdam, D-14473 Potsdam, Germany
[3]Geozentrum der Universität Frankfurt, D-60438 Frankfurt a. M., Germany
[4]Senckenberg Naturhistorische Sammlungen Dresden, D-01109 Dresden, Germany

In alkali basaltic rocks scarcely appear accessory minerals such as zircon and corundum. The origin of these mostly gem stone like mega-crystals is unknown and discussed controversial. Host magmas of the zircon mega-crystals are normally SiO_2 undersaturated (basanites and nephelinites).

In several localities we could observe some zircon mega-crystals and in a quarry in Saxony (eastern Germany) we collected about 40 crystals up to 15 mm in size *in situ* from the basanitic rock [1]. Zircons occur in agglutinates of lower crater facies of a scoria cone. The related lava flows are almost free of zircons and their Zr contents reaches up to 900 ppm [2]. There is a good correlation between Ar/Ar data of the basanites (30 to 31 Ma) and the zircon U/Pb data which show ages about 30.5 Ma.

First investigations indicate two different alkaline sources for zircons which origin possibly from syenitic, phonolitic or trachytic melts. This is evidenced by zircon-typology, mineral chemistry and analyses of mineral inclusions [3]. Preliminary *in situ* Hf-isotopic analyses of zircons indicate an origin from the lithospheric mantle.

The crystals show an intensive magmatic corrosion in alkalibasaltic rocks (including nephelinites), whereas zircons out of phonolites are mostly euhedral. Zircons in basaltic rocks have more or less evolved reaction rims, composed mostly of baddeyleit. Zr-contents in the rims of clinopyroxene phenocrystals decreases rapidly with the distance from the zircon inclusions. This indicates late entrainment of zircon crystals into the basanitic melt.

The age data of the zircons in relation to that of the host rocks as well as the mineral chemical and isotopic data imply a cogenetic development of both.

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Petit spot-like volcanoes exposed in Costa Rica

D.M. BUCHS[1]*, S. PILET[1], P.O. BAUMGARTNER[1], M. COSCA[2], K. FLORES[1] AND A. BANDINI[1]

[1]IGP/IMG, University of Lausanne, Switzerland (correspondence: dbuchs@ifm-geomar.de)
[2]US Geological Survey, USA

The study of volcanism in the ocean is fundamental to better understand the dynamics of the Earth mantle and plate tectonics. However, our understanding of this volcanism is limited by difficulties to access the roots of ocean volcanoes and the ocean floor. Recent results in Panama shown that exposed accreted volcanoes can provide another way of understanding volcanism in the oceans [1].

Petit spot volcanoes found on the subducting plate off Japan are considered to reflect volcanism in response to plate flexure [2]. However, petit spot volcanoes are very small and it remains unclear if they are a common feature on the ocean floor; documenting new occurrences of petit spot volcanoes is a key multidisciplinary issue. We recognize here ancient petit spot-like volcanoes accreted in Costa Rica based on new geochemical, geological, ^{40}Ar-^{39}Ar, and biochronologic data.

Petit spot-like volcanoes acccreted in Costa Rica consists of tectnonic stacks of volcano-sedimentary material that includes vesiculated pillow lavas, volcanic breccias and thick radiolarite beds. Igneous sills compositionnally similar to the lavas are common in the radiolarite beds. Major and trace element contents of the igneous rocks indicate an alkalic, moderately fractionated composition, and support very low degrees of partial melting in the garnet stability field. Normalized trace element patterns are very similar to those of petit spot volcanoes in Japan, and distinct from those of typical OIB, MORB and off-axis seamounts.

Step-heating ^{40}Ar-^{39}Ar dating on co-magmatic amphiboles gave two ~175 Ma ages of formation for the petit spot-like volcanoes in Costa Rica. Tectonostratigraphic and biochronologic data clearly document a ~110 Ma age of accretion, and indicate that the volcanoes did not formed close to a subduction zone or a mid-ocean ridge. Therefore, we propose that petit spot-like volcanoes may represent a ubiquitous feature on the ocean floor, which can form far from mid-ocean ridges and subduction zones. Possibly, petit spot-like volcanoes exposed in Costa Rica reflect tectonically-induced leaking of melts pre-existing at the base of the lithosphere.

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Cross calibration of a Pb Multi Ion Counting array on TIMS

NADINE BUCHS, DIETMAR TUTTAS AND CLAUDIA BOUMAN*

Thermo Fisher Scientific, Hanna-Kunath-Str. 11, 28199 Bremen, Germany.
(*correspondence: claudia.bouman@thermofisher.com)

Multicollector instruments using arrays of Faraday detectors are the first choice for high precision isotope ratio measurements. With decreasing sample sizes, the noise level of the Faraday detectors becomes the limiting factor for high precision isotope ratio measurements. The new TRITON *Plus* TIMS provides Multi Ion Counting with up to eight ion counters in addition to its variable multicollector array of nine Faraday cups. Classical large scale SEMs can be combined with the newly introduced compact discrete dynode electron multipliers (CDDs). The performance of these small electron multipliers is directly comparable to the classical large-scale SEMs. Both show identical stability and linearity. Also dynamic range and noise characteristics are equal for both ion counter types.

In case of Faraday detectors, precise cross calibration is guaranteed by the gain calibration and baseline measurements. In a Multi Ion Counting array, individual yield factors must be taken into account, but the stability of the yield factors needs to be assessed as well to obtain ultimate precision for isotope ratio measurements.

This study presents two strategies for precise cross calibation of all ion counting channels. The first one includes a calibration up-front; the second strategy involved an in-run calibration to control yield drift. Experiments were done on a TRITON *Plus* setup with four ion counting detectors to collect ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. Internal correction for mass fractionation was done using ^{208}Pb/^{206}Pb.

Probing the Toba super-eruption: Oxygen isotope geochemistry of zoned quartz phenocrysts

D.A. BUDD[1]*, V.R. TROLL[1,4], E.M. JOLIS[1], F.M. DEEGAN[1], V.C. SMITH[2], M.J. WHITEHOUSE[3], C. FREDA[4], C. HARRIS[5] AND D.R. HILTON[6]

[1]Dept. of Earth Sci., CEMPEG, Uppsala University, Sweden
(*correspondence: david.budd.0339@student.uu.se)
[2]Research Lab. for Archaeology, University of Oxford, UK
[3]Swedish Museum of Natural History, Stockholm, Sweden
[4]Istituto Nazionale di Geofisica e Vulcanologia, Roma, Italy
[5]Dept. Geol. Sci, University of Cape Town, South Africa
[6]Scripps Institute of Oceanography, UCSD, California, USA

The Toba caldera located in Sumatra (Indonesia) is the source of the largest volcanic eruption in the Quaternary [1]. We present oxygen isotope data for a suite of zoned quartz phenocrysts (n=8) erupted as part of the Young Toba Tuff (YTT), an eruption event of approximately 2800 km^3 some 75 ka ago [1, 2]. Oxygen isotope data has been obtained by SIMS (n=92) in combination with cathodoluminescence (CL) imaging in order to establish the role of shallow level processes such as magmatic fractionation, magma-crust interaction and crystal recycling occurring in the Toba magmatic system. The CL images exhibit defined patterns of magmatic zoning which broadly coincide with fluctuations in δ^{18}O values in the quartz crystals, allowing correlation of textural and compositional data. Measured $\delta^{18}O_{quartz}$ values range from 6.7 ‰ to 9.4 ‰, independent of position on crystal core or rim. Values for $\delta^{18}O_{magma}$ have been calculated from quartz phenocrysts (assuming $\Delta_{quartz\text{-}magma}$ is 0.7 ‰ at magmatic temperatures). The lowest magma value is 6.0 ‰, apparently reflecting a primitive isotopic signal [3]. The maximum calculated magma value is 8.7 ‰ and the average is 7.2 ‰, indicating multiple sources to the Toba system including a significant crustal component. These new data allow us to unravel the heterogeneous magmatic system at Toba volcano, involving an evolved but dominantly magmatic melt and crustal partial melts reflected in elevated δ^{18}O crystal zones. Several crystals, however, show gradually lower values towards the rims pointing to either input from a less evolved magma or, more likely, a low-δ^{18}O contaminant from the shallow volcanic edifice. The crystals therefore record a complex and heterogeneous origin of the YTT magma, comprising an evolved igneous component and several substantial crustal contributions to finally assemble the massive volume of the Toba eruption.

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Microbial diversity and physiology of Alberta coal seams

K. BUDWILL[1]* AND S.P. KOZIEL[2]

[1]Alberta Innovates – Technology Futures, Edmonton, AB T6N 1E4, Canada
(*correspondence: Karen.Budwill@albertainnovates.ca)
[2]Alberta Innovates – Technology Futures, Vegreville, AB T9C 1T4, Canada (Susan.Koziel@albertainnovates.ca)

We have begun to map, using 16S pyrosequenicng and traditional enrichment culturing techniques, the microbial diversity and metabolic activities of coal from different Alberta coal zones. Results have implications for optimizing the bioconversion of coal to methane and other products.

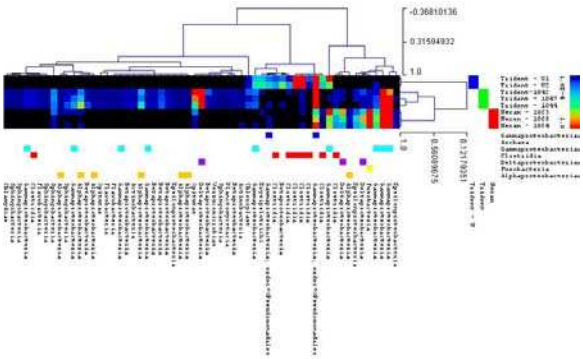

Figure 1: Hierarchical clustering tree (Linear Models for Microarray data significant taxons analysis) of 3 well sites from Mannville coal formation, Alberta.

Culture	μmol CH_4/mL culture
Coal + Tryptone	42.9
Tryptone only	11.7
Coal only	0

Table 1: CH_4 and CO_2 production at 55 days incubation in methanogenic cultures amended with 5 g coal and/or 0.05 g/mL tryptone.

Cluster analysis of microbial DNA sequences shows distinct microbial communities exist in Alberta coal deposits. The geochemical environment (e.g. salinity) likely influences community composition. Anaerobic culturing of the coal with 0.05 g/ml tryptone resulted in significant methane production and sequence reads related to *Methanobacter* increasing up to 30% from less than 1% of the total sequences detected in uncultured coal. GC-MS analysis of culture fluids provides evidence the microbial community uses coal as a carbon substrate in the presence of the nutrient.

Dynamics and evolution of the Earth's core and lowermost mantle

BRUCE BUFFETT

Earth and Planetary Science, University of California, Berkeley, CA 94720 USA (bbuffett@berkeley.edu)

Transport properties control many processes in the deep Earth. For example, the geodynamo is crucially dependent on electrical conductivity in the core. A typical estimate at relevant pressure and temperature is $5x10^5$ S m^{-1}, although this value is probably uncertain by a factor of two. At first glance a higher electrical conductivity might be expected to enhance the geodynamo. However, a higher electrical conductivity also implies a higher thermal conductivity, which suppresses the geodynamo. According to the Wiedemann-Franz law, an electrical conductivity of $5x10^5$ S m^{-1} corresponds to a thermal conductivity of 50 W K^{-1} m^{-1} at 4000 K. Approximately 8 TW of heat is carried by conduction toward the core-mantle boundary when the core is well mixed (i.e. adiabatic). This conductive transport represents a large fraction of the total core heat flow, suggesting that the transport due to convection is relatively small. Even modest changes in thermal conductivity can substantially alter the vigor of thermal convection. Present uncertainties in thermal conductivity permit widely varying estimates for the power available to drive the geodynamo.

Mass transport across the core-mantle boundary can also affect the dynamics and evolution of the core. Chemical disequilibrium between the core and mantle inevitably drives a flux of mass across the boundary, but the rate of transfer is limited by diffusion. Recent suggestions that the core is undersaturated in O and/or Si implies a flux of light elements into the core. Downward diffusion through the liquid core can produce a stratified layer 50 to 70 km thick if the flux of light elements from the mantle is sufficiently large. Dynamical arguments suggest that the residence time of material at the base of the mantle is 40 to 80 Ma. Steep chemical gradients in the mantle can drive a large mass flux, especially in the presence of partial melt or an interconnected ferropericlase phase. Local depletion of Si by transfer to the core would likely promote interconnection as the volume fraction of ferropericlase increases. Alternatively, a randomly oriented post-perovskite phase could permit a large flux. On the other hand, a large volume fraction of silicate perovskite at the boundary would likely suppress mass transfer. Differences in the mineralogy could have important implications for both the composition and dynamics of the core.

Net redistribution of ^{137}Cs over Australia

E.N. BUI AND A. CHAPPELL

CSIRO Land and Water, GPO Box 1666 Canberra, ACT 2601, Australia. (elisabeth.bui@csiro.au, adrian.chappell@csiro.au)

Cesium-137 (^{137}Cs), a radionuclide by-product of atomic testing, is a stratigraphic marker specific to the period of above-ground nuclear tests (1950s-70s), used to trace the movement of surficial material in terrestrial landscapes [1]. Its half-life is short (30.2 y) and its utility as a tracer will be of limited duration. We show here that its geographic pattern can shed valuable insight into contemporary geomorphic processes. We use geostatistics and estimates of net ^{137}Cs redistribution relative to a baseline reference fallout level to quantify and map topsoil erosion over Australia between 1950 and 1990. We show that net soil loss occurs in the main cultivated areas along the coastal regions of Western Australia, South Australia, Victoria, New South Wales, and Queensland. The most eroded area is in the Pilbara region of Western Australia, with median erosion rates > 6 t ha^{-1} yr^{-1}. The coincidence of net gain areas with eolian deposition in southeastern Australia suggests that the map is identifying wind-borne transport patterns. Eolian deposition in the Wet Tropics World Heritage Area supports the theory that dust is a major source of nutrients on ancient highly weathered soils where rainforests grow [2]. The potential for eolian deposition over the Wet Tropics is evident from an animation of MODIS imagery from the late September 2009 dust storm across Australia. However this is the first time that dust deposition over NE Australia has been substantiated.

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The first stepwise crushing data on C, N and Ar isotopic and elemental ratios in Guli carbonatites

A.I. BUIKIN[1], A.B. VERCHOVSKY[2], V.A. GRINENKO[1] AND L.N. KOGARKO[1]

[1]Vernadsky Institute of Russian Academy of Sciences, Moscow, Russia (bouikine@mail.ru)
[2]The Open University, Milton Keynes, UK

To get insight into the fluid regime evolution during formation of Guli massif (Maymecha-Kotuy magmatic complex, Syberia) carbonatites we have studied C, N and Ar isotopic and elemental ratios in foure carbonatite samples by stepwise crushing method. Mineral separates representing different formation stages of the massif have been selected for the investigation: two early calcites (Cal) and a late stage dolomite (Dol) and siderite (Sid).

The early calcites are carachterized by significantly lower CO_2 content and lower $\delta^{13}C$ values than the late Dol and Sid (-14.1, -13.6‰ and -9.0, -10.5‰ in average respectively). Fractionation during melt degassing (when system is closing) could lead to a higher CO_2 content with higher $\delta^{13}C$ values in the late minerals. But the results on C, N and Ar elemental compositions in the fluid inclusions have shown that C/N and C/Ar ratios also dramatically increase from the early to the late samples (C/N: from 7 in Cal to 210 in Sid and 2100 in Dol; C/Ar ; from 870 in Cal to 12300 in Sid and 159000 in Dol), which could not be caused by a simple magmatic fractionation. An additional source of CO_2 could appear at the late stages of the fluid-magmatic evolution of the massif. The data on C, N and Ar concentration variations in crushing steps support this assumption: well-defined correlations between concentrations of these elements in fluid inclusions are observed in the early Cal (i.e. all gases in the inclusions have the same elemental composition and concequently the same source). For the late Sid and Dol the situation is different: when N and Ar concentrations decrease with crushing steps, the C concentration is increasing, suggesting different sources for (N+Ar) and for most of CO_2. Moreover, $^{40}Ar/^{36}Ar$ ratios in early and late samples are quite different: 3680 in Cal and 657 and 549 in Sid and Dol, respectively. This suggests the air-like argon component to be domineted in fluids during formation of the late minerals.

Thus, relationships between C, N and Ar concentrations as well as differences in C and Ar isotopic compositions in fluid inclusions of the early and late carbonitites suggest that at the late stages of Guli massif carbonatites formation an additional CO_2 source with havier carbon and atmosphere-like Ar have contributed to the system.

The expansion of metal stable isotope biogeochemistry into biomedicine

T.D. BULLEN* AND M-N. CROTEAU

US Geological Survey, Menlo Park, CA 94025, USA (*correspondence: tdbullen@usgs.gov, mcroteau@usgs.gov)

Numerous metals are essential nutrients for human health, while others are toxic even at extremely low concentrations in body fluids and tissues. Moreover, a variety of metals and most recently nanometer-sized metals are increasingly being used as components of diagnostic and therapeutic agents to study or treat diseases and metabolic disorders as well as for drug and gene delivery, tissue engineering and pathogen detection. Several of the metals studied in the field of biomedicine, including Li, Ca, Fe, Cr, Zn, Cu, Mo, Ni, Cd and Hg, have variable stable isotope composition in natural materials which can now be measured accurately. Application of stable isotope tracing techniques normally used to study biogeochemical systems could be invaluable to biomedical research. Metal stable isotopes can be used to understand processes such as metal transfer among body pools, and may uniquely identify the fate of toxic metals delivered to the body in different forms such as nanoparticles or aerosols. Initial work has focused on Ca and Fe stable isotope variations in humans, reflecting the importance of bone mineral balance and blood chemistry to human health as well as the advanced state of analytical techniques for the determination of Ca and Fe stable isotope compostions.

Both natural abundance and enriched stable isotopes can be used to provide increased understanding of metabolic processes and pathways at a mechanistic level. Natural abundance stable isotope variations between ingested and excreted metals may prove useful for determining the onset of and recovery from metabolic disorder or disruption of homeostasis. Enriched stable isotopes may be particularly useful for studying processes involving metals in the body, since only very small quantities of enriched tracer are needed in the exposure media in order to create a signal in body tissues and fluids above background levels. Carefully crafted laboratory experiments with lower trophic level organisms will help guide the application of these tools to biomedicine. Coupled with continual advances in mass spectrometry, expansion of metal stable isotope biogeochemistry into the field of biomedicine will be an exceptional research opportunity for the coming years. Involving experts from the medical and other professions in this work and learning their "language" will be essential for success.

Vertical distribution of Fe and S species in anoxic water column of Pavin Lake (France): Electrochemical evidence for nanoparticulate FeS

E. BURA-NAKIĆ[1]*, I. CIGLENEČKI[1] AND E. VIOLLIER[2]

[1]Ruđer Bošković Institute, Bijenička 54, 10 000 Zagreb, Croatia (*correspondence: ebnakic@irb.hr, irena@irb.hr)

[2]Université Paris Diderot – IPGP-UMR CNRS, Cas Courrier 7052, 75205 Paris Cedex 13, France (viollier@ipgp.jussieu.fr)

Recently it has been shown that anodic oxidation of Hg by FeS at around -0.45 V can be used as an analytical protocol for electrochemical determination of FeS nanoparticules in natural waters [1]. The proposed protocol was tested on anoxic samples of Pavin Lake (France) where anodic waves were observed at -0.45 V (vs. Ag/AgCl); these correspond to an electrochemical transformation of particulate and/or nanoparticulate FeS to HgS.

A vertical profile of S(-II) obtained by voltammetric measurements showed that through the whole Pavin Lake monimolimnion layer a majority (~70 %) of S(-II) is in the form of FeS nanoparticulates. Concentrations of dissolved Fe(II) in the Pavin Lake monimolimnion layer are extremly high (up to the 1 mM) supporting our previous conclusion that Fe(II) is controling the speciation and distribution of S(-II) between dissolved and particulate phases [2,3]. At the oxia-anoxia boundary (from 61 to the 64 m), electrochemical measurements indicate presence of colloidal Fe(III) and /or Fe(III) organic species [2].

Thermodynamic calculations predict precipitation of FeS with log Ks value between -3.6 and -3.8 in the Pavin Lake monimolimnion layer. In the upper part of monimolimnion layer most probably precipitation of greigite is proceeding.

It was shown that modification of an Hg electrode with surface formed FeS has significant influence on the voltammetric Fe(II) determination, since cathodic reduction of Fe(II) in such conditions is occuring both on bare (-1.4 V) and on FeS modified Hg surfaces (-1.1 V)[1]; Fe(II) may be underdetermined when only the -1.4 V peak is measured.

This research was suported by COGITO and UKF grant 62/10.

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Inverse modelling of gas chemistry measurements

ALAIN BURGISSER, MARINA ALLETTI AND CLIVE OPPENHEIMER

ISTO-CNRS, 1A rue de la Férolerie, 45071 Orléans, France (burgisse@cnrs-orleans.fr; marina.alletti@cnrs-orleans.fr, co200@cam.ac.uk)

We illustrate the inverse modelling of gas chemistry measurements by using gas compositional data for both quiescent and explosive emissions from the lava lake at Erebus volcano, Antarctica. The multi-component degassing model used needs calibration with experimental data in order to partition correctly the volatile species between their gaseous and dissolved forms. Solubility experiments were made on phonolite lava from the lake for H_2O, and data from the literature were reformatted to obtain the fugacity-based solubilities of CO_2 and S.

The degassing model is based on the hypothesis that the gas phase is buffering the system and controls the balance of volatile species. Two types of calculations are performed, depending on whether the measured gas was in equilibrium with the surrounding melt at the lake surface (case 1), or was emitted in isolation from the lava contained in the lake (case 2). The inversion procedure starts by calculating the equilibrium composition of all the species assumed to coexist at atmospheric pressure. This is not straightforward, as the species that are best measured at the vent and those best constrained in the model do not always match. At Erebus, such discrepancy occurs for H_2S, which is simulated but not measured, and OCS, which is measured but not simulated. Compression is then performed by assuming mass conservation of the volatile elements, either applied to the mixture of melt and gas (case 1), or only to the gas (case 2).

Model results are projections at higher pressures (up to 3 kbar) of the gas composition measured at the surface. At Erebus, we find that the difference between the gas emitted explosively and that emitted passively can be explained by a common source situated at depths corresponding to as little as 300 bars pressure. While quiescent, the lake is either degassing in fully open system, or by the means of a convective system restricted between the surface and depths equivalent to 60 to 300 bars. Additional constraints on the magmatic system are obtained by comparing the simulated melt volatile contents with those measured in melt inclusions. We will discuss the limitations of the main model assumptions (chemical equilibrium, gas buffering of the redox state, and temperature effects).

Electrical resistivity imaging of a deep coal mine discharge

W. BURGOS[1]*, M. FITZGERALD[2], L. LARSON[1], L. HERWEHE[2], K. SINGHA[2], AND M. GOOSEFF[1]

[1]Dept. Civil Environ. Eng., Pennylvania State University, University Park, PA 16802, USA (*correspondence: wdb3@psu.edu, lnl5053@psu.edu, mng2@psu.edu)

[2]Dept. of Geosciences, Pennylvania State University, University Park, PA 16802, USA (mxf218@psu.edu, lmh5193@psu.edu, ksingha@psu.edu)

The biogeochemistry of iron cycling in acidic environments is quite complex where aerobic surface sediments and anaerobic subsurface sediments are often separated by only a steep redox gradient. The hydrodynamic conditions in these systems affect geochemical conditions that in turn affect microbial community structure. Hydrodynamic conditions can be observed directly at the surface, however, identification of e.g. areas of “fast” vs. “slow” flow are more difficult in the subsurface. To characterize flow paths and hyporheic exchange in the surface and shallow groundwater at an acid mine drainage (AMD) site, we used electrical resistivity imaging (ERI) at a stream emanating from a large abandoned deep coal mine in Cambria County, Pennsylvania. Because of the high conductivity (2,000 μS/cm) of the emergent AMD, we added clean fresh water (30 μS/cm) as a tracer to visualize the spatial and temporal distribution of the hyporheic exchange. Two-dimensional imaging of stream-groundwater exchange was collected from three locations in the study reach using three electrode transects across the stream. We were able to identify the location and spatial extent of a large artesian spring of AMD that contributed significant flow to the stream. Concurrent measurements of in-stream and in-well water chemistry were in good agreement with the inverted models of electrical resistivity. We believe this is the first report of a dilution tracer coupled with ERI for 2-D imaging of hyporheic extent in an acidic stream environment.

Uranium valence cycling with iron-rich phyllosilicates

W. BURGOS[1]*, F. LUAN[1], M. BOYANOV[2], K. KEMNER[2] AND H. DONG[3]

[1]Dept. Civil Environ. Eng., Pennylvania State University, University Park, PA 16802, USA (*correspondence: wdb3@psu.edu, ful6@psu.edu)
[2]Biosciences Division, Argonne National Laboratory, Argonne, IL 60439, USA (mboyanov@anl.gov, kemner@anl.gov)
[3]Dept. Geology, Miami University, Miami, OH 45056, USA (dongh@muohio.edu)

Iron-bearing phyllosilicate minerals are widely distributed in soils and sediments and often account for about half of the iron in soil. These minerals help establish the physical/hydrogeological conditions of subsurface redox transition zones because of their small size and limited hydraulic conductivity, and disproportionately buffer the redox conditions through the transition zone because they provide a large solid-phase reservoir of Fe(III)/Fe(II) (e.g., they are less susceptible to reductive dissolution as compared to oxides). We previously demonstrated that metal-reducing bacteria preferentially reduce soluble U(VI) over structural-Fe(III) in phyllosilicates; uraninite ($U^{IV}O_2(s)$) is rapidly reoxidized by phyllosilicate-Fe(III) (allowing U to serve as an electron shuttle); but at some thermodynamic endpoint, corresponding to an elevated concentration of structural Fe(II), phyllosilicate-Fe(III) can no longer oxidize uraninite. To better characterize this thermodynamic endpoint we conducted a series of abiotic experiments with synthetic uraninite and specimen phyllosilicate minerals, and with synthetic uraninite and clay-sized fractions from sediments collected from redox transition zones. We conducted these experiments using the unaltered clays (highest Fe(III) contents) and chemically-reduced clays (incremental increases in Fe(II) contents) to evaluate both kinetic and thermodynamic behaviour of their reactions with uraninite. Identical experiments were conducted where uraninite was replaced with non-sorbing, colorimetric redox indicators to quantify the reduction potential of the clays. Reaction products were characterized by U L_{III}-edge and Fe K-edge EXAFS spectroscopy and by TEM-electron energy loss spectroscopy.

Mixing of radiocarbon from high latitude oceans through the atmosphere and ocean during the last deglaciation: Results from Iceland and the Drake Passage

ANDREA BURKE[1,2]*, LAURA F. ROBINSON[2] AND NICKY J. WHITE[3]

[1]MIT/WHOI Joint Program (*correspondence: aburke@whoi.edu)
[2]Woods Hole Oceanographic Institution, 360 Woods Hole Rd. Woods Hole, MA. 02543 USA.
[3]Bullard Laboratories, Madingley Rise, Madingley Road, Cambridge, CB3 0EZ, UK

Radiocarbon is a sensitive tracer of carbon cycle processes over the last ~40 kyr. We present new radiocarbon reconstructions from U-Th dated deep-sea corals from the Reykjanes Ridge off Iceland. These results are compared to radiocarbon reconstructions from deep-sea corals in the Southern Ocean and published radiocarbon records from benthic foraminifera to further our understanding of the transfer of carbon between different reservoirs during the last glacial period and deglaciation.

Our dataset from Iceland comes from solitary and colonial corals collected by dredge from water depths ranging between 770 to 1680 m. U-Th ages of these corals range from modern to 40 ka. During the last glacial period at ~35 ka, radiocarbon reconstructed at 1680 m water depth was ~100‰ more depleted from the contemporaneous atmosphere than it is today. However at the Bolling-Allerod and throughout the Holocene these sites were better ventilated, with radiocarbon offsets from the contemporaneous atmosphere similar to those observed in this region today (~70‰).

Radiocarbon reconstructions from Iceland and the Southern Ocean do not show extreme radiocarbon depletions of the magnitude oberved in some intermediate-depth deglacial records (e.g. [1]). A comparison of $\Delta^{14}C$ records to other proxy data suggests that these large depletions cannot be explained by a common water mass (e.g. Antarctic Intermediate Water), since mixing of this water mass would dissipate any extremely depleted radiocarbon signature. However, the radiocarbon depletions that we do observe throughout the glacial ocean are large enough to explain the atmospheric drop in $\Delta^{14}C$ over the 'Mystery Interval' if we allow some direct transfer of carbon from the deep ocean to the atmosphere, such as through the Southern Ocean.

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Speciation of contaminant metals in red mud from Ajka, Hungary

I.T. BURKE[1]*, W.M. MAYES[2], C.L. PEACOCK[1], A.P BROWN[4], A.P. JARVIS[3] AND K. GRUIZ[5]

[1]Sch. Earth & Environ. and [4]Sch. Process, Environ. & Materials Eng., University of Leeds, UK (*correspondence: I.T.Burke@leeds.ac.uk)
[2]Centre for Environ. & Mar. Sci., University of Hull, UK.
[3]Sch. Civil Eng. & Geosci., Newcastle University, UK.
[5]Dept Appl. Biotechnol. & Food Sci., University of Technology and Economics, Budapest, Hungary.

The catastrophic failure of the sludge dam at the Ajkai Timfoldgyar Zrt alumina plant in Hungary on the 4th October 2010 resulted in the release of 700000 m^3 of caustic metalliferous red mud. Red mud leachate is hyperalkaline (pH 13) has elevated concentrations of metals and metalloids such as Al (1000 ppm) As, V, and Mo (4 - 6 ppm) and the red mud itself has elevated concentrations of As, V, Cr, Co, Ni and U (100-1000 ppm). These contaminants persist in water and sediment samples for up to 100 km downstream of the source. The long term effects of the red mud spill on the environment remain largely unknown, especially with respect to the behaviour of the toxic elements present. Here we describe the results of experiments using sequential extraction, electron microscopy and X-ray absorption spectroscopy techniques to characterise the occurrence of metal(loids) within the red mud.

SEM and TEM analysis of red mud material sampled from the dyke breach at Ajka was composed primarily of 10-100 nm haematite particles occurring as 100-700 nm aggregates and 1-4 μm sodium aluminosilicate particles. Transported samples also contain 10-40 μm silt particles, presumably entrained from local soils and sediments. In EDS analysis Cr, Ti, Al, Si, and Mn were associated with aggregates of nano-crystalline (~ 5 nm) haematite. Discrete 2-10 nm Ce-rich particles were also present. At Ajka, acid dosing and gypsum addition were extensively used to lower pH and precipitate soluble Al, As, V and Mo. Sequential extractions performed on transported red mud deposits determined that 70-90 % As and V are present in residual hard-to-leach phases. The remaining 10-30 %, however, occurred in weak acid / hydroxylamine HCl leached phases, which may represent the presence of freshly precipitated metal(loid) containing phases. XAS analysis of red mud samples and leachate precipitates focused on determining As and V speciation in both the labile and refractory phases present. This baseline information will help in predicting the likely environmental mobility, fate and the long term hazards from metal(loid) contamination associated with the spill.

Nucleosynthetic Mo and W isotope anomalies in Murchison leachates

C. BURKHARDT[1]*, T. KLEINE[2], N. DAUPHAS[3], F. OBERLI[1] AND R. WIELER[1]

[1]Institute of Geochemistry and Petrology, ETH Zurich, CH-8092 Zurich (*correspondence: burkhardt@erdw.ethz.ch)
[2]Institute for Planetology, University of Muenster, D-48149 Muenster
[3]Origins Laboratory, The University of Chicago, IL 60637, USA

Nucleosynthetic isotope anomalies at the bulk meteorite scale exist for several elements (e.g., Ti, Mo, Ru) and most likely reflect incomplete mixing of diverse presolar components in the solar nebula [e.g. 1]. These isotope heterogeneities contrast with uniform and terrestrial isotope composition for other elements (e.g., Hf, W, Os [2]). Constraining why planetary-scale nucleo-synthetic isotope anomalies exist for some elements but not for others can provide clues to understanding the early evolution of the solar nebula. To address this important issue we obtained Mo and W isotope data for acid leachates of the Murchison chondrite. About 16 g of Murchison was sequentially digested using acids of increasing strengths. Aliquots of these leachates were previously analysed for Os isotopes [3]. Here, in addition, the acid-resistant residue was completely digested after fusion with a laser.

The Mo and W isotope data, obtained by MC-ICP-MS at ETH Zurich, reveal large anomalies that correlate with each other as expected from nucleosynthetic theory [4] and can be accounted for by variable amounts of s-process Mo and W. A regression of ^{182}Hf-decay corrected W data in ε^{182}W-ε^{186}W space yields an initial ε^{182}W consistent with the solar system initial value [5]. The Mo and W anomalies do not correlate with Os isotope anomalies reported for the same samples [3], indicating that Mo and W are hosted in different carriers than Os. This can explain why planetary-scale isotope anomalies exist for Mo but not for Os. Furthermore, the well-correlated Mo and W isotope anomalies in the Murchison leachates combined with the observation that planetary-scale isotope anomalies exist for Mo but not for W suggests that Mo and W are hosted in distinct but chemically similar carriers. The different patterns of planetary-scale nucleo-synthetic anomalies thus seem to reflect the presence of distinct generations of presolar dust that have been homogenized to different degrees.

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Oxygen fugacity-dependence of zircon-melt trace element partitioning

A.D. BURNHAM[1,2]* AND A.J. BERRY[1,2]

[1]Department of Earth Science and Engineering, Imperial College London, SW7 2AZ, UK (correspondence: a.burnham08@imperial.ac.uk)
[2]Department of Mineralogy, Natural History Museum, London, SW7 5BD, UK.

A common feature of terrestrial igneous zircons is a marked excess of Ce over La and Pr, and a deficit of Eu relative to Sm and Gd. This Ce anomaly is attributed to the presence of Ce^{4+}, and this Eu anomaly attributed to the presence of Eu^{2+}; all other REE occur exclusively as M^{3+}. Therefore, the magnitude of these anomalies may record the oxygen fugacity (fO_2) at which the magma crystallised. It is often unclear, however, whether the Eu anomaly reflects directly the Eu oxidation state ratio of the melt from which the zircon crystallised, or whether the Eu content of the melt was depleted by fractional crystallisation of plagioclase (or other Eu^{2+}-bearing minerals) prior to zircon growth. The present study presents the first systematic data on the dependence of zircon-melt REE partitioning on fO_2.

Synthetic zircons were grown at 1 atmosphere from a flux-free melt of 'natural' composition, over a range of 14 log units in fO_2 (IW-4 to QFM+6). The resulting crystals were characterised by cathodoluminescence and analysed by secondary ion mass spectrometry (SIMS) and laser ablation ICP-MS for P, Sc, Ti, Y, REE, Hf, Th and U.

Increasing fO_2 results in the Ce and Eu anomalies becoming more and less pronounced, respectively. There is a narrow fO_2 range over which both anomalies were observed; however the two anomalies do not covary in the same manner as natural samples. Therefore, either partitioning depends strongly on temperature and/or melt composition, or most natural samples suffer removal of Eu from the system before zircon saturation. The Ce and Eu data will be combined with direct determinations by XANES (X-ray absorption near edge structure) spectroscopy of the effects of fO_2, temperature and melt composition on the redox state ratios of Ce and Eu.

The partitioning of Sc, Y, other REE and Hf is fO_2-independent, as expected. The presence of P in the melt does not affect partitioning. Ti partitioning remains constant, indicating that Ti^{3+} (likely to represent 10-20% of Ti at the most reduced conditions studied) shows similar partitioning behaviour to Ti^{4+}. The U/Th ratio of zircon varies systematically over more than one order of magnitude with fO_2.

Mantle controls on the geochemistry of Kīlauea lavas erupted over the last millennium

D.H. BURNS[1], A.J PIETRUSZKA[1], M.D. NORMAN[2], J.P. MARSKE[3], M.O. GARCIA[3] AND J.M. RHODES[4]

[11]Department of Geological Sciences, San Diego State University, San Diego, CA 92182-1020, USA
[2]Research School of Earth Sciences, Australian National University, Canberra ACT 0200, Australia
[3]Department of Geology and Geophysics, University of Hawaii, Honolulu, HI 96822, USA
[4]Department of Geology and Geography, University of Massachusetts, Amherst, MA 01003, USA

Lavas from Kīlauea Volcano display rapid geochemical variations on a time scale of decades to centuries. The wall of Kīlauea Caldera at Uwekahuna Bluff exposes a 135-m thick sequence of recent prehistoric lavas (erupted mostly between AD 900-1400) and tephra from an explosive eruptive sequence at the volcano's summit (the Uwekahuna Ash). This stratigraphic section allows us to re-create a detailed temporal record of the mantle controls on the geochemical evolution of Kilauea lavas erupted over the last millennium. Previously [1], we analyzed the Pb, Sr, and Nd isotope ratios and major-element abundances of a series of 24 successive lava flows from the upper portion of Uwekahuna Bluff. The $^{206}Pb/^{204}Pb$ and $^{87}Sr/^{86}Sr$ ratios of these lavas were found to converge with prehistroic Mauna Loa lavas of the same age. This observation was attributed to the rapid passage of a small-scale compositional heterogeneity through the melting regions of both volcanoes. Here we present a detailed geochemical study (major- and trace-element abundances, and Pb, Sr, and Nd isotope ratios) of four glass separates from the Uwekahuna Ash and the remaining 38 lavas exposed lower in the Uwekahuna Bluff, along with trace-element abundances for the upper 24 lava flows from Uwekahuna Bluff. These prehistoric lavas and glasses display a small, but systematic, temporal variation in ratios of highly over moderately incompatible trace elements (e.g. La/Yb) that correlates with fluctuations in the Pb and Sr isotope ratios. These correlations suggests that the lithology of the mantle source controls the degree of partial melting at Kīlauea. The origin of these differences in source lithology will be explored using the major- and trace-element abundances of the lavas.

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Mechanisms of deep crustal subduction and exhumation: Insights from numerical modelling

EVGUENI BUROV

ISTEP, UMR 7193 UPMC-CNRS, Case 129, T46-00 e2, University of Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris (evgenii.burov@upmc.fr)

The dynamic processes leading to syn-convergent crustal subduction and consequent exhumation of high pressure low and high temperature rocks in continental collision zones remain poorly understood. Using results of thermo-mechanical thermodynamically coupled numerical models, we here discuss different possible mechanisms of crustal subduction and exhumation. To reach that goal, oceanic subduction-continental subduction and collision is modelled using a forward viscous-elastic-plastic thermo-mechanical models and synthetic petrology models allowing to trace P-T-t paths, generated out of numerical simulations, and compare them with natural P-T-t paths. Different collision scenarios, as function of the convergence rate and thermo-rheological profile are also discussed. It is shown that crustal subduction may occur only at very specific conditions in terms of crustal rheology, structure, subduction rate and thermal regime. It is also noteworthy that the models predict strong variations in the exhumation rates during the subduction-collision stage, and indicate that UHP rocks are likely to be exhumed at the earlier stages of continental subduction. Several additional mechanisms related to strain localization due to strain softening, metamorphic reactions, heat dissipation and fluids are also discussed. A particular attention is paid to the role of surface processes, sedimentary content and inherited structures. The experiments also show that the dynamic pressure in the subduction channel is unlikely to deviate by more than ± 10% from the lithostatic approximation. The models are applied to a number of regions such as the Alpes, Zagros and Hymalaya showing each time a significant difference in the mechanisms of subduction and exhumation.

GEO-CARS: 3-D, chemically selective imaging of fluid inclusions with multimodal nonlinear optical microscopy

R.C. BURRUSS[1]*, A.D. SLEPKOV[2], A.F. PEGORARO[2] AND A. STOLOW[2]

[1]USGS, Reston, VA 20191 USA, (*correspondence: burruss@usgs.gov)

[2]National Research Council of Canada, Ottawa, Ontario, Canada (Aaron.Slepkov@nrc-cnrc.gc.ca; Adrian.Pegoraro@nrc-cnrc.gc.ca; Albert.Stolow@nrc-cnrc.gc.ca)

3-D images and spectra of methane-rich fluid inclusions have been recorded for the first time with coherent anti-Stokes Raman scattering (CARS) and associated nonlinear optical methods (second harmonic generation, SHG, and two-photon excitation fluorescence, TPEF). Laser scanning confocal microscopy (LSCM) with CARS was developed for biomedical imaging of lipids [1] (based on C-H stretching vibration) suggesting that we could image CH_4 in fluid inclusions. The CARS microscope uses a single ultrafast laser source that simultaneously generates additional nonlinear imaging modes (SHG and TPEF) [1]. All three signals are generated in the same focal volume and collected on separate detectors, creating high-resolution 3-D images with complimentary information such as evidence of aromatic hydrocarbons (TPEF) and sub-micrometer crystallographic disorder and internal surfaces in host minerals (SHG), in addition to the chemically-specific Raman spectral information from CARS at 2100 to 4500 cm^{-1}.

CARS images and spectra of CH_4-rich inclusions in sedimentary, igneous, and metamorphic rocks provide new information on methane in the crust. 3-D images of CH_4 and water clearly identify aqueous inclusions with CH_4-rich vapour bubbles that coexist with one-phase CH_4-rich inclusions. In crude oil inclusions, CARS spectra of CH_4 are clearly separated from fluorescence emission of the oil, allowing us to record, for the first time, the pressure sensitive peak position of CH_4 [2] in oil inclusions for input to PVT models of oil migration. Healed microfractures are visible in SHG allowing identification of distinct generations of CH_4-rich inclusions associated with specific fracture orientations. Some CH_4-rich inclusions in metamorphic and igneous rocks show TPEF signals that indicate the presence of aromatic hydrocarbons associated with CH_4. We believe this work demonstrates the broad potential of multimodal nonlinear optical microscopy and spectroscopy to provide new insight to the geochemistry of carbon in the crust and upper mantle.

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The role of microbial sulfidogenesis in shaping iron-sulfur-arsenic interactions within floodplain soils

EDWARD D. BURTON*, SCOTT G. JOHNSTON AND RICHARD T. BUSH

Southern Cross GeoScience, Southern Cross University, Australia; (*correspondence: ed.burton@scu.edu.au)

Introduction and objectives

Dissimilatory SO_4^{2-}-reducing bacteria play a key role in shaping the biogeochemical behaviour of Fe and As in floodplain wetland soils. These bacteria gain metabolic energy by coupling the anaerobic oxidation of organic C or H_2 with the reduction of SO_4^{2-}. This results in the generation of sulfide, which can interact via a series of often competing and complex reactions with both Fe and As. Here we discuss our recent research aimed at unraveling the role of microbial sulfidogenesis in shaping Fe-S-As interactions within flooded soils. More specifically, we examine how the onset of sulfate-reduction in floodplain soils can drive transformations in Fe mineralogy and cause associated changes in As mobility.

Methodological approach

To address this issue, we have employed a multi-scale approach spanning (1) field-scale investigations that include an essential integration of hydrological, geomorphological and geochemical observations, (2) a series of controlled advective-flow experiments with a pure culture of a sulfate-reducing bacteria (*Desulfovibrio vulgaris*) and (3) relatively simple batch-type incubations with a natural assemblage of anaerobic microorganisms.

Results and discussion

Aqueous sulfide is a powerful and facile reductant of Fe(III) that can drive the rapid reductive dissolution of poorly ordered ferric (hydr)oxides, such as ferrihydrite and schwertmannite. In the case of these poorly-ordered phases, the resulting production of Fe(II) can drive rapid formation of goethite – an Fe mineralogical transformation that appears to significantly retard As mobility. Under strongly sulfidogenic conditions, magnetite formation occurs preferentially along with the accumulation of Fe sulfide minerals.

Whilst sulfidogenesis initially causes pH-dependent release of Fe(II), sulfidogenesis can eventually sequester Fe via the the precipitation of Fe sulfide minerals. These minerals include mackinawite, greigite and pyrite – which appear to exhibit vastly contrasting affinities for As. Hence, the effect that Fe sulfide accumulation has on As mobility within floodplain soils is heavily dependent on Fe sulfide mineralisation rates.

Ancient lead trapped in the Earth's upper mantle

KEVIN W. BURTON[1,2], BENEDCITE CENKI-TOK[1,3], FATIMA MOKADEM[1,2], JASON HARVEY[1,4] AND IAN J. PARKINSON[1]

[1]Department of Earth and Environmental Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK.
[2]Department of Earth Sciences, University of Oxford, South Parks Road, Oxford OX1 3AN, UK.
[3]Géosciences Montpellier, UMR 5243 - CC 60, Université Montpellier 2, Place E. Bataillon, 34095 Montpellier cedex 5, France.
[4]School of Earth & Environment, University of Leeds, Leeds LS2 9JT, UK.

The isotope compostion of lead (Pb) the Earth's upper mantle (sampled by oceanic basalts) is far too radiogenic for evolution from chondritic (primitive solar system) material over 4.57 billion years, the so called 'Pb paradox' [1]. Loss of Pb to the core [2] or arrival in a late veneer [3], have both been proposed as mechanisms to account for this imbalance. Alternatively, recent Pb isotope data for orogenic peridotites suggests that such rocks could serve as a complentary reservoir of unradiogenic Pb [4]. However, orogenic peridotites may not be representative of the asthenopshere underlying present-day mid-ocean ridges, furthermore, it is unclear why such material is not sampled by oceanic basalts.

Here we show that sulphides trapped as inclusions in silicate minerals in abyssal peridotites from the North Atlantic ocean (ODP Leg 209; Site 1274A) preserve extremely unradiogenic Pb isotope compositions, some corresponding to an age of ca 1.8 billion years. These ages are indistinguishable from those preserved by Os isotopes in sulphides from the same abyssal peridotites [5], and demonstrate that both Pb and Os isotopes preserve an unequivocal record of ancient melt depletion in the sub-oceanic mantle. Therefore, at least, some of the Pb in the Earth's mantle is unradiogenic and complements the composition of oceanic basalts. That these sulphides contribute little of their Pb to the isotope composition of oceanic basalts may be due either to their entrapment in host silicate phases or else that they are generally present in refractory domains in the mantle that are little sampled by later melting events.

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Fe isotope cycling in ferruginous and anoxic Lake Pavin (France) from water column to sediment

V. BUSIGNY[1], N. PLANAVSKY[2], D. JÉZÉQUEL[1], P. LOUVAT[1], G. MICHARD[1], E. VIOLLIER[1] AND T. LYONS[2]

[1]IPGP, 1 rue jussieu, 75005 Paris, France; (busigny@ipgp.fr)
[2]Earth Sciences, Univ. of California Riverside, USA

Fe isotopes are an emerging biogeochemical paleoproxy that can improve our understanding of the Fe cycle in early Earth's ocean and early microbial evolution. Sediments deposited during the Precambrian record a large range of δ^{56}Fe values, with an exceptional negative excursion (down to -3.5‰) between 2.9 and 2.3 Ga, a transition period believed to be marked by stratified redox ocean basins. The origin of this negative excursion is still debated but may be linked to a unique period of water column Fe cycling or a time of enhanced microbial Fe reduction in Fe-rich sediments.

Lake Pavin is a unique stratified aquatic system characterized by permanent anoxic and ferruginous deep water (from 60 to 92 m depth) topped by oxic shallow water (from 0 to 60 m), and can thus be regarded as a modern analog for Archean ocean. In the present work, we have studied Lake Pavin Fe isotope cycling along a profile in the water column down to the sediment in order to bring new insights into the record of ancient rocks. Four sediment cores were drilled and analyzed: (1) in the oxic zone, (2) at the oxic-anoxic boundary, (3) under the peak of H_2S production from SO_4^{2-} reduction and (4) at the bottom of the lake. In the water column, dissolved Fe concentration increases with depth from 2 μM at the oxic-anoxic boundary to 1200 μM at the lake bottom, with δ^{56}Fe increase from -1.67 to +0.31‰. The very negative δ^{56}Fe of the oxic-anoxic boundary reflects the residue of Fe oxidation and precipitation. The δ^{56}Fe increase with depth is interpreted as a coupling between (1) diffusion of Fe enriched in heavy isotopes from the bottom of the lake towards the oxic-anoxic boundary and (2) a combination of Fe reduction of downgoing Fe(III) particles and ferrous-ferric Fe interations. Analyses of bulk sediment show δ^{56}Fe values close to the purported detrital source (i.e. basalts with δ^{56}Fe ~ 0.20‰). In contrast, Fe sequential extraction in sediments shows a significant variation in δ^{56}Fe. Iron isotope mass balance calculation in both water column and pore waters of the sediment cores indicate that Fe isotope variability in iron sulfides reflects mostly Fe chemistry in the water column rather than isotopic fractionation during diagenetic processes or sulfide precipitation in the sediment.

Long-term versus short-term weathering fluxes in contrasting lithologies at the Luquillo Critical Zone Observatory, Puerto Rico

H.L. BUSS[1,2]*, A.F. WHITE[1], A.E. BLUM[3], M.S. SCHULZ[1] AND D. VIVIT[1]

[1]U.S. Geological Survey, Menlo Park, CA 94025, USA
[2]Department of Earth Sciences, University of Bristol, Bristol, BS8 1RJ, UK (*correspondence: h.buss@bristol.ac.uk)
[3]U.S. Geological Survey, Boulder, CO 80303, USA

(Bio)geochemical and physical weathering processes in tropical watersheds produce most of the solutes and sediments discharged to the oceans. Thus, relative to their area, tropical systems are disproportionately important in terms of weathering, erosion, and global CO_2 cycles. In addition to influencing stream and ocean chemistry and sediment loads, weathering processes exert control over chemical transport in soils and regolith (e.g., saprolite), soil and saprolite formation rates, mineral nutrient availability, and microbial growth rates. Currently, the volcaniclastic Río Mameyes watershed is being investigated as a comparison to the nearby, well-studied, granitic Río Icacos watershed in order to better understand the influence of lithology on weathering processes, weathering fluxes, and mineral nutrient availability.

Both watersheds are located in the Luquillo Critical Zone Observatory in Northeastern Puerto Rico and are characterized by similar humid, tropical climate; high annual rainfall, high year-round temperatures, tropical montane vegetation, and high relief. In both watersheds, thick (37+ m in places) saprolites blanket the ridges, but the majority of the chemical weathering occurs at the bedrock-saprolite interface. Long-term weathering fluxes are calculated from mass losses in the weathering profiles between the bedrock and the saprolite and from the age of the regolith surface (determined by cosmogenic nuclides or U-Th disequilibria). Short-term weathering fluxes are calculated from solute chemistries and infiltration rates and can be compared to watershed flux rates. Comparison of these three calculations for each watershed can be used to identify the changes in weathering regime and environment over time. Comparison of the two different watersheds demonstrates the influence of lithology on weathering fluxes on different timescales.

Defining a landscape for microbial electron transfer to extracellular minerals

JULEA N. BUTT[1]*, ANDREW J. GATES[1], SOPHIE J. MARRITT[1], MARCUS EDWARDS[1], THOMAS A. CLARKE[1], LIANG SHI[2], JAMES K. FREDRICKSON[2], JOHN M. ZACHARA[2] AND DAVID J. RICHARDSON[2]

[1]School of Chemistry and School of Biological Sciences, University of East Anglia, Norwich NR4 7TJ, United Kingdom (*correspondence: j.butt@uea.ac.uk)
[2]Biological Sciences Division, Pacific Northwest National Laboratory, Richland, WA, USA

The respiratory reduction of extracellular minerals poses a considerable challenge to microbes. Redox events associated with generating proton motive force across the inner membrane to drive ATP synthesis must be coupled to transfer of electrons to the extracellular matrix. In *Shewanella* multi-heme cytochromes are support this translocation of electrons. The tetraheme containing protein CymA moves electrons from inner membrane quinols to the periplasm. Porin wrapped decaheme cytochromes provide a conduit for electron transfer across the outer membrane while additional cytochromes interface with the extracellular matrix. The redox activity of each of these cytochromes spans a distinct window of potential. Consequently when present together these cytochromes can provide both a reservoir to accommodate electrons arriving from quinol oxidation at the inner membrane and a variable driving force for delivering electrons to extracellular minerals.

Coevolution of early animals and environment

N. J. BUTTERFIELD

Department of Earth Sciences, University of Cambridge, Cambridge, UK CB2 3EQ (njb1005@cam.ac.uk)

Large scale coevolution of organisms and environment is conventionally viewed from the bottom up – with microbially driven biogeochemical cycles providing the ecological oportunity, and larger, more physiologically constrained organisms rapidly evolving in response. Nowhere has this approach been more popularly applied than in oxygen-limitation hypotheses aimed at the seemingly delayed appearance of large and/or predatory animals. In this presentation I consider the nature of biological/environmental coevolution through the Proterozoic-Phanerozoic transition.

There is no question that planetary environments and biogeochemical cycling changed dramatically through the the Ediacaran and early Cambrian, an interval also marked by the first significant appearance of macroscopic organisms in the fossil record. More significantly, fundamental shifts in the the composition and evolutionary dynamics of contemporaneous microfossils attests to the genuine absence of eumetazoans prior to the Ediacaran. If oxygen availability was a first-order constraint on animal evolution, then the critical threshold was crossed in the early Ediacaran. Evidence for earlier oxygen limitation comes from geochemical proxies for deep-water anoxia, though it is notable that these same signatures extend into early Palaeozoic strata – while evidence of significant surface water oxygenation extends well back into the Neoproterozoic.

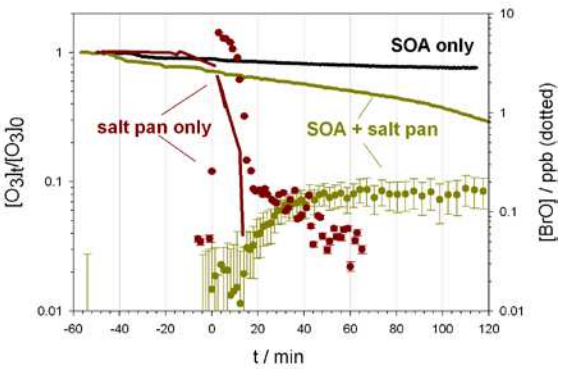
Such geochemical expression is difficult to reconcile with oxygen limitation hypotheses – particularly in light of the modest oxygen demand of most animals, and the conspicuous monophyly of the Metazoa. As such, the delayed appearance of eumetazoans is more convincingly ascribed to the extraordinary complexity of gene regulatory networks underlying organ-grade multicellularity; i.e., internal rather than external constraints. Once these developmental schemes were established, however, they opened up a new universe of ecological, evolutionary and biogeochemical phenomena, ranging from bioturbation and faecal pellets to the coevolutionary forcing of biomineralization, large body size, eukaryotic dominated phytoplankton and fundamental shifts in oceanic structure. Unlike the exclusively bottom-up microbial world of the pre-Ediacaran, the Phanerozoic biosphere must also be viewed from the top down – with animals playing a key role in the construction and definition of environments.

Influence of secondary organic aerosols (SOA) on "Bromine Explosion" in smog-chamber experiments

J. BUXMANN[2]*, N. BALZER[1], J. OFNER[1], U. PLATT[2] AND C. ZETZSCH[1]

[1]Atmospheric Chemistry Research Laboratory, BayCEER, University of Bayreuth, Germany
[2]Institute of Environmental Physics, University of Heidelberg, Germany
(*correspondence: joelle.buxmann@iup.uni-heidelberg.de)

It is assumed that SOA slow down the catalytic bromine release via "Bromine Explosion" (auto catalytic release of reactive bromine from salt surfaces). Based on this theory a new experimental setup was developed, in which a substrate NaCl/NaBr=300:1 mixture was placed on a teflon pan located in an aerosol smog-chamber [1]. Direct observation of BrO is possible using an active Differential Optical Absorption Spectroscopy (DOAS) instrument [2] in combination with a multi-reflection cell. SOA was formed during the ozone-initiated oxidation of α-pinene, catechol and guaiacol,



respectively [3].

Figure 1: Time profile of O_3(lines) and BrO(dotted) during experiments with different initial composition: with salt pan as halogen source (red), with SOA only (black) and with both (green). At t=0 the solar simulator was switched on.

The experiments showed that the presence of SOA modifies the kinetics of halogen cycles in the gas phase: With salt pan only a complete ozone depletion was observed within first 10 minutes due to "Bromine Explosion" with up to 6ppb BrO. With salt pan and SOA the BrO formation showed a delay and its maximum mixing ratio of 150 ppt was one order of magnitude lower than without SOA.

[1] Siekmann 2008), PhD-thesis, University of Bayreuth [2] Platt and Stutz (2008) Volume. ISBN 978-3-540-21193-*Springer-Verlag Berlin Heidelberg* [3] Ofner *et al*. (2011) *Atmos. Chem. Phys*., **11**, 1-15

Dissolved organic carbon and soil respiration release in undisturbed columns from SE Spain

A. BÜYÜKKILIÇ YANARDAĞ*, M. GÓMEZ-GARRIDO, M. D. ESTÉVEZ RODRÍGUEZ, I. H. YANARDAĞ AND A. FAZ CANO

Universidad Politécnica de Cartagena, Agrarian Science and Technology Department Research Group: Sustainable Use, Management and Reclamation of Soil and Water, Murcia/España (*correspondence: ab16@alu.upct.es)

When pig slurries (PS) are applied to agricultural fields at different rate, large amounts of carbon can be introduced into soils. Better knowledge land application of pig slurry is important to know influence on carbon in leaching experiment. This study assessed the leaching potential of carbon cycle after an intensive farm pig manure at rates of control, single, triple doses are applied and investigated 'how is the relation between leaching of dissolved organic carbon (DOC) and soil respiration in the laboratory leaching experiment in silty loam soil?'.

Leaching was carried out weekly using distilled water to simulate the monthly rainfall events in the study area. Experiment was carried out for 12 weeks rainfall. Soil solutions and CO_2 were analyzed in each week. The results showed that; DOC are changed between 1.1 and 24.3 ppm, DIC are changed 20.5 and 47.8 ppm, NT are changed 2.3 and 55.9 ppm. during leaching experiment. Soil respiration varied between 10 and 150 mg C-CO_2 kg^{-1} soil h^{-1} in the control, between 10 and 250 mg C-CO_2 kg^{-1} soil h^{-1} in single plots, between 10 and 450 mg C-CO_2 kg^{-1} soil h^{-1} in triple plots.

Dissolved Organic and Inorganic Carbon, Dissolved Nitrogen, are effected temperature, and pH in the leaching system. pH is a more important factor for DOC leaching than temperature. Soil respiration is not significantly affected by pig manure application even during the four weeks, which is found balance and hold C in the soil with application. In single doses plots, respiration values are strongly correlated with time and also this dose is the agronomic rate of N-requirement (170 kg N/ha/yr) [1]. Finally, single application doses to silty loam soils have positive effect on carbon to the atmosphere and ground water.

[1] Directive 91/676/EEC (1991), *Concerning the protection of waters against pollution caused by nitrates from agricultural sources*. Ofic. J.L 375, 31.12. European Union, Brussels.

Inorganic and organic occurences from diagenesis of the Güvenç formation shales in the Adana basin, Turkey

A. BUYUKUTKU[1]* AND M. ALBAYRAK[2]

[1]Ankara University Engineering Faculty, Department of Geological Engineering, 06100 Besevler, Ankara, Turkey (*correspondence: butku@eng.ankara.edu.tr)

[2]General Directorate of Mineral Research and Exploration, Sogutozu, Ankara, Turkey (mustafa_albayrak@hotmail.com)

In the study, shale diagenesis of Güvenç Formation in Adana Basin was determined on the surface samples. Güvenç shales consist of organic matter (% 0.3-0.4) for hydrocarbon formation. X-Ray Diffractometer, Scanning Electron microscope equipped with an energy dispersive analyzer were used for detailed mineralogical, microstructural and elemental analysis for shale diagenesis. Fourier transform infra red spectroscopy (FTIR) was used for organic sample origin in the Güvenç Shales.

Diagenesis in the shales principally involves the progressive development of various types of cements in the following order: Calcite and feldspar formation, mixed layer smectite-illite and smectite-chlorite authigenesis, illite, chlorite authigenesis, quartz.

The C-H peak at 860 cm^{-1} shows the occurrence of aromatic groups (Fig. 1).

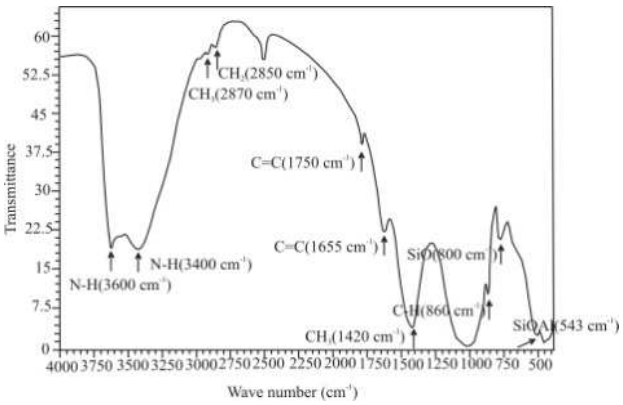


Figure 1: FTIR spectrum of the sample

Gallium oxide solubility in vapor and indicators of heterogeneous fluid filtration

A.YU. BYCHKOV, S.YU. NEKRASOV, I.YU. NIKOLAEVA AND S.S. MATVEEVA

Moscow State Universiy, Moscow,Russia (bychkov@geol.msu.ru)

The solubility of gallium and aluminum oxides in gas phase in the system Ga_2O_3 (Al_2O_3)-HCl-H2O was studied at 200-350ºC and pressure up to saturated vapor. The concentration of gallium increases with the increasing of HCl pressure. The formulae of gallium gaseous specie was determined as $GaOHCl_2$. The constant of gallium oxide solubility reaction was calculated at 200, 250, 300 and 350ºC. The concentration of aluminum in gas phase is insignificant in the same conditions. The possibility of gallium transportation in gas phase with small quantity of Al allow to separate this elements in hydrothermal processes with gas phase. The Ga/Al ratio can be used as the indicator of gas phase separation and condensation. The separation of gas and liquid phases was determined on greisen deposits by carbon isotope fractionation of carbon dioxide in fluid inclusion. The important feature of both ore mains is heterogenization and boiling of ore-forming fluids. Greisen ore bodies are formed as a result of strongly focused fluid flow in the T-P gradient fields. Gas and liquid phase separation specifies the vertical zonality of quartz type veins. The gas phase with the high gallium concentration is separated from a flow of liquid phase. Liquid phase react with the granites forming greisen metasomatites. Condensation of the gas phase in upper parts of massive produces the increasing of Ga/Al ratio in muscovite 3-5 times more, then in granites and bottom part of vein (from $2 \cdot 10^{-4}$ to $8 \cdot 10^{-4}$ mass ratio). The muscovite type veins has no separation between gas and liquid due to there thickness and small pressure gradient. There is no difference in Ga/Al ratio in muscovite from this veins. The Spokoinoe deposit is classified by mineralized dome type. The heterogenization of fluid occurs in H_2O-CO_2 system for water phase and carbon dioxide with temperature decreasing. Two-phase flow is separated in granite, forming greisen metosomatites. The Ga/Al ratio in rock increase up to 3 times to the upper part of metasomatitic zone. The Ga/Al ratio in muscovite can be applied for other hydrothermal systems for geochemical indicator of gas phase separation and condensation zone determination.

Geochemical evidence for lithosphere delamination beneath the central Rio Grande rift

B.L. BYERLY* AND J.C. LASSITER

Geological Sciences Department, University of Texas at Austin, Austin, TX, USA
(* correspondence: benbyerly@utexas.edu)

Seismic studies have shown a low-velocity zone in the mantle that extends up to the Moho (~40km) beneath the central Rio Grande rift (RGR). Gao *et al*. [1] interpreted the low velocity zone to be the result of delamination of the original (≥100km thick) Proterozoic lithosphere and replacement with hot asthenosphere. However, hydration or melt infiltration of the lithosphere could also produce the observed low wave speeds. We have examined the geochemical signatures of spinel peridotite xenoliths hosted in alkalic basalts erupted near Elephant Butte, NM, USA in the central RGR in order to determine their chemical affinity (old continental lithosphere or young asthenosphere), and thereby test the delamination hypothesis.

Peridotite xenoliths from Elephant Butte can be divided into two distinct groups. One group is commonly fine grained and displays foliation. These are relatively fertile (3.5-4.5 wt.% Al_2O_3), have depleted Sr- and Nd-isotope signatures (e.g. $^{87}Sr/^{86}Sr \approx 0.7018$-$0.7025$), $^{187}Os/^{188}Os$ ranging from 0.124-0.130, and are LREE depleted with flat M-HREE. These signatures are similar to fertile abyssal peridotites, thought to represent the convecting upper mantle. In contrast, the other group are coarser grained, more refractory (~1.5wt. % Al_2O_3), display LREE enrichment, unradiogenic $^{187}Os/^{188}Os$ (~0.120), radiogenic $^{87}Sr/^{86}Sr$ (0.7041-0.7043) and lower modal abundance of CPX. These signatures are characteristic of Proterozoic SCLM. Two-phase pyroxene geothermometry of xenoliths from Elephant Butte shows no significant difference in temperature (~1000°C) between the two groups. Based on a local heat flow of 90mW/m^2 these temperatures correspond to a depth of ~45km.

The fertile xenoliths most likely represent convecting asthenospheric mantle that has recently replaced the lithosphere. The refractory xenoliths represent Proterozoic lithosphere which has undergone varying degrees of ancient melt depletion and metasomatism. This indicates that lavas from Elephant Butte are sampling the lithosphere asthenosphere boundary which lies at ~45km depth and that significant thinning of the lithosphere has occurred, consistent with the delamination hypothesis of Gao *et al*. [1].

[1] Gao *et al*. (2004) *J Geophys Res* **109**, B03305.

Using bacteria to produce tailored magnetic nanoparticles

J.M. BYRNE[1]*, V.S. COKER[1], N.D. TELLING[2], G. VAN DER LAAN[1,3], D. J. VAUGHAN[1], R.A.D. PATTRICK[1] AND J.R. LLOYD[1]

[1]SEAES, Williamson Research Centre for Molecular Environmental Science, University of Manchester, M13 9PL, UK
(*correspondence: James.Byrne@postgrad.manchester.ac.uk)
[2]Institute for Science & Technology in Medicine, Keele University, Stoke-on-Trent ST4 7QB, UK
[3]Diamond Light Source, Didcot, Oxfordshire OX11 0DE, UK

Magnetic iron oxide nanoparticles of the form $M_xFe_{3-x}O_4$ (M = Co, Zn, Cr, Mn etc.) are useful for a wide range of applications including targeted cancer therapies, remediation of contaminated ground waters and data storage devices. Many current production processes use chemical and mechanical methods which often use toxic reagents and are expensive. This work presents an alternative biotechnological approach, harnessing the reductive capabilities of the subsurface Fe(III) reducing bacterium *Geobacter sulfurreducens* which yields relatively large quantities of magnetite nanoparticles at ambient temperatures.

The intrinsic magnetism and small size of the nanoparticles are paramount to their commercial use, and must be optimised during production for specific applications. In this study, the incorporation of dopants including zinc and cobalt into the structure of the biomagnetite nanoparticles was studied, and changes in the magnetic and structural properties of the resulting iron oxide minerals quantified. We demonstrated a significant increase in the magnetic moment of the particles at 5K and room temperature by doping with relatively low quantities of zinc, whilst cobalt induced large increases in coercivity. The inclusion of dopants also significantly affected the size of the nanoparticle crystals, with decreases from ~20nm to 8nm observed as dopant concentration increased.

Analytical methods including x-ray absorption, (XAS and XMCD), SQUID magnetometry and Mössbauer spectroscopy were used to provide important information about the mineral structure and indications of where in the crystal the dopants were incorporated, i.e. tetrahedral or octahedral components of the magnetite. Such techniques are vital to better understand how to improve bioproduction methods in order to maximize the potential of biogenic nanoparticles.