Los Morros olivine basalts from the Domeyko Cordillera in the Antofagasta region, northern Chile

O.M. RABBIA1*, C. JARA2, L.B. HERNÁNDEZ1 AND E. ARAGÓN3
1Instituto GEA, Universidad de Concepción, P.O. Box 160c, Concepción, Chile
*correspondence: rabbia@udec.cl)
2Cía. Minera Barrick Ltda. Barrio Industrial Alto Peñuelas Sitio 58, Coquimbo, Chile (cjara@barrick.com)
3Centro de Investigaciones Geológicas (UNLP-CONICET), La Plata, Argentina (earagon@cig.museo.unlp.edu.ar)

In the eastern flank of the Domeyko Cordillera at 23º45' S two types of olivine basalts crop out as lava flows covering the Permian crystalline basement and as sills in Jurassic limestones. The basalts lay on an uplifted crustal block within the transpressional Domeyko fault system (DFS).

One type is an olivine-phyric alkali basalt, with Mg# 62-67, Ni 120-190 ppm and Cr 205-338 ppm. The Ta/Hf (>0.4); La/Nb (<2) and Ba/Nb (12-31) ratios suggest an intraplate-like affinity (OIB-type mantle source).

The other, is an olivine-clinopyroxene-phyric transitional basalt (in TAS diagram), with high Ba/Nb (90-100) and Th/Nb (>0.2) ratios indicating an arc affinity. A primitive character is suggested by: Mg# 70-74; Cr 870-1100 ppm, Ni 220-300 ppm and olivine phenocrystal with core compositions (2300-3200 ppm Ni and Fo88-92) in the range of mantle olivines. Its source is more refractory than that of the alkali basalt.

New 40Ar/39Ar step-heating ages ranging from 55.6±1.4 to 56.7±1.0 Ma (this work) place the alkaline magmatism in the Palocene-Eocene transition. These ages are close to, but slightly older than the 52.5±1.8 Ma (K/Ar, [1]) for the spatially associated transitional basalts with arc-affinity.

The nature and close relationship in space and time of these basalt types is consistent with short crustal residence time and deep major faults in extensional zones. The Los Morros basaltic magmatism may imply that the inverse structures of the DFS associated to these mafic rocks may represent step-inverted normal faults inherited from Paleocene and/or previous extensional episodes, later reactivated by the transpressional Incaic tectonic event, which uplifted the Domeyko Cordillera during the Eocene-Oligocene time.


Metal isotope fractionation during microbial processes in the Critical Zone

K. RABE1*, A. SCHIPPERS2, S. WEYER1, S. SCHUTH1 AND M. LAZAROV1
1Leibniz Universität Hannover, Institut für Mineralogie, Callinstr. 3, 30167 Hannover, Germany
*correspondence: k.rabe@mineralogie.uni-hannover.de)
2Bundesanstalt für Geowissenschaften und Rohstoffe, Stillweg 2, 30655 Hannover, Germany (Axel.Schippers@bgr.de)

Oxidation of sulfide minerals (e.g. pyrite) in sulfidic mine waste leads to the formation of acid mine drainage [1]. Herbert and Schippers (2008) found large Fe isotope fractionations (Δ⁸⁶Fe: -1.4‰ to -2.4‰) between pore water and Fe(oxy-)hydroxides in mine tailings and concluded that this was the product of microbially catalyzed iron cycling [2].

In this study the potential of Fe and Cu isotope fractionation analysis is investigated to fingerprint microbial oxidation of metal sulfides in mine tailings. We focus on the investigation of the metal isotope fractionation between the sulfides and the metal(oxy-)hydroxides. We tested the selectivity of a sequential extraction method consisting of six extraction steps, to distinguish between sulfates, carbonates, Fe(oxy-)hydroxides, oxides, sulfides and silicates [3, 4]. For this test we used a synthetic test sample with known Fe isotope ratios of the components. The first results show that for Fe isotopes no significant isotope fractionation occurs during the extraction.

In the next steps we will adopt this sequential extraction method to natural samples from a porphyry copper mine tailings in Chile [5, 6] and determine the Fe and Cu isotope compositions of the particular fractions. In addition, we will perform laboratory experiments of microbial mineral oxidation and compare the isotope fractionation with that in the mine tailings.

Groundwater Resource Management of Rampurbaghelan Area, Satna District, Madhya Pradesh India

RABINDRA N. TIWARI
Department of Geology, Govt. P.G. Science College Rewa, Madhya Pradesh (email: geogppandey@gmail.com)

The paper deals with management of groundwater resource of Rampurbaghelan area Satna district, Madhya Pradesh. Geologically, the area is a part of Bhandar Group of Vindhyan Supergroup. The limestone and shale are the main aquifers of the area. For the assessment of groundwater resource, groundwater recharge, groundwater development stage, water table trends, water table fluctuation etc. have been studied. The Pre and Post monsoon water tables are falling. The calculated stage of groundwater development suggests that the area falls in semicritical category. However due to decline in water level, quality and quantity of groundwater have been adversely affected. For scientific management, utilization and augmentation of groundwater resource, the following suggestions have been recommended:

Artificial recharge structures like percolation pond, check dam and contour trenches should be preferred at suitable sites with the help of geological and geomorphological data.

The area having moderate slope can be utilise for contour bunding. The soil taken from the trenches may be placed down the hill in the form of bund. The soil erosion and vegetation cover can be controlled by growing such seeds of grasses and shrubs on the bunds which are suitable to the area.

Recharge augmentation is positive may, while pumpage control is negative way of management. In extreme cases, when pumpage control is to be observed in the area, the best way of monitoring is at the level of Gram Panchayat.

The groundwater management policies and practices should transcend from academic echelon to actual field implementation. All the related departments publics, stake holders and research institution should be jointly initiate the sustainable action plan with short term and long term plan strategy. Besides these, NGO's may play vital role to conserve the groundwater resource of the area.

The awareness programme is honestly and urgently needed.

Proteogenomic insights into completely oxidizing sulphate reducers (Desulfobacteriaceae)

RALF RABUS¹

¹Institute for Chemistry and Biology of the Marine Environment (ICBM), University Oldenburg, Oldenburg, Germany; rabus@icbm.de

Sulfate-reducing bacteria are pivotal to carbon turnover in marine sediments, as Jørgensen (1982) demonstrated in his seminal work on organic carbon rich shelf sediments. The observed high in situ activities could concurrently be explained best by the key properties of newly discovered sulphate reducers belonging to the family Desulfobacteriaceae (Widdel 1988): (i) capacity to completely oxidize organic carbon to CO2, and (ii) broad nutritional versatility spanning from simple fermentation end-products to less well degradable substrates such as aromatic compounds. These early findings and concepts motivated more recent genomic and proteomic investigations to further our molecular understanding of this group’s physiological capacity. The first published genome of a Desulfobacteriaceae member was that of Desulfobacterium autotrophicum HRM2 (Strittmatter et al. 2009), which degrades long-chained fatty acids and is capable of chemolithoautotrophy (with H2 and CO2). The 5.6 Mbp genome displayed an unusually high degree of plasticity and contains a large suite of genes for regulation and electron transport. The recently completed genome of Desulfobacula toluolica Tol2 (Wöhlbrand et al. 2012) in combination with sub-proteomics and metabolite analysis allowed a detailed reconstruction of the catabolic network for aromatic-compound utilization and discovery of new degradative capacities. Taken together first genome-based insights are emerging that causally explain the ecosystems function of Desulfobacteriaceae.


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Sedimentary and diagenetic features of the Oolithe Blanche formation (Middle Jurassic): New contribution from Ca, Sr, C, O isotopic compositions

SETAREH RAD1, YASIN MAKLHOUFI2, CATHERINE GUERROT1, CHRISTINE FLEHOC1 and PIERRE-YVES COLLIN3

1BRGM, 3, avenue Claude-Guillemin, Orléans, France
2UPMC Univ. Paris 06, UMR 7193, ISTeP, Paris, France
3Université de Bourgogne, UMR CNRS 5561, Dijon, France

The Oolithe Blanche formation is present in the Paris Basin at more than 1500 m depth in the middle of the basin and on outcrops at the basin edges. This Bathonian formation (Middle Jurassic) is composed of very shallow marine oolithic and bioclastic limestones, located within a shoreface depositional environmental (Casteleyn et al., 2010).

Calcium, strontium, carbon and oxygen isotopes have been analysed both in ooids and interparticular cement directly extracted from the limestone in order to study sedimentary and diagenetic environment.

The $^{44}\text{Ca}/^{40}\text{Ca}$ ratios (expressed as $\delta^{44/40}\text{Ca}_\text{SW}$) were measured by TIMS using a $^{42}\text{Ca}-^{48}\text{Ca}$ double-spike. Carbon and oxygen isotopic ratios were measured by IRMS.

Preliminary results show a range of $\delta^{44/40}\text{Ca}_\text{SW}$ from -0.74‰ to -1.09‰ in the cement and from -0.85‰ to -1.05‰ in ooids. Carbon isotopic signature show a range of $\delta^{13}\text{C}_\text{vs PDB}$ range from 1.5‰ to 2.7‰ in the cement and from 1.5‰ to 2.4‰ in ooids while $\delta^{18}\text{O}_\text{vs SMOW}$ vary from 21.5‰ to 23.9‰ in the cement and from 21.2‰ to 24.9‰ in ooids.

This first multi-isotopic approach on Oolithe Blanche formation seems to be consistent with the diagenetic evolution of Paris Basin. Effects of diagenesis on the isotopic signatures will be discussed.


Role of small urban reservoirs in regulating watershed quality

L.K. RADEMACHER1* AND K.L. FAUL2

1University of the Pacific, Stockton, CA, 95211, USA
(*correspondence: lrademacher@pacific.edu)
2Mills College, Oakland, CA, 94613, USA (kfaul@mills.edu)

Many coastal creeks in California drain small upstream reservoirs. These reservoirs were originally created to store drinking water, but many are currently maintained for recreation, irrigation, and other purposes. More than 200 of these reservoirs are located within the San Francisco Bay (SFB) area, which is western North America’s second largest urban area. As a result, these small individual reservoir/creek systems contribute a significant proportion of pollution to the coastal ocean. Understanding modern and historic biogeochemical cycling in urban watershed/reservoir systems provides new insight into anthropogenic influences on the function of these systems, how differing management strategies in these systems may mitigate or exacerbate contaminant discharge to the urban-influenced coastal ocean, and how best to manage these systems for improved water quality and beneficial use in the future.

The present study investigates three watershed/reservoir systems in the east SFB region to better understand biogeochemical cycling in disturbed urban environments. For example, Lion Creek/Lake Aliso is an acid mine drainage impacted system and the Don Castro/San Lorenzo Creek system is influenced by freeways and residential land uses. In comparison, the relatively undeveloped Lake Anza/Wildcat creek is primarily surrounded by parkland. Water quality data (including standard geochemistry, as well as nutrient and trace element concentrations) from reservoir inlets and outlets at each of these systems is collected biweekly. Depth profiles of pH, conductivity, temperature, and dissolved oxygen within each lake are also collected biweekly. In addition, sediment cores from multiple locations in each lake were collected and analyzed for nutrient and trace element concentrations.

Preliminary results indicated urban reservoirs play an important role in biogeochemical cycling in urban watershed and downstream water quality. Lake water column structure varies over the course of a year with reducing conditions prevailing during warm summer months and more oxidizing conditions occurring during more winter months. The oxygenation state of these lakes ultimately plays a significant role in whether metals and nutrients are mobilized or retained. In addition, sediment cores from each of the lakes indicate changes in how these lakes cycle elements has changed through time in response to differing managing strategies.
FTIR imaging of carbon dioxide diffusion in cordierite-like structures

F. RADICA1,*, F. BELLATRECCIA1, G. DELLA VENTURA1, C. FREDA2, G. CINQUE3 AND M. CESTELLI GUIDI4

1Università degli Studi Roma Tre, 00146 Rome, Italy
(*correspondence: fradica@uniroma3.it, bellatre@uniroma3.it, dellaven@uniroma3.it)
2INGV, 00143 Roma, Italy
3INFN-LNF, 00044 Frascati (Rome), Italy
4Diamond Light Source, OX11 0DE Didcot, UK

Cordierites and beryls are isostructural minerals that may diffuse significant amounts of H2O and CO2 through their structural channels, running along the c axis, [1]. Experimental introduction of CO2 in cordierite-like structure was studied by several authors [2, 3], who pointed out the extreme difficulty to reach sample saturation and homogenization.

In this work we treated cordierite and beryl volatiles-free single-crystals in CO2-saturated environment at different PTt conditions. The run products were analyzed via micro-FTIR spectroscopy in order to quantify the CO2 content and its distribution across the sample.

Preliminary results show that pressure plays a major role in diffusing gaseous CO2 across both cordierite and beryl, whereas the effect of temperature is less pronounced. Detailed FPA (focal-plane-array of detectors) imaging shows that the diffusion occurs along the structural channels starting from the basal pinacoids along the c-axis direction. As expected, no diffusion occurs perpendicularly to the c-axis. The diffusion path of CO2 does not exceeds 200 µm even after 10 days. Sample cracks formed during the experimental runs speed up diffusion; measured CO2 contents along these cracks are even 4 times higher than in the rest of the sample.


Figure 1 - FPA image and single spot IR transect of a single-crystals in CO2-saturated environment at different PTt conditions. The run products were analyzed via micro-FTIR spectroscopy in order to quantify the CO2 content and its distribution across the sample.

Glacial-interglacial changes in ocean carbonate chemistry constrained by boron isotopes, trace elements, and modelling

JAMES W.B. RAE1, JESS F. ADKINS1, ALAN FOREMAN2, CHRISTOPHER CHARLES2, ANDY RIDGWELL3, GAVIN L. FOSTER4, DANIELA N. SCHMIDT3 AND TIM ELLIOTT3

1Geological and Planetary Sciences, Caltech, Pasadena, USA jamesrae@caltech.edu
2SCRIPPS Institution of Oceanography, UCSD, La Jolla, USA
3University of Bristol, Bristol, UK
4School of Ocean and Earth Science, National Oceanography Centre, University of Southampton, Southampton, UK

Deep ocean carbon storage and release is commonly invoked to explain glacial-interglacial CO2 cycles, but records of the carbonate chemistry of the glacial ocean have, until recently, been scarce. Here we present new boron isotope (δ11B) data from detailed depth profiles and time series, that record the pH of the deep ocean at the last glacial maximum (LGM), and how it evolved over the deglaciation. We examine these data using a recently developed tracer fields modelling approach [1]. This has previously been applied to δ18O data to investigate changes in circulation at the LGM. Here we extend this method to the non-conservative tracers δ11B and δ13C, allowing us to constrain the roles of circulation, the biological pump of organic carbon and CaCO3, and carbonate compensation, in setting deep ocean carbon storage at the LGM. Finally, we show how deep ocean carbon storage evolved over the deglaciation, with pulses of stratification breakdown in the Southern Ocean and North Pacific causing CO2 release from the deep ocean to the atmosphere.

Revealing Pacific Ocean organic matter remineralization and circulation using the dual isotopic composition of nitrate

PATRICK A. RAFTER1 AND DANIEL M. SIGMAN1
1Department of Geosciences, Princeton University

Here we show that the difference between the N and O isotopic composition of nitrate, or $\Delta^{15}(15-18)$, is sensitive to organic matter remineralization and largely reflects known patterns of surface ocean nitrogen cycling. For example, incomplete nitrate consumption in high latitude surface waters and N fixation in the subtropical North Pacific lowers subsurface $\Delta^{15}(15-18)$, while complete consumption in the lower latitudes elevates subsurface $\Delta^{15}(15-18)$ (see Figure 1 below). This sensitivity is exploited to estimate the $^{15}N/^{14}N$ of sinking organic matter and to track the modification of nitrate as it passes from the deep Pacific Ocean, through the Southern Ocean surface, and into intermediate-depth waters—a pathway that is necessary for resupplying the low latitude surface ocean with nutrients (Figure 1).

Figure 1: Nitrate $\Delta^{15}(15-18)$ along $150^\circ W$ in the Pacific Ocean (see colour bar) and potential density (lines). Deep-sea nutrients are brought to the high latitude surface ocean and transported to lower latitudes within the potential density range of 26.5 to 27.1 kg/m$^3$ (arrows). Changes in nitrate $\Delta^{15}(15-18)$ along these isopycnals largely result from organic matter remineralization.

Growth medium and carbon source of unusual rounded diamonds from alluvial placers of the North-East of Siberian Platform

A.L. RAGOZIN1*, V.S. SHATSKY1,2, D.A. ZEDGENIZOV1 AND W.L. GRIFFIN3
1V.S. Sobolev Institute of Geology and Mineralogy SB RAS, Koptyuga Ave. 3, Novosibirsk 630090, Russia, (*correspondence: ragoz@igm.nsc.ru)
2A.P. Vinogradov Institute of Geochemistry SB RAS, Favorsky str. 1a, Irkutsk 664033, Russia
3CCFS/GEMOC, Macquarie University, NSW 2109, Australia

About 70% of diamond placer deposits of the Siberian platform are concentrated in the northeastern part. Primary sources of diamonds of these placers have not yet been established. Some diamonds are neither characteristic to the pipes located nearby nor to any of the known kimberlite pipes of Yakutia. A significant part of the diamonds belongs the variety V [1]. These diamonds are characterized by rounded morphology and radial mosaic-block internal structure. The diamonds enriched in isomorphic nitrogen (up to 3500 ppm) and have light carbon isotopic composition ($^{13}C$: -19.6÷-24.1‰). The Coe inclusions suggests eclogite paragenesis also supported by the light carbon isotopic composition. Moreover, diamonds contain numerous microinclusions (<1 µm). Rt, Grt, Ap, Kfs, Dy, Omph and Jd have been identified among microinclusions associated with fluid (or melt) inclusions of composition varied from carbonatitic (enriched in Ca, Mg, Fe, Cl, Ba and Sr) to silicic (enriched in Si, Al, Ti, K). Bulk trace element patterns of microinclusions as determined by LA-ICP-MS are similar to that observed in cuboid diamonds from Siberian Platform. Fluid inclusions have demonstrated that growth environment involved H$_2$O, CO$_2$, N$_2$, CH$_4$ and heavier hydrocarbons [2]. The compositions of fluid inclusions in one crystal could change from CO$_2$ to essentially hydrocarbons from center to the periphery.

Thus the obtained data for unusual rounded diamonds (variety V) indicates the possible connection between the formation of diamonds and subduction events. Variations of the growth media composition may be caused by the interaction between the metasomatizing fluids and silicate substrate.

Petrological and Geochemical Evidences for the Origin of the Neyriz Ophiolites, SE Zagros, Iran

MOHAMMAD RAHGOSHAY and IMAN MONSEF

1Shahid Beheshti University, Earth Sciences Faculty, Tehran, Iran (M-Rahgoshay@sbu.ac.ir)
2Industrial and Mining Research Center, ZaminOmran, Shiraz, Iran, (*Correspondance: Iman_monsef@yahoo.com)

The Late Cretaceous Neyriz ophiolites in south eastern of Zagros are a remnant of Neo-Tethyan oceanic lithosphere with nearly continuous NW-SE-trending belt. The ophiolite consists chiefly of mantle (ultramafic) and crustal (cumulates, volcanic and sub-volcanic rocks) sequences.

The mantle sequences consist of harzburgite, dunite, pyroxenite, gabbroic pockets, diabasic dykes and chromitite presented by mantle deformation conditions. Chromitite ore deposits with podiform and lenses structures are located in dunitic envelope of ultramafic host rocks. The chromitites are alpine type with high values of Cr#, Mg# and Fe^2+/Fe^3 ratio and low values of Al_2O_3 and TiO_2.

The crustal sequences consist of layered gabbros, isotropic gabbros, plagiogranites, sheeted dykes, and pillow lavas. Most of the mafic rocks have flat chondrite-normalized REE patterns and are strongly depleted in incompatible elements (negative Ta-Nb anomalies), similar to depleted tholeiites affinity.

The Neyriz oceanic lithosphere was probably formed within marginal basin system that was later accreted to the northern margin of the Arabian plate.


Tracing the time-resolved magmatic evolution of the Hegau volcanic field (Southern Germany) through apatites

MEINERT RAHN and ANETTE VON DER HANDT

1Swiss Federal Nuclear Safety Inspectorate, Brugg, Switzerland, meinert.rahn@ensi.ch
2Albert-Ludwigs-Universität, Freiburg, Germany
3University of Minnesota, Department of Earth Sciences, avdhandt@umn.edu

Major outcrops of Tertiary–Quaternary mafic alkaline volcanic rocks form the Central European Volcanic Province (CEVP). The Hegau volcanic field is found at the southern periphery of the CEVP, around 60-70 km to the east of the Upper Rhine graben. Age dating suggests a period of volcanic activity between 15 and 7 Ma [1-3]. Three main lithological units can be distinguished, i.e. from old to young: (1) tuff layers (so-called “Deckentuff”) intercalating with surrounding Miocene sediments, (2) olivine melilitites forming cones, but no lava flows, and (3) isolated phonolite peaks. Carbonatites occur subordinately in the Hegau province, mostly evidenced by calcite-apatite-magnetite aggregates, but suggesting the coexistence of silicate and carbonate melts in the source area.

We investigated apatites from Deckentuffs and phonolites, as their composition is expected to reflect whole rock compositional variation and in particular any changes between silicate and carbonate melt origin [4]. Apatites are often the only fresh remnants of the associated volcanic products; they occur in all lithological units and commonly display a complex internal growth pattern. EPMA and SIMS techniques are applied to decipher the major and trace element compositional evolution. The combination of fission track age dating with chemical composition allows a time-resolved investigation of the evolution of the Hegau volcanic field and its relation to the Kaiserstuhl volcanism.

In addition, apatites with Hegau compositional patterns can be found as thin tuff layers intercalated with sediments as much as 60 km away from the Hegau volcanic field. This suggest a more explosive volcanism which is corroborated by the occurrence of diatreme breccias in the Hegau. Multiple magmatic cycles can be discerned on the basis of apatite composition.


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Journal paper isotopic composition as climate proxy

P RAHUL1, P GHOSH1* AND SNEHA SURESH2

1Centre for Earth Sciences, Indian Institute of Science, Bangalore (* pghosh@ceas.iisc.ernet.in)
2Pondicherry University, Pondicherry

The increasing use of fossil fuels mainly due to burning of coal and petroleum since the beginning of industrial revolution has caused steady rise in CO2 concentrations in the atmosphere. CO2 is well mixed in global atmosphere through general circulation. There is a consistent pattern observed between concentration rise and carbon isotopes in atmospheric CO2. The isotopic signature seen in CO2 of atmospheric air is transferred to the biosphere through exchange mechanisms. The 

13C signature of fossil fuel derived CO2 being lighter than other natural sources and preferential uptake of 12CO2 from atmosphere by plants, provide us an opportunity to understand its fluctuations over time through stable isotopic analyses of plant materials [1]. In the present study we investigated the transfer of 

13C signal from raw plant material to paper in archives of periodicals and magazines. Study by Yakir (2011) [2] shows a depleting trend in 

13C of paper cellulose through time and linked it to global-scale increases in plant intrinsic water-use efficiency. In our study we have investigated the 

13C of paper produced from Europe and America capturing atmospheric CO2 trends mimicking the rise in global temperature for time period of last 100 years. The representative samples of journal papers are retrieved from the library at four to five year resolutions avoiding any ink contamination. We recorded a sudden drop in 

13C value (-22.9‰ to -24.39‰) in cellulose composition coinciding with the time period from 1920 to 1925. The global temperature anomalies for the same period ranges from -0.25°C to -0.14°C. Detailed examination of 

13C variability revealed impacts of historically important events on atmospheric CO2 via cellulose in paper. Analyses performed on archives of a regionally published journal confirms global patterns and along with the capturing signatures of regional industrial revolution. Analyses of 

18O in the cellulose further confirm the signature of global climatic events due to its linkage with the hydrological cycle. The study identified a potential new reliable archive which can supplement proxy records at much higher time resolutions.


Crustal structure beneath the Dharwar craton, India

S. S. RAI*, KAJALIYOTI BORAH, S. GUPTA AND K. S. PRAKASAM
National Geophysical Research Institute, Hyderabad-50007 India
(*Correspondence: shyamsrai@gmail.com)

We report significant lateral variability in shear wave velocity and Moho depth in the Archean crust beneath the Dharwar craton, India using earthquake waveform data recorded over 50 broadband seismographs (Figure a). The craton is a continuously exposed Archean continental fragment from north to south, and divided into the west Dharwar craton (WDC) of age 2.7-3.6 Ga, and the east Dharwar craton (EDC) of age, dominantly, 2.5 Ga. The craton progressively transition into the Southern Granulite Terrain (SGT) with age of metamorphism around 2.6 Ga.

The inversion of receiver function data reveals significant variation of Moho depth, viz., 38-54 km in the WDC, 40-46 km in SGT, and 32-38 km in the EDC. The average shear wave velocity of crust beneath the WDC is ~3.85 km/s as compared to ~3.60 km/s in the EDC. We infer highly variable thickness (16-30 km) of mafic cumulate (Vs ~4.0 km/s, Vp ~7.0 km/s) beneath the WDC, in contrast with a thin one (<5 km) beneath the late Archean EDC. The 3.36 Ga greenstone belt in WDC has maximum basal layer thickness of ~30 km. The result suggest the mafic crust and exceptional thickness of crust beneath the WDC (>50 km) as compared to felsic to intermediate composition for the EDC crust with almost flat Moho (~36 km) (Figure b). Considering the surface exposure of 15-20 km crust, based on P-T condition, in the southern segment of WDC, we speculate a Himalaya-like crustal thickness (50-70 km) beneath the mid-Archean crust pointing towards a plate-tectonic like scenario at ~3.0 Ga. In contrast, the EDC is possibly evolved as a consequence of subduction and delamination that led to a felsic crust with a nearly flat Moho.

Figure: (a) Tectonic map of Dharwar craton. Seismic stations are shown as black triangles (b) Schematic showing distinct crust-mantle character of the WDC and EDC.

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Kinetic parameters of pelagic nitrifying communities: consequences on nitrite dynamics in the Seine River downstream of Paris

M. RAIMONET1, L. VILMIN2, N. FLIPO2, T. CAZIER1, V. ROCHER3 AND A. M. LAVERMAN1
1UMR 7619 Sisyphe, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris, France (melanie.raimonet@upmc.fr)
2Centre de Géosciences, MINES ParisTech, 77300 Fontainebleau, France
3SIAAP-Direction du Développement et de la Prospective, 82 avenue Kléber, 92700 Colombes, France

Elevated nitrite concentrations are observed in the Seine River downstream of Paris and its main waste water treatment plants (WWTP). In order to understand the persistence of nitrite in the Seine, we determined kinetic parameters of pelagic ammonia- and nitrite-oxidizing communities. In situ ammonia- and nitrite-oxidation rates were deduced by determination of the kinetic parameters of the two processes combined with modeling. We compared the in situ rates and kinetic parameters upstream and downstream of the WWTPs during different seasons. The results showed both spatial and temporal variations of the in situ nitrification rates and kinetic parameters (e.g., maximal oxidation rate, half-saturation constant). At each given site and season, the in situ ammonia- and nitrite-oxidation rates were however similar, most likely resulting in little changes in water column nitrite concentrations. The results confirm that the elevated nitrite concentrations monitored in the Seine River are due to high nitrite released by the WWTP. In addition, the low nitrification rates and the equilibrium between ammonia- and nitrite-oxidation rates appear to prevent the elimination of nitrite from the system, leading to its persistence over more than 100 kilometers. The spatial and temporal variations of kinetic parameters reflect the dynamic microbial community structure and activity and may have implications on biogeochemical models.

Computer simulations of carbonates in water

PAOLO RAITERI1*, RAFFAELLA DEMICHELIS1 AND JULIAN D. GALE1
1Nanochemistry Research Institute and Department of Chemistry, Curtin University, Perth WA 6845, Australia (*correspondence: p.raiteri@curtin.edu.au)

Over the last thirty years a lot of effort has been made to understand the structural, surface and crystal growth properties of carbonates in aqueous environments, both experimentally and computationally. The ever increasing resolution of experimental techniques and power of supercomputer are rapidly closing the gap between what the two approaches can achieve. Arguably calcium carbonate is among the most studied minerals, but while there is a general consensus that its crystalline phases grow via an amorphous precursor, there is still much debate about the existence of pre-nucleation clusters and whether the nucleation follows a classical or non-classical pathway. Moreover, other carbonates are comparatively less studied and less understood.

Here we will present a recent force field developed to reproduce the thermodynamic properties of the alkaline-earth carbonates X-CO3 (X=Mg, Ca, Sr and Ba). This force field is used to study the different stages of the crystallisation mechanism, from isolated ions in solution to pre-nucleation clusters, nanoparticles and the growth of fully developed crystals. These studies include the calculation of reaction free energies (Figure 1), IR spectra and both structural and dynamical properties, and they demonstrate that carefully developed computational models are capable of quantitatively reproducing experimental observations.

Figure 1 Ca-CO3 pairing free energy calculated using the metadynamics technique with 2 collective variables.
Presence of > 3.3 Ga old crust and Neoarchean juvenile magmatic accretion in eastern most part of the Dharwar craton: Evidence from Peddavura greenstone belt.

M. RAJAMANICKAM1 AND S. BALAKRISHNAN1,*

1Department of Earth Sciences, Pondicherry University, Puducherry-605014
(*correspondence: balakrishnan.srinivasan@gmail.com)

Neoarchean witnessed rapid growth and stabilization of continents. The Dharwar Craton had significant addition of juvenile material and consequent crustal growth during 2.9 to 2.5 Ga ago in greenstone-granite terrains. [1, 2, 3]. Rocks of Peddavura greenstone belt in eastern Dharwar craton was studied for Rb-Sr and Sm-Nd systematics to understand crustal growth in the Dharwar Craton.

Peddavura greenstone belt consists of pillowed basalt, basaltic andesite and rhyolites inter-layered with ferruginous chert. Basalt and basaltic andesite define a Rb-Sr isochron age of 2551±19 Ma (MSWD=1.16), whereas, rhyolites were scattered and do not show any age. Sm-Nd system also does not yield any age for both the rock types.

The Rb-Sr age could represent time of thermal event that was strong enough to completely reset the Rb-Sr isotopic system in the basaltic rocks. The scattering of samples in Sm-Nd evolution diagram could be due to either low-temperature alteration or heterogeneity in their sources. Basalt and basaltic andesites show variation in their $\varepsilon_{Nd}$ values, whereas they have similar $\varepsilon_{Sr}$. This implies that magmas representing these rocks might have derived from variably LREE enriched and depleted mantle sources. Rhyolites show larger variation in their $\varepsilon_{Nd}$ as well as in $\varepsilon_{Sr}$, which are negatively correlated. Parental magmas of rhyolites derived by partial melting of short-lived basaltic rocks were contaminated with older crustal rocks similar to the Gorur-Hasan gneisses. Thus, we infer presence of older crust, > 3.3 Ga, in the eastern most part of the Dharwar Craton.


Microbial mobilization of arsenic for bioremediation of contaminated soils

LIWIA RAJPERT1,2, ŁUKASZ DREWNIAK2, ALEKSANDRA SKŁODOWSKA2 AND MARKUS LENZ1,3,*

1Institute for Ecopreneurship, School of Life Sciences, University of Applied Sciences and Arts Northwestern Switzerland, Grunendenstrasse 40, CH-4132 Muttenz, Switzerland (*correspondence: markus.lenz@fhmw.ch)
2Laboratory of Environmental Pollution Analysis, Faculty of Biology, University of Warsaw, 03-982 Warsaw, Poland
3Sub-Department of Environmental Technology, Wageningen University, 6700 EV Wageningen, The Netherlands

Arsenic contamination of soil and drinking water is a serious problem of worldwide concern [1, 2]. The efficiency of a novel combined strategy relying on enhancing microbial As mobilization with subsequent immobilization on nanosized iron phases for the treatment of mining impacted soil (As >2000 ppm; Lower Silesia, Poland) was evaluated.

Three bioreactors were operated in parallel assessing 1) inherent As reducing capacity of the soil; 2) biostimulation with external electron donor and 3) bioaugmentation with dissimilatory arsenate reducing microorganisms. Mobilization rates of As, Fe, Mn were analyzed using ICP-MS, whereas aqueous As speciation was analysed by LC-ICP-MS. Potentially formed hazardous As volatiles were trapped in 1% H2O2 (Fig.1). Addition of an external electron donor resulted in both lower total and bioavailable As fraction in soils. Different iron phases were evaluated for their As sorption/desorption capacity of different As species following microbial mobilization. Nanosized ferrihydrite proved to be the most effective and cheap As sorbent evaluated.

Elevated pressure of carbon dioxide affects growth of thermophilic *Petrotoga* sp.

**JANA RAKOCZY**1*, **CLAUDIA GNIESE**2, **AXEL SCHIPPERS**1, **MICHAEL SCHLÖMANN**2 AND **MARTIN KRÜGER**1

1Bundesanstalt für Geowissenschaften und Rohstoffe (BGR), Stilleweg 2, D-30655 Hannover
2Institut für Biowissenschaften, TU Bergakademie Freiberg, Leipziger Str. 29, D-09599 Freiberg

Carbon capture and storage (CCS) is considered a promising new technology which reduces carbon dioxide emissions into the atmosphere and thereby decelerates global warming. However, with CCS being a very young technology, there are yet a number of factors that need to be investigated before declaring CCS as being safe. Our research investigates the effect of high carbon dioxide concentrations and pressures on an indigenous microorganism that colonises a potential storage site.

Growth experiments were conducted in liquid culture using the thermophilic thiosulphate-reducing bacterium *Petrotoga* sp., isolated from formation water of the gas reservoir Schneeren (Lower Saxony, Northern German Plain). Growth (OD<sub>600</sub>) was monitored over 10 days at different carbon dioxide concentrations (50%, 100%, and 150% in the gas phase), and was compared to cultures grown with 20% carbon dioxide. An additional growth experiment was performed over a period of 145 days with repeated subcultivation steps to detect long-term effects of carbon dioxide. Short-term cultivation at 50% and 100% carbon dioxide slightly reduced cell growth. In contrast, long-term cultivation at 150% carbon dioxide reduced cell growth and finally led to cell death. This suggested a more pronounced effect of carbon dioxide at prolonged cultivation and stresses the need for closer consideration of long-term effects.

Experiments with supercritical carbon dioxide at 100 bar completely inhibited both growth of a freshly inoculated culture and a pre-grown culture demonstrating the lethal effect of supercritical carbon dioxide. This effect was not observed in control cultures with 100 bar of hydrostatic pressure.

Evaluating the Role Mafic Crustal Assimilation in the Generation of Western US Continental Basalts

**RAMOS, FRANK C., GLADISH, E., SLATER, N. AND PALIEWICZ, C.**1

1New Mexico State University, Las Cruces, NM 88003 USA

Western US continental basalts are generally thought to reflect pristine geochemical and isotopic signatures inherited from heterogeneous mantle sources. Such thoughts rely on a lack of magmatic interactions with crustal sources. Assessments for the role of potential crustal interactions typically focus on modifications expected for Si-rich materials such as increased SiO<sub>2</sub> or highly elevated trace elements such as Ba. In contrast, mafic crustal assimilation may impart only limited SiO<sub>2</sub> and trace element variations depending on the exact nature of the mafic crust and the degree to which the mafic materials are melted. Tholeiites and alkaline basalts erupted along and the Colorado Plateau-Rio Grande rift transition zone and within the Rio Grande rift itself retain geochemical and isotopic variations that are similar to those expected to result from mafic crustal assimilation. Results allow for the possibility that asthenospherically derived magmas assimilated variable amounts of mafic crust resulting in a range of isotopic and geochemical characteristics that are similar to those expected for trace element enriched heterogeneous subcontinental lithospheric mantle sources. Whole rock isotope signatures in a few of the younger flows (e.g., Bandera and McCartys flows, Zuni-Bandera volcanic field, and the Carrizo flow, Rio Grande rift) vary extensively (e.g., 87Sr/86Sr of 0.7028 to 0.7035 for the Bandera flow, 0.7037 to 0.7084 for the McCartys flow, and 0.7044 to 0.7052 for the Carrizo flow) and are consistent with more complicated petrogenetic histories involving a range of potential mantle and crustal sources. Here, we present phenocryst and melt inclusion major and trace element compositions to identify and track chemical variations retained in whole rocks and melt inclusions and integrate isotopic signatures of these components imposed during crystallization. Additional mineral signatures of plagioclase and xenocrystic materials will be discussed and the petrogenetic histories of selected young alkaline and tholeiitic basaltic from the Rio Grande rift and Zuni-Bandera volcanic field will be assessed to evaluate the potential role of mafic crustal assimilation in the genesis of respective trace element and isotopic signatures of these continental basalts.
Melt-rock reaction in oceanic troctolites (Ligurian ophiolites, Italy) as revealed by trace element chemistry of olivine

E. RAMPONE1*, G. BORGHI1,2, L. CRISPINI1, M. GODARD1, B. ILDEFONSE3 AND P. FUMAGALLI2
1DISTAV, University of Genova, I-16132 Genova, Italy (*correspondence: betta@dipteris.unige.it)  
2University of Milano, I-20133 Milano, Italy  
3UMR CNRS, Université Montpellier 2, Montpellier, France

Several recent studies have documented that reactions between melt and crystal mush in primitive gabbroic rocks (via reactive porous flow) has an important control in the formation of the lower oceanic crust and the evolution of MORBs. In this context, an open issue concerns the origin of olivine-rich rocks, whether they formed by fractional crystallization of primitive melts or by open system reactive percolation of pre-existing (possibly mantle-derived) olivine matrix. To address this topic, we performed high-quality in-situ trace element analyses (by LA-ICP-MS) of olivine in the ideal case study of the Erro-Tobbio ophiolite Unit (Ligurian Alps), where mantle peridotites show gradational contacts with an hectometer-scale body of troctolites and plagioclase wehrlites, and both are cut by later decameter-wide lenses and dykes of olivine gabbros. Previous studies [1] inferred that they represent variably differentiated crystallization products from primitive MORB-type melts. Olivines in the three rock types (mantle peridotites, troctolites, ol-gabbros) exhibit distinct geochemical signature and well-defined elemental correlations. As expected, compatible elements (e.g. Ni) show the highest contents in peridotites (2580-2730 ppm), intermediate in troctolites (2050-2230 ppm) and lowest in gabbros (1355-1420 ppm), whereas moderate incompatible elements like Zr, Hf, Ti, HREE elements (e.g. Mn, Zn) show the opposite behaviour. By contrast, highly incompatible elements like Zr, Hf, Ti, HREE are variably enriched in olivines of troctolites and the enrichment in absolute concentrations is coupled to development of significant HFSE/REE fractionation (ZrN/NdN ratios in olivines are consistent with a process of olivine assimilation and plagioclase crystallization at decreasing melt mass, in agreement with textural observations. In-situ trace element geochemistry of olivine, possibly combined with CPO measurements, thus appears a powerful tool to investigate reactive percolation and the origin of olivine-rich rocks in the lower oceanic crust.

Quantification of the in situ heterogeneity of RMs for microanalytical methods

MICHAEL H. RAMSEY1 AND MICHAEL WIEDENBECK2*
1University of Sussex, UK; (m.h.ramsey@sussex.ac.uk)  
2Helmholtz Zentrum Potsdam, Germany (*correspondence: michael.wiedenbeck@gfz-potsdam.de)

A range of laboratory techniques is available for the geochemist wishing to characterize the chemical and/or isotopic compositions of solid materials at the nanogram or smaller sampling mass range. Examples of widely available techniques are based on the electron probe, laser ablation ICP-MS and secondary ion mass spectrometry (SIMS).

When operating at such small test portion masses there are three fundamental requirements that a reference material (RM) should enable: (1) method calibration, which is typically based on one or a few discrete fragments of the RM, (2) evaluation of method repeatability, which is commonly based on multiple analyses on a single RM fragment, and (3) method development and validation. An additional consideration is that most such materials must necessarily be characterized using laboratory methods operating at the milli-gram or larger sampling scale.

In order to meet all of these requirements it is evident that a microanalytical RM must be assessed for heterogeneity in-situ at a variety of scales, and that the corresponding heterogeneity component must be considered for each application being undertaken. When calibrating an instrument it is essential to know the likely variation between the mean content of individual sample aliquots (chips or fragments). This information can commonly be obtained from “bulk sample” analyses conducted on mm-sized units, be it via wet chemical, gas source mass spectrometer or other methods. For evaluating the repeatability of a microanalytical method it is necessary that the in situ heterogeneity of the material be quantified at the equivalent sampling scale. For method development and validation a detailed knowledge of a RM’s major element composition, as well a knowledge of its heterogeneity at the given sampling scale, are both necessary.

Our work focuses on developing experimental and mathematical tools that will quantify in situ heterogeneity at the various sampling scales while taking into account the analytical uncertainties intrinsic to the laboratory method being used to characterize such variations. The ultimate goal of our work is to enable SIMS to assess in detail the isotopic characteristics of candidate RMs at sampling masses well below 1 ng and with overall heterogeneity being evaluated at the < 0.1 % level.
Cryo-XPS monitoring of cell wall compositional changes for *Bacillus subtilis* as a function of pH and Zn\(^{2+}\) exposure

MADELEINE. RAMSTEDT*, LAURA. LEONE, ANDREY. SHCHUKAREV AND PER. PERSSON

Department of Chemistry, Umeå University, 90187 Umeå, Sweden,

correspondance: madeleine.ramstedt@chem.umu.se

Bacteria such as *Bacillus subtilis* and *Escherichia coli* adjust and alter their gene transcription and protein production depending on the environment they are exposed to. For example, membrane-bound protein complexes are up-regulated at high pH in *B. subtilis* and several enzymes that reduce acidity and transport metals out of the cell are up-regulated at low pH [1]. It has also been reported that building blocks in the cell wall change with varying pH.

X-ray Photoelectron Spectroscopy (XPS) is a surface sensitive analysis method that has been used by several researchers to successfully analyze the chemical composition of bacterial cell walls [e.g. 3,4,5]. In this presentation we will show how we have used cryo-XPS together with a recently developed curve fitting model to predict the chemical composition of the surface of bacterial cells [2]. We have used this to study changes in the surface composition of *B. subtilis* exposed to environments with varying pH and/or Zn\(^{2+}\) content. We will also compare the obtained ratios of different substances with ratios obtained using previously published methods based on equation systems [3,4,5].


Alkenones and hydrogen stable isotopic composition of n-alkane as indicators of past temperature and salinity in Lake Van sediments

M.È. RANDLETT1*, M. J. L. COOLEN2, A. BECHTEL3, M. STOCKHECKE1, O. KWIECIEL1, Y. TOMONAGA1, B. WEHRLI1 AND C. J. SCHUBERT1

1Swiss Federal Institute of Aquatic Science and Technology EAWAG, Switzerland
2Woods Hole Oceanographic Institution (WHOI), MA 02543, United States
3Montanuniversität Leoben, Leoben A-8700, Austria

(*correspondence: marie-eve.randlett@eawag.ch)

The successful drilling operations of the International Continental Scientific Drilling Program (ICDP) PaleoVan project allowed the recovery of 220-m long sediment cores, which represents approximately the last 600 ka. This exceptional climatic archive was investigated for two relevant organic molecular proxies; alkenones and hydrogen stable isotopic composition of n-alkanes C29 (\(\delta D\) of n-C\(_{29}\)). The potential of unsaturation patterns in alkenones for reconstructing past temperatures in Lake Van was assessed through investigation of algae types responsible for alkenones biosynthesis using ancient DNA stratigraphy. The diversity of alkenones producers within the core hampered the use of a single calibration curve for reconstructing temperature based on alkenone unsaturation patterns, as found elsewhere [1,2]. On the other hand, the \(\delta D\) of n-C\(_{29}\) co-vary with the salinity of the pore water profile in Lake Van. The latter organic proxy therefore seems to be a promising tool for reconstructing changes in the source water salinity due to variable precipitation/evaporation ratio, as previously suggested [3].


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Δ¹⁷O, δ¹⁷O, δ¹⁸O variation in precipitated water at Jungfraujoch (3571 m) - relation to meteorological parameters and low altitude stations

S. RANJAN1 AND M. LEUENBERGER1

1Climate and Environmental Physics, Physics Institute and Oeschger Centre for Climate Change Research University of Bern, Bern, Switzerland
shyam@climate.unibe.ch (* Presenting Author)

We have analysed precipitated water sample of seven stations from high altitudes Jungfraujoch (3571 m) to low altitudes Basel (292 m). Δ¹⁷O, δ¹⁷O, δ¹⁸O was analysed for Jungfraujoch (A) from 1983 to 2011 and Grimsel (B), Guttanen (C), Meiringen (D), Locarno (E), Bern (F) and Basel (G) from 2003 to 2005. pH, temperature, relative humidity, air pressure and precipitation data was available through MeteoSwiss. Δ¹⁷O, δ¹⁷O, δ¹⁸O and pH variations were analysed by using the conventional CO₂-equilibrium method and a pH sonde with a repeatability of ± .01 pH unit. Positive correlation were found between δ¹⁸O & δ¹⁷O, temperature and relative humidity, while poor correlation were found between δ¹⁷O & δ¹⁸O, δ¹⁷O & δ¹⁹O, pH & relative humidity, air pressure and precipitation of all station. Year 2003, one of the hottest period of Europe and at the same period, highest δ¹⁷O values were observed at station A, C, D, G but not at station B, E & F which require further in-depth research. Interestingly, the decreasing trend of pH was observed at all stations. Except at the station G, highest pH of all stations was greater than 10 pH unit while lowest pH was less than 3 units at station A. Only station A is mostly exposed to the free troposphere and receive signals at a continental scale. Contrary to all others stations, low pH was observed mainly during 1991 to 1993 period at station A, which is originating most probably from multiple large volcanic eruptions (Pinatubo, which was 2nd largest eruption of 20th century). Increasing concentration of atmospheric CO₂ have only a small effect on pH changes in precipitated water compared to the results we have observed. Further explanations will be given in the presentation.

U-Pb Dating of Carbonates and Fluorite: Prospects for Understanding Fluids from Deposition Through Burial

E. T. RASBURY1, R. R. PARRISH2, W. AUSTIN-GIDDING3, A. LANZIROTTI4, P. TOMASCAK5 AND J. R. KYLE6

1Department of Geosciences, Stony Brook University, Stony Brook NY, *corresp: troy.rasbury@stonybrook.edu
2Dept Geology U. Leicester, UK and NIGL, British Geol Survey, Keyworth, Notts, rrp@nigl.nerc.ac.uk
3Institute of Geography and Earth Science, Aberystwyth University, Aberystwyth, Wales wea2@aber.ac.uk
4Center for Advanced Radiation Sources, University of Chicago, lanzirotti@uchicago.edu
5Department of Earth Sciences, SUNY Oswego, Oswego, NY, paul.tomascak@oswego.edu
6Dept Geological Sciences, Jackson School of Geosciences, University of Texas at Austin, rkyle@jsg.utexas.edu

Minerals such as carbonates and fluorite record information about the fluids from which they formed such as the salinity, temperature, degree of rock-water interaction, as well as details of the source(s) of these fluids. The U and Pb concentrations, U oxidation state and molecular speciation and Pb isotope compositions in these minerals may reveal important information about the nature of the fluids and, in favorable cases, can be used to date the time of mineral formation. The application of emerging in situ microbeam analytical techniques such as synchrotron XRF, LA-ICP-MS, and SIMS offers the possibility of tracking the mineralogical and geochemical evolution of these minerals from the time of deposition of limestones through burial diagenesis, faulting and vein formation. Dating of the time of deposition provides a framework for understanding the climate history and fossil information encoded in the rock. Key genetic aspects for ore and hydrocarbon deposits could be provided by a more thoroughly dated history of formation. The timing of tectonic events may be constrained by dating vein fillings of associated fault and fracture systems.

Studies have shown great potential for U-Pb and U-series dating of carbonates precipitated from meteoric fluids and for dating of vein calcite, associated with faulting and with ore mineralization. We will review these studies with insights based on synchrotron and laser ablation work, and present new work on the application of U-Pb dating of fluorite and calcite from a variety of settings, and discuss the expanding applications of these methods to geological problems.
The selective sorption of K⁺ from water solutions by Ca-zeolites

SERGEY V. RASHCHENKO12* AND LIDIA K. KAZANTSEVA1

1Sobolev Institute of Geology and Mineralogy SB RAS, 3 Koptyug Avenue, 630090 Novosibirsk, Russia
(*Correspondence: rashchenko@igm.nsc.ru)
2Novosibirsk State University, 2 Pirogov Street, 630090 Novosibirsk, Russia

The geochemistry of potassium during subduction-related processes does not seem to be a solved problem yet. The important role of subducted oceanic lithosphere as a potassium source for alkali-rich subduction magmatism was repeatedly discussed [1]. However, MORB basalts contain less than 0.16% of K₂O [2] and so cannot be considered as important source of this component. To avoid such discrepancy, some authors consider terrigenous sediments to enrich subducting lithosphere in K₂O [3]. We suggest the alternative mechanism of this enrichment consisting in cation exchange between seawater and zeolitized rocks of the ocean floor. To prove the probability of such process we carried out the experimental modeling of interaction between Na⁺/K⁺ water solutions and Ca-zeolites as common secondary minerals appearing during hydrothermal alteration of basalts.

The water solution with Na⁺/K⁺ molar ratio close to that of seawater (0.06) was used in our experiments. The obtained results for laumontite and stellerite are given in the Table 1.

<table>
<thead>
<tr>
<th>%</th>
<th>Laumontite</th>
<th>Stellerite</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>7.34 → 5.51</td>
<td>8.03 → 2.27</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.56 → 2.67</td>
<td>0.14 → 4.71</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.47 → 1.43</td>
<td>0.05 → 2.46</td>
</tr>
</tbody>
</table>

Table 1: The change in the cation composition of Ca-zeolites due to 30 days of hydrothermal treatment by Na⁺/K⁺ solution.

As one can see, a significant change in cation composition of Ca-zeolites occurs after interaction with Na⁺/K⁺ water solution. Moreover, the K⁺/Na⁺ molar ratio of alkali cations absorbed by laumontite (0.58) and stellerite (0.35) clearly demonstrates the selective sorption of K⁺ from solution with low K⁺/Na⁺ ratio (0.06). Such phenomenon caused by features of zeolites crystalline frameworks probably plays an important role in interaction of zeolitized rocks of ocean floor with seawater and enriches the sedimentary part of oceanic lithosphere in potassium.

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Algal biofuels: A sustainable pathway to mitigate energy demand

MOHAMMED ABDUL RASHEED*, SYED ZAHEER HASAN AND B.KUMAR

Petroleum Research Wing, Gujarat Energy Research and Management Institute, Gandhinagar, Gujarat, India.

*(Correspondence: abdul@germi.res.in)

Algal fuels are generating considerable interest around the world. These fuels may represent a sustainable pathway for helping to meet the energy demand. Algae is a preferred biodiesel base because algae grow more rapidly and occupy less space compared to other plants used for biodiesel such as corn, soy, canola and other lipid producing organisms. The algae strain, *Chlorella vulgaris*, contains 30% lipids by mass. Thus, a common goal is to create a manageable and cost effective process for manufacturing biodiesel on a large scale. Microalgae are single-cell, photosynthetic organisms known for their rapid growth and high energy content. Some algal strains are capable of doubling their mass several times per day. In some cases, more than half of that mass consists of lipids or triacylglycerides—the same material found in vegetable oils. These bio-oils can be used to produce such advanced biofuels as biodiesel, green diesel and green oil [1]. Algae consume carbon dioxide as they grow, so they could be used to sequester CO₂ being released from power stations and other industrial plant that would otherwise go into the atmosphere. Meeting the world’s fastly growing energy demands will require a multitude of sources. Several private and government agencies are putting efforts to reduce capital and operating costs and make algae fuel production commercially viable. The challenges that need to be addressed are, the exploitation of naturally occurring photosynthetic microalgae, which provides a green and renewable resource of feedstock biomass to meet increasing energy needs and especially the demand for liquid fuels thereby isolation, screening and evaluation of naturally occurring algal strains which exhibit high growth rate and large-scale photo bioreactor design and optimization, to outdoor mass culture and downstream processing. Challenges to be addressed include refinement of the cultivation process, downstream processing of biomass, and development of an economic feasibility model for commercialization of algae-based biofuels and biomaterials.


Evidence for increased Southern Ocean waters in the tropical intermediate Indian Ocean during the last deglaciation

HARUNUR RASHID1*, HARRY ELDERFIELD2, ALEXANDRA GOURLAN3 AND MARY SMITH4

1Memorial University of Newfoundland, Corner Brook, Canada hrashid@grenfell.mun.ca*
2University of Cambridge, Cambridge, UK, he101@cam.ac.uk
3Maison des Geosciences, Grenoble, France alexandra.gourlan@ujf-grenoble.fr
4Indiana State University, Terre Haute, USA, msmith157@sycamores.indstate.edu

Oxygen isotopes (δ¹⁸O) and Mg/Ca in the *Globigerinoides ruber* (w) are analysed from the Bay of Bengal and Andaman Sea sediments. Mg/Ca, Cd/Ca and B/Ca are also determined in *Cibicidoides wuellerstorfi* and *Uvigerina peregrina* in two cores from the same basins. Furthermore, neodymium isotopic ratios (ɛNd) of seawater in two sediment cores are determined. Our results show that seawater oxygen isotope values were most enriched between 17.8 and 14.6 ka. We also find coincidence between the onset of intermediate water warming at 17.8 ka, and the onset of increase in atmospheric CO₂. In the tropical Indian Ocean, the deep water (>2,200 m) warmed after the surface, in sharp contrast with the warming found in the intermediate water which occurs earlier. Furthermore, an inverse relationship between the intermediate and surface waters is also found during the Bolling-Allerod and Younger Dryas periods in which surface water warmed (cooled) and intermediate water cooled (warmed). We hypothesize that the cause of warming of the northern tropical Indian Ocean intermediate water does not lie within the tropics, rather an increase in Southern Hemisphere spring insolation combined with sea-ice albedo feedbacks, consistent with the hypothesis suggested earlier. The hypothesized mechanism involves an increase in upper circumpolar deep-water circulation into the Indian Ocean.
Nitrate- and nitrite dependent anaerobic oxidation of methane

OLIVIA RASIGRAF1, BAOLI ZHU1, DORIEN M. KOOL2, MIKE S. M. JETTEN1 AND KATHARINA F. ETTWIG1

1Department of Microbiology, IWW, Radboud University Nijmegen, The Netherlands
2Royal NIOZ, Department of Marine Organic Biogeochemistry, Texel, The Netherlands

The first described enrichment culture capable of anaerobic oxidation of methane (AOM) coupled to nitrite and nitrate reduction was a consortium of *Methylomirabilis oxyfera* bacteria (80%) and archaea (10-20%) [1], the latter later named AOM-associated archaea (AAA) [2]. However, after prolonged incubation (several months) with elevated nitrite the AAA disappeared from the enrichment culture, and *M. oxyfera* bacteria were shown to oxidize methane without an archaeal partner. Subsequent isotope labeling studies with *M. oxyfera* showed that it can produce oxygen from nitric oxide, which is then used for methane oxidation via a monoxygenase reaction [3]. The isotope fractionation factors for carbon and hydrogen during methane oxidation by *M. oxyfera* were determined, and were in the same range as previously reported for aerobic methanotrophs [4]. Recently we investigated the capacity of *M. oxyfera* bacteria to fix CO₂ via the Calvin-Benson-Bassham cycle and their unusual lipid composition. Furthermore, based on the genomic information and physiological studies, the AAA were shown to possess the capacity for reverse methanogenesis and nitrate reduction. AOM by both *M. oxyfera* and AAA is of great interest for the understanding of and the linkage between the biogeochemical cycles of methane and nitrogen.


Deposition of the precursor sediments of banded iron formations

B. RASMUSSEN1*, B. KRAPEZ1, J.R. MUHLING1,2 AND D.B. MEIER3

1Dept of Applied Geology, Curtin University, Kent Street, Bentley, WA 6102, Australia
(*correspondence: b.rasmussen@curtin.edu.au)
2CMCA, The University of Western Australia, Stirling Highway, Crawley, WA 6009, Australia
3School of Earth and Environment, The University of Leeds, Leeds, LS2 9JT, United Kingdom

Banded iron formations (BIFs) are derived from iron-rich chemical sediments whose composition is used to make inferences about the early Precambrian ocean, atmosphere and biosphere. Before geochemical information from BIFs can be reliably interpreted, their origin and post-depositional history must be understood. However, the identity of the original sediments and how those sediments were deposited is contentious due to a long history of post-depositional overprinting and the absence of direct modern analogues. Most depositional models are based on the interpretation that the initial precipitate comprised ferric oxyhydroxides that formed when ferrous iron was oxidized in the water column and settled on the seafloor. The lack of well-defined grain-shapes and current-generated structures has been used to infer a pelagic origin for the primary sediments.

New sedimentological and petrographic studies of well-preserved intersections of BIF in the 2.63-2.45 Ga Hamersley Group, Western Australia, show the presence of abundant silt-sized spherical particles (or microgranules) in mm-thick chert microbands. The microgranules are most common in the least-altered BIF where they define sedimentary laminations, implying a depositional origin. They were deposited in lamina sets comprising a basal microgranule-rich lamina overlain by amorphous mud with dispersed microgranules. Seafloor silicification is interpreted to have preferentially replaced the amorphous clay matrix, implying that the precursor sediment must have comprised two particle sizes: silt and clay. Micrograding is interpreted to record plane laminations resulting from deposition of iron-rich muds entrained in dilute turbidity currents. The presence of micrograded structures in other BIFs, implies that resedimentation of precursor sediments was common.

A model is proposed in which ferruginous oceans with elevated silica favoured the growth of iron-silicate minerals proximal to active ridge systems. The hydrothermal muds accumulated on a sloping seafloor and were resedimented by dilute turbidity currents, and deposited on the basin floor as thin, laterally extensive sheets.

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Mantle Source Characteristics and Petrogenesis in the Lunar Crater Volcanic Field


1Department of Geology, Miami University, Oxford, USA, widome@muohio.edu (*presenting author)
2Department of Geology, State University of New York, Buffalo, USA, gav4@buffalo.edu
3Department of Geoscience, University of Nevada, Las Vegas, USA, gene.smith@unlv.edu

The nature of the mantle sources and the role of lithospheric assimilation in producing compositional variations in basaltic monogenetic volcanic fields remains controversial. To address these issues, we have performed major and trace element and Sr, Nd, Pb, Hf and Os isotope measurements on 19 mafic lavas from 4 volcanic centers in the northern Lunar Crater Volcanic Field (LCVF), Nevada. Three eruptive centers (Giggle Springs, ~<100 Ma; and Hi Desert and Mizpah, ~620-740 Ma) are located within ~500 m of each other; the Marcath volcano (~40 ka), the youngest eruptive center in the field, is located ~6 km SW of these cones. The lavas have essentially constant Nd and Hf isotope ratios, but significant heterogeneity in Sr and Pb isotopes, and superchondritic Os isotope ratios. The older Mizpah and Hi Desert lavas exhibit HIMU-like trace element and Sr-Pb isotope signatures, with Nb-Ta enrichment, Rb, Cs and K depletion, and high 206Pb/204Pb but low 87Sr/86Sr. In contrast, the younger Marcath and Giggle Spring lavas have enriched mantle (EM) type signatures with high Ba, Rb and Cs, and lower 206Pb/204Pb and higher 87Sr/86Sr. Together, the LCVF lavas produce a negative correlation between Sr and Pb isotopes that could be attributed to lower crust assimilation. However, the lack of correlation of isotopes with indices of fractionation, OIB-like Nb/U ratios, and a positive correlation of 187Os/188Os with Nb/U argue against an important role for crustal assimilation. Instead, the compositional variations are attributed to heterogeneous mantle sources. Mixing models indicate that incorporation of ~18% of 0.8Ga recycled oceanic crust into a depleted mantle source can explain the trace element and isotopic signatures of the HIMU lavas. Subsequent addition to the HIMU-like source of minor (~1%) hydrous fluid derived from subducted oceanic crust could account for the chemical and isotopic compositions of the EM lavas. Our data indicate that the mantle source region in the LCVF is characterized by chemical and isotopic heterogeneity over a very small spatial scale (~<500m), and that the nature of the mantle source and the depth of melt generation has changed systematically with time.

Compositions and zoning of coexisting minerals in alkaline-ultrabasic rocks, phoscorites, and carbonatites from the Kovdor Complex, Kola Peninsula

I. RASS AND E. KOVALCHUK
Institute of Geology of Ore Deposits, Petrography, Mineralogy & Geochemistry, Russ. Acad. Sci., 35 Staromonetny, 119017 Moscow, e-mail: rass@igem.ru

The compositions of coexisting pyroxene, magnetite, perovskite, schorlomite, titanite, and apatite in silicate and carbonate rocks were studied by electron-probe microanalysis (EPMA) techniques. The principally different major- and trace-element compositions and zoning of the above minerals from magmatic and metasomatic rocks reflect their different crystallization circumstances (P, T, fO2, pCO2, aSiO2) in the Earth’s crust. Magnetite in silicate rocks is noticeably richer in Ti than this mineral in carbonatites and phoscorites. The Ti content decreases from the cores to rims of magnetite crystals in any magmatic rock but shows the opposite tendency in magnetite of metasomatic Ne-Px rocks. A higher proportion of the magnesioferrite component in magnetite from phoscorites compared to that in silicate rocks is likely attributed to higher oxygen fugacity during the crystallization of the former. Apatite in younger derivatives of silicate rocks bears higher Sr concentrations. Its crystals exhibit core-to-rim variations in the contents of F (by up to 3.2 wt.%), REE, and SiO2. The F content increases in apatite from magmatic rocks and decreases in that mineral from metasomatic ones. The SiO2 content of apatite in silicate rocks reaches ~1 wt.% and shows a core-to-rim increase, whereas its concentrations in carbonatitic and phoscoritic rocks are noticeably lower. The presence of Si-rich apatite suggests its crystallization at shallower depths, at which CO2 activity is lower. The occurrence of Ti-rich andradite and titanite in Px-Ne rocks instead of perovskite is due to a higher aSiO2.

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Diurnal Chemical Characteristics of PM$_{2.5}$ over a Source Region of Biomass Burning Emissions in the Indo-Gangetic Plain

RASTOGI N$^1$, SINGH A$^2$ AND SINGH D$^2$

$^1$Geosciences Division, Physical Research Laboratory, Ahmedabad, India
$^2$Department of Physics, Punjabi University, Patiala, India
nrastogi@prl.res.in

Wintertime haze/fog has been observed every year over the Indo-Gangetic Plain (IGP); however, the understanding on corresponding particulate composition is meager. The diurnal chemical characteristics of PM$_{2.5}$ were investigated during October-2011 to March-2012 at a site (Patiala, 30.2 oN, 76.3 oE; 250 m amsl) located in the source region of biomass burning emissions over IGP. The study period covers characteristic emissions from post harvest paddy-residue burning during October-November (P1), from fossil, wood, and bio-fuel burning during December-February (P2), and from variable regional sources during March (P3).

A striking diurnal variability was observed in PM$_{2.5}$ mass, SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, K$^+$, OC, EC, and WSOC during P1 with ~30 to 300% higher concentrations of species in nighttime samples. The averaged WSOC/OC ratios for daytime and nighttime samples were ~0.65 and 0.47, respectively in all seasons, suggesting the enhanced daytime secondary organic aerosols formation. The NO$_3^-$ was comparable and OC was higher than SO$_4^{2-}$, indicating their importance as scattering species over IGP. The averaged (OC + SO$_4^{2-}$ + NO$_3^-$)/EC ratios for the daytime samples were ~12, 15 and 5.5, and for the nighttime samples were ~18, 14, and 6 during P1, P2 and P3, respectively, indicating the dominance of scattering type species in all the seasons with noticeable diurnal difference during P1, and the contribution of absorbing species (EC) increases from P1 to P3. A strong linear correlation ($r^2 = 0.86$) has been observed between all daytime and nighttime OC and K$, suggesting that the K$^+$ can be used as a tracer for biomass burning emissions over IGP with the OC/K$^+$ characteristic ratio of ~16. Water-soluble species were dominant (~55%) in PM$_{2.5}$ during winter (P2), and could be the major contributor to fog formation over IGP under favourable meteorological conditions. This study has implications in understanding the effects of biomass burning emissions on regional air quality and climate over IGP, and designing appropriate mitigation strategies.

Isotopic evidence for a crustal Pb source in the giant Broken Hill Pb-Zn-Ag deposit, NSW, Australia

MASSIMO RAVEGGI$^1$, DAVID GILES$^2$, JOHN FODEN$^2$, SEBASTIEN MEFFRE$^3$, MIKE RAETZ$^1$ AND IAN NICHOLLS$^1$

$^1$School of Geosciences, Monash University, Melbourne, Australia.
$^2$School of Earth and Environmental Sciences, The University of Adelaide, Adelaide, Australia
$^3$CODES, The University of Tasmania, Hobart, Australia.

The Paleo to Meso-Proterozoic Willyama Supergroup, together with the Broken Hill Pb-Zn-Ag deposit, hosts a wide variety of unusual rocks with mineralogical compositions comprising various proportions of quartz ± Fe-oxide ± garnet ± accessories (QFeGA), as well as mafic and felsic orthogneisses that intruded at ca. 1685 Ma. Major, trace, REE and U/Pb zircon geochronology data suggests that the QFeGA lithologies are syn-sedimentary, hydrothermal meta-sediments with limited detrital input, similar to hydrothermal sediments forming at present day spreading centers. Neodymium isotope data suggests that the hydrothermal fluids responsible for their deposition were in equilibrium with the Willyama Supergroup (meta)sedimentary sequences.

Lead isotope data from the mafic and felsic ortho-gneisses lie within error on the same 1685 Ma $^{207}$Pb/$^{206}$Pb reference isochron with an initial Pb isotope composition of Broken Hill orebody (galena). This is inconsistent with independent geochemical evidence showing that the mafic and felsic orthogneisses were derived from end-member mantle and crustal sources respectively. It is inferred that Pb isotope data is the result of a period of regional homogenisation due to pervasive crustal hydrothermal flux at the time of emplacement of the mafic and felsic rocks (ca. 1685 Ma). This is coincident with formation of the QFeGA rocks and the Broken Hill deposit. It is interpreted that the Pb (and other metals) scavenged by this hydrothermal system from the Willyama Supergroup (meta)sedimentary sequences, provided the metals for the Broken Hill orebody.

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Field evidence, modeling results, and new investigative strategies shed light on the timing and amplitude of sea level change during past interglacials

M.E. RAYMO1, A. ROVERE1, J.X. MITROVICA2, M. O’LEARY3, P. HEARTY4 AND J. INGLIS5

1Lamont-Doherty Earth Observatory of Columbia University, raymo@ldeo.columbia.edu
1Lamont-Doherty Earth Observatory of Columbia University, roverere@ldeo.columbia.edu
2Harvard University, jxm@eps.harvard.edu
3Curtin University, Perth, mickoleary.sci@googlemail.com
4University of North Carolina, Wilmington, kaisdad04@gmail.com
5University of North Carolina, Chapel Hill, jezinglis@gmail.com

Oscillations of sea level, whether rapid or gradual, influence the degree and style of shoreline formation including reef framework construction, destruction, and preservation. Using insight from modern shoreline systems, members of the PLIOMAX project have mapped mid-Pliocene, MIS11, and MIS5e shorelines at numerous localities around the world and modeled the effects of subsequent glacial isostatic adjustment (GIA) on their current position. For both MIS5e and MIS11 we conclude that an ice sheet stability threshold was crossed in the last few kyr of each interglacial resulting in the catastrophic collapse of polar ice sheets with a rise in eustatic sea level to ~9m or more above present. We further show that dynamic topography, supported by convectively maintained stresses generated by viscous flow in the mantle and associated buoyancy variations in the lithosphere, plays a significant role in the post-depositional displacement of Pliocene and even much younger Pleistocene shorelines. We will discuss how we are using predicted global patterns of GIA and dynamic topography to guide field efforts aimed at extracting the eustatic component of sea level change during past warm climates. We also discuss how our field data is helping, in turn, to constrain uncertainties in models of both GIA and the long-term convective evolution of the Earth (uncertainties in mantle viscosity, for instance).

Giving microbial communities a solar supercharge: does the transition to photosynthesis in extreme environments drive taxonomic, biochemical, and metabolic novelty?

JASON RAYMOND, ERIC ALSOP AND MATTHEW KELLOM
School of Earth & Space Exploration, Arizona State Uni.

A combination of prolific biological diversity and steep physical and geochemical gradients make hydrothermal ecosystems outstanding environments for understanding the dynamic interplay between life and environment. Our work investigates taxonomic (e.g. 16S rRNA), metagenomic, and transcriptomic profiling of microbial communities in extreme environments. One such study focuses on communities occurring along a 40+ degree C temperature gradient in a geochemically well-characterized alkaline hot spring in Yellowstone National Park (YNP). The communities along this single outflow channel show changes in community organization, metabolism, and (taxonomic) biodiversity that can be directly related to changes in the geochemistry of their aqueous environments.

One unexpected result of this work comes at the so-called photosynthetic fringe, where “hot” chemotrophic metabolism gives way to “cool” phototrophy. This transition occurs between 55 and 73 degrees C in alkaline YNP springs—an apparent upper temperature limit on photosynthesis that is still poorly understood. While in general, biodiversity increases as temperature decreases, 16S analysis reveals that community diversity—quite unexpectedly—peaks not below but rather just above the onset of photosynthesis, tapering off at both higher and lower temperatures. This increase in biodiversity is not simply the union of lower T photosynthetic and higher T chemotrophic communities; intriguingly, new species not observed in any other communities occur only at this intersection.

We are integrating molecular genetic data with geochemical analyses to investigate several plausible hypotheses for this boost in diversity. Furthermore, this integrated approach provides unprecedented resolution of how the onset of photosynthesis in complex, natural communities results in a dramatic shift not only in the overall numbers but also in the distinct types of biomolecules able to be synthesized by the community at large. Whereas taxonomic diversity is at a maximum above the photosynthetic fringe, biochemical and metabolic diversity is highest below the fringe, where the energetic supercharge provided by photosynthesis makes accessible new and otherwise costly metabolic capabilities.

Finally, we hypothesize that the transitions associated with the photosynthetic supercharge may provide important insights into how the invention of photosynthesis (oxygenic photosynthesis in particular) provided the molecular underpinnings for early life on Earth to achieve new levels of complexity and stands as the single most important biological innovation since the origin of life itself.

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STXM characterization of fossil organic matter from the Montceau-les-Mines Lagerstätte (France)

A. Recanati¹, S. Bernard¹, D. Germain², S. Charbonnier² and F. Robert¹

¹LMCM, UMR 7202, MNHN and CNRS, Paris, France (arecanati@mnhn.fr, sbernard@mnhn.fr, robert@mnhn.fr)
²CR2P, UMR 7207, MNHN and CNRS, Paris, France (scharbonnier@mnhn.fr, germain@mnhn.fr)

The fossil record contains key information regarding the evolution of life and environment on Earth. However, decoding this record can be quite challenging as biogenic organic matter (OM) is inevitably altered during fossilization processes. The combination of transmission electron microscopy (TEM) with synchrotron-based scanning transmission X-ray microscopy (STXM) and X-ray Absorption Near Edge Structure (XANES) spectroscopy now offers valuable capabilities for the in situ characterization of heterogeneous and organic-rich samples such as fossilized remains [1]. TEM provides spatially-resolved information on organic constituent texture at the sub-nanometer scale, and allows for crystallographic determination. STXM and XANES enable spatially-resolved characterization of organic constituent speciation at the 15 nanometer scale.

Here we report the multiscale characterization of exceptionally preserved soft-bodied plants and animals fossilized within carbonate concretions from the Carboniferous Montceau-les-Mines Lagerstätte [2]. SEM and TEM investigations have revealed mineralogical and textural heterogeneities at all scale of observations, likely explaining the exceptional morphological preservation of the investigated fossils. STXM experiments (performed using the 5.3.2.2. ALS STXM Polymer beamline [3]) have allowed to evidence the similar molecular signatures of the OM composing the vegetal and the animal remains. We interpret this surprising homogeneity as resulting from the replacement of the initial biogenic OM by newly condensed recalcitrant geopolymer compounds during early diagenesis. Altogether, this study illustrates the capabilities of synchrotron-based STXM and XANES spectroscopy to provide molecular-level information on natural OM.

A Simple Method to Filter Arsenic From Water using CuO Nanoparticles

K.J. REDDY AND K.J. MCDONALD

1Department of Ecosystem Science and Management, University of Wyoming, Laramie, WY 82071, USA (katta@uwyo.edu)

A continuous flow-through reactor with CuO nanoparticles (NPs) was developed to filter arsenic (As) from groundwater samples. Natural groundwater samples as well as spiked with 100 µg/L of As were passed through (1L per hr) the flow-through reactor to filter As. Samples from the flow-through reactor were collected at a regular interval and analyzed for As and other chemical components (e.g., pH, major and trace elements). The CuO NPs adsorbed with As were regenerated with a sodium hydroxide (NaOH) solution and tested again in the flow-through reactor. The continuous flow-through reactor was effective in filtering As from spiked or natural groundwater samples. The regenerated CuO NPs were also effective in filtering As from groundwater. The CuO nanoparticle treatment did not show any discernible effects on the chemical quality of groundwater samples. Results of this study suggest that CuO NPs show potential for developing a simple process for field applications to remove As from water (Table 1) [1].

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Volume (L)</th>
<th>CuO NP (As, µg/L)</th>
<th>RegenCuO NP (As, µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Control</td>
<td>109</td>
<td>110</td>
</tr>
<tr>
<td>5</td>
<td>0.1</td>
<td>1.5</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>30</td>
<td>0.5</td>
<td>2.5</td>
<td>&lt;1.0</td>
</tr>
<tr>
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<td>3.0</td>
<td>3.0</td>
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</tr>
<tr>
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<td>15.0</td>
<td>19.0</td>
<td>10.0</td>
</tr>
<tr>
<td>1200</td>
<td>20.0</td>
<td>23.0</td>
<td>14.0</td>
</tr>
</tbody>
</table>

Table 1. Effect of CuO NPs in removal of As from groundwater samples with continuous flow-through system.

Partial melting and melt loss: Migmatites from Val Strona di Omegna (Ivrea Zone, NW Italy)

CHARELTE REDLER

1Institute of Earth and Environmental Sciences, Mineralogy-Petrology-Geochemistry, University of Freiburg, Albertstrasse 23b, D-79104 Freiburg, Germany (charlotte.redler@minpet.uni-freiburg.de)

The mid to lower crustal field gradient through amphibolite to granulite facies rocks in the Ivrea Zone [1] offers the potential to study classical high-grade metamorphic processes such as partial melting and melt loss. Metapelitic rocks in Val Strona di Omegna show a progressive development in structures, starting with typical amphibolite facies mica-schists at lowest grades that change to metatexites with rare isolated leucosome veins at medium grades and diatexites in high-grade granulite facies rocks.

The first field evidence for partial melting is given by narrow discontinuous leucosomes that coincide with the fluid-absent breakdown of muscovite and the prograde appearance of K-feldspar. Towards high grades the consumption of biotite lead to more extensive melting and the formation of garnet-bearing leucosomes. Zones of diatexite in the highest-grade rocks indicate that melt loss was inefficient and/or accumulation of melt occurred. These zones are common at boundaries between diatexitic metapelitic rocks and metatexitic metagreywacke and may indicate that the metagreywacke formed a low-permeability barrier that restricted melt flow.

Field and petrographic evidence for melting can also be seen by crossing the position of the modelled wet solidus, which is consistent with the small amounts of melt predicted to occur by H2O-saturated melting. In addition, calculated P-T pseudosections show that the metapelitic rocks have produced up to 30-40 mol.% melt at peak metamorphic conditions of around 11 kbar and 900°C. Modelling of granulite facies samples suggest a significant melt loss prior to cooling by showing elevated solidi. This is consistent with a depletion in SiO2, Na2O and K2O and an enrichment in FeO, MgO and TiO2 relative to amphibolite facies samples.


Peloid mud maturation, a mineralogical and health hazard point of view

MARCO REDOLFI

1Dipartimento di scienze, Univ. Roma3, Roma 00146 Italia (*correspondence: marco.redolfi@uniroma3.it)

One of the main topic in medical spa is understanding the health hazard correlated to the presence of heavy metal cations in the thermal mud that can be absorbed by the skin associated with the more desirable cations who have beneficial property for some chronic diseases. I develop a standard protocol for analysis of the thermal mud during the maturation for better understanding the characteristic and eventually change in mineralogical and metal available parameter.

I used a maturation protocol developed at Salsomaggiore Terme [1] Italy, mixing a common clay, obtain in Tor Caldara Regional park, Anzio with 11 thermal water collected in the Lazio region in Italy plus distillate water. These mud has been put at 40°C in sealed container for all the maturation period.

After one month and three month of maturation I sample the mud for XRD analysis and heavy metal sequential extraction plus “sweat” extraction [2] to understand the change in these parameter with the progress of the maturation process. These parameter were compered each other, to see the modification of the mineralogy and heavy metal availability during the different stage of mud maturation.

The first data are under integration with new data obtain in these days. But avaialbe data demonstrate the formation of gypsum inside the clay, and the partial reduction of some more complex mineral, like plagioclase. The data of the metal and “sweat” extraction are under processing phase and will be ready for the end of June.

Active and Total Microbial Community Structure in relation to Metal Availability within Subsurface Sediments

BRANDI KIEL REESE¹, LAURA ZINKE², HEATH J. MILLS³ AND KATRINA EDWARDS⁴

¹Department of Biological Sciences, University of Southern California, Los Angeles, CA (brandi.reese@usc.edu)
²Department of Earth Sciences, University of Southern California, Los Angeles, CA (laurazinke@neo.tamu.edu)
³Department of Oceanography, Texas A&M University, College Station, TX (hmills@ocean.tamu.edu)

To understand the role of biology over geologic time scales and to appreciate past, current and future processes, the total microbial community (including metabolically active and dormant populations) must be characterized. The total microbial community is composed of varying metabolically active and dormant populations based on geochemical conditions. While metabolically active populations change the current geochemical conditions, understanding the total community structure can determine the potential processes available when geochemical conditions change in the future or when geochemical conditions were different in the past. Unlike surface populations that may experience rapid geochemical shifts, timescales for change in the deep subsurface may be over geologic time scales. Thus, dormant populations may become members of a seed bank, which can contribute to the diversity of future microbial communities while remaining examples of past conditions.

Sediment was collected during IODP Expedition 336 on the western flank of the mid-Atlantic ridge (North Pond) and was immediately cryogenically frozen. DNA and RNA were simultaneously isolated from the same sample at eight depths downhole using a uniquely developed extraction method. The V1-V3 region of the 16S gene and gene transcript was targeted using universal Bacteria specific primers. This approach targeted the active microbes via rRNA transcripts and the total population (live, dormant, dead) via DNA targets. X-ray Absorption Spectroscopy (XAS) was also used to map elements within the sediment samples chosen for molecular analysis. 16S rRNA gene transcripts extracted were quantified using quantitative rt-PCR. Greater microbial activity was observed at the sediment surface and diversity decreased with depth into the sediment. A majority of the lineages detected were heterotrophic, despite reduced metal species being present, suggesting the overall influence of very low carbon concentrations on community structure and function.

Holocene climate variability from Rio Martino Cave (Western Alps, northern Italy)

REGATTIERI E.¹,², ZANCHETTA G.¹,², ISOLA I.², DRYSDALE R.N.³, ZANELLA E.⁴, LANZA R.⁴, HELLSTROM J.C.³, DALLAI L.⁵, PERRETTE Y.⁶, COUCHoud I.⁷, MAGNY M.⁸ AND VANNIÈRE B.⁹, LANCI L.⁹

¹Department of Earth Sciences, University of Pisa, Italy. (regattierid@dst.unipi.it)
²Istituto Nazionale di Geofisica e Vulcanologia, Pisa, Italy.
³School of Earth Sciences, University of Melbourne, Australia.
⁴Department of Earth Sciences, Università degli Studi di Torino, Italy.
⁵Department of Resource Management and Geography, University of Melbourne, Australia.
⁶Istituto di Geoscienze e Georisorse, CNR- Pisa, Italy.
⁷EDYTEM, CNRS, Université de Savoie, France.
⁸Chrono-Environment CNRS, Besancon, France.
⁹Department of Earth Sciences Universita’ degli Studi di Urbino, Italy.

The Alpine region of Europe currently experiences complex climatic conditions and this is also apparent during the Holocene. With this in mind, several flowstone cores were retrieved from Rio Martino Cave (Piemonte, Northern Italy, ca. 1530 m a.s.l.) in the western Alps, where the climate is dominated by North Atlantic synoptic systems. U/Th dating of several flowstones indicates that deposition started at the beginning of the Holocene. One core has been intensively studied using a multi-proxy approach (stable isotopes and rock magnetism). The δ¹⁸O record show substantial variability through the Holocene, which is interpreted as changes in rainfall δ¹⁸O recharging the cave catchment. Variations in δ¹³C instead are interpreted as different degrees of soil development. A long-term trend in δ¹⁸O is apparent, with relatively low values persisting from the commencement of deposition until ca. 6 ka. From 6 to 3 ka the δ¹⁸O increases gradually before decreasing again from 3 ka onward. δ¹³C shows a good degree of correlation with δ¹⁸O. This long-term trend may be related to changes in the seasonal patterns of precipitation. Superimposed on this trend there are numerous centennial scale oscillations which may reflect alternating periods of drier and wetter conditions.

Both stable isotope records and magnetic susceptibility, which mainly depend on the detrital content, show good correlations with lake level record and flood events in Lake Ledro.

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Results of an Interdisciplinary Research Project on Soil Aggregate Formation in CZO’s

INGE REGELINK1, GEORG LAIR2, TARU LEHTINEN23, JEROEN VAN LEEUWEN1, BAS VAN DER ZAAAN2, JASMIN SCHIEFER2, SVETLA ROUSSEVA5, AIMERIC BLAUD6, MENOJ MENNONS4 AND STEVE BANWART6

1Wageningen University, Wageningen, The Netherlands, (*correspondence: inge.regelink@wur.nl)
2University of Natural Resources and Life Sciences, BOKU, Vienna, Austria
3University of Iceland, Reykjavik, Iceland
4Deltares, Utrecht, The Netherlands
5Nikola Poushkarov Institute of Soil Science, Sofia, Bulgaria
6University of Sheffield, Sheffield, UK

Soil physical properties such as aggregate stability and porosity are crucial for the soil’s agricultural productivity, carbon sequestration capacity and water holding capacity. The formation of soil aggregates is the result of complex interactions between biological, chemical and physical soil processes. Therefore, multi-disciplinary research on Critical Zone Observatories (CZO’s) is needed to unravel the key-processes. Therefore, multi-disciplinary research on Critical Zone Observatories (CZO’s) is needed to unravel the key-processes. These data are the result of the joined efforts from soil chemists and biologist collaborating within the SoilTrEC project [2]. We show that organic-mineral interactions and solution chemistry are important for formation of primary soil aggregates. Especially Fe-(hydr)oxides play a crucial role because of their strong interactions with organic substances in the soil [3]. Macro-aggregates are formed when both organic matter, clay minerals and Fe-(hydr)oxides are present in sufficient amounts. These soil macro-aggregates act as habitats for micro-organisms which may in turn alter the organic substances within the soil aggregates. The microbial communities within the macro-aggregates are affected by the land use. Furthermore, land use shows pronounced effects on the structure of the pores within the soil macro-aggregates.

Overall, we want to highlight the importance of multi-disciplinary research in understanding the complex interactions between chemical and biological processes within the critical zone.


Reconstructing subducted sediment fluxes using ancient arc lavas

MARCEL REGELOUS1, CHRISTOPH BEIER1
AND KARSTEN HAASE1

1GeoZentrum Nordbayern, Universität Erlangen-Nürnberg, Schlossgarten 5, 91054 Erlangen, Germany (correspondence: marcel.regelous@fau.de)

Previous studies have shown that there exists a relationship between the fluxes of trace elements contained in subducting sediments at active subduction zones, and the trace element composition of the associated arc lavas, after correction for melting and fractionation effects [1]. This relationship apparently holds despite the wide range in thermal structure of present-day subduction zones resulting from variations in subduction rate, slab dip and the age of the subducting plate and could be used, together with trace element analyses of ancient arc lavas, to estimate past sediment fluxes at former subduction zones.

This method might be used to test the hypothesis that high atmospheric CO₂ concentrations in the late Mesozoic–early Cenozoic was maintained by subduction and decarbonation of large volumes of carbonate-rich sediment deposited in the former Tethys Ocean [2-4]. If this were the case, then ancient arc lavas from the margins of Tethys would be expected to have relatively high Sr and Ba, and low Th normalised concentrations. The approximate mass of carbonate subducted could be estimated from the Sr concentration of Tethyan carbonate.

The volume and average composition of deep-sea sediment available for subduction at ancient subduction zones has likely varied over time-scales that are long compared to the average age of the oceanic crust (~60 Ma) [5]. Biogenic sediments, which are important hosts of some trace elements, would not have been available for subduction before 500 Ma. The mid-Mesozoic proliferation of planktic calcifiers resulted in a larger carbonate component in deep-sea sediments available for subduction. If carbonate makes up 7-15% of the average subducting sediment and has Sr contents an order of magnitude higher than the detrital fraction, then sedimentary Sr fluxes into subduction zones may have been ~50% lower than present before 500 Ma (i.e. for much of Earth's history).

Occurrence and distribution of natural occurring radioactive materials at a geothermal facility in the North German Basin

SIMONA REGENSPURG1, JÖRG DILLING2, JÜRGEN MIELCAREK2, RUDOLF NAUMANN1 AND UWE-KARSTEN SCHKADE2

1Helmholtz Centre Potsdam, German Research Centre for Geosciences, Telegrafenberg, D-14473 Potsdam, Germany; regens@gfz-potsdam.de
2Federal Office for Radiation Protection, Köpenicker Allee 120-130, D-10318 Berlin, Germany

The occurrence of mineral precipitates with elevated activity concentrations of radionuclides of natural origin is a well known observation from wells of the oil and gas industry. Similar natural occurring radioactive materials (NORM) were found at some deep geothermal facilities. Presumably, these radionuclides are transported with the geothermal fluids and co-precipitate upon change of thermodynamic conditions with the respected oversaturated mineral.

On the one hand, the occurrence of NORM offers the identification of geochemical processes, but on the other hand elevated activities might lead to an enhanced exposure due to radiation. At the geothermal research facility in Groß Schönebeck (North German Basin) the mobility of potassium (40K) and radionuclides of the natural uranium- and thorium decay series was intensively monitored. Radionuclide concentrations were measured by gamma-ray spectrometry in samples from reservoir rocks, scalings, filter residues and fluids. Additionally the ambient gamma dose rate of several plant components was monitored. It was found that the content of natural radioactivity in the reservoir rocks is relatively low, whereas a strong enrichment was detected for 210Pb and especially for the radium isotopes 226Ra and 228Ra in the filter residues of the plant. Filter residues and fluid samples were not in equilibrium with respect to these nuclides.

Since these residues consist mainly of the mineral barite (BaSO4) and Ra is known as substitute for barium in minerals, barite precipitates apparently act as scavenger for these radionuclides. Further, it was found, that in sandstone reservoir rocks the radionuclides 226Ra and 210Pb are in deficiency compared to their parent 238U.

REE mobility in carbonatites: insights from the trace-element composition of dolomite

E.P. REGUIR* AND A.R. CHAKHMOURADIAN

1Department of Geological Sciences, University of Manitoba, Winnipeg, MB, Canada, R3T 2N2 (*correspondence: umreguir@cc.umanitoba.ca)

Dolomite is a principal constituent of many carbonatites. Whereas the major-element chemistry of this mineral has been studied reasonably well, its trace-element variations have not. Here, we examined the trace-element composition of dolomite from carbonatites at Aley (British Columbia, Canada) to improve the current understanding of the processes that affected these rocks after their emplacement.

The examined dolomite shows extremely variable levels of Mn, Co, Sr, Ba, Sc and REE (900-13500, 0-15, 22-7000, 0-600, 0-60 and 0-400 ppm, respectively). Late-stage rhombohedral dolomite associated with quartz and chlorite (±REE minerals) is consistently enriched in REE relative to the groundmass. The pattern of enrichment varies from light-REE dominated to heavy-REE dominated. The former type correlates with enrichment in Mn, Sr, Co and Ba. Late-stage dolomite enriched in heavy REE contains lower levels of these elements. There is a general increase in REE content from the core of rhombohedral crystals toward their rim. The groundmass dolomite is characterized by relatively flat chondrite-normalized profiles, which are, in some cases, interrupted by a small negative Y anomaly. With the exception of one sample, REE patterns of the late-stage dolomite show appreciable positive Eu and Y anomalies.

The observed trace element characteristics of dolomite indicate an influx of REE, possibly scavenged from fluorapatite and transported by F-bearing crustal fluids under reducing conditions. The trace-element composition of the late-stage dolomite was further influenced by the precipitation of other associated phases, such as monazite and chlorite.

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Crustal thickness estimation from GOCE satellite mission gravity data

M. REGUZZONI1 AND D. SAMPIETRO2*

1DICA, Politecnico di Milano, Piazza Leonardo Da Vinci, 32
20133, Milano, Italy
(mirko.reguzzoni@polimi.it)
2GReD - Geomatics Research & Development srl, via Valleggio 11, 22100, Como, Italy
(*correspondence: daniele.sampietro@g-red.eu)

The boundary between Earth crust and mantle, the so-called Moho, is commonly estimated by means of seismic or gravimetric methods. The former methods can be locally very accurate since seismic profiles give an almost direct observation of the actual crustal structure, but can be quite far from reality in large regions where no data are available. The latter methods, although often based on simplified hypotheses to guarantee the uniqueness of the solution, are nowadays becoming more and more important thanks to the improved knowledge of the gravitational field. In particular satellite gravity missions, like the European Space Agency mission GOCE (Gravity field and steady-state Ocean Circulation Explorer) [1], provide a very accurate and spatially homogeneous dataset that can be used to validate the existing global crustal models or to estimate a new one by constraining the relation between Moho depth and crustal density.

In this work a new crustal model (GEMMA model) with a spatial resolution of 0.5°x0.5° and constrained with GOCE observations is computed. For this purpose several additional external information has been used, such as topography, bathymetry and ice sheet models from SRTM, a recent 1°x1° sediment global model and some prior hypotheses on crustal density. In particular the main geological provinces, each of them characterized by its own relation between density and depth, have been considered. A model describing lateral density variations of the upper mantle is also taken into account. Starting from this prior information, an inversion algorithm is applied to the GOCE space-wise grid of second radial derivatives of the gravitational potential [2] to estimate the bottom of the crust. The computed Moho global model is well consistent not only with other global/regional models, but also with the actual gravity field, thus overcoming the main limitation of seismic Moho models (e.g. CRUST2.0).


Stable Isotope Tracing of Manufactured Nanoparticles

M. REHKÄMPER12, A. LAYCOCK12, F. LARNER13, A. DYBOWSKA2, Y. DOGRA4, B. STOLPE5, M. DIEZ ORTIZ6, J.R. LEAD7, C. SVENDSEN6, E. VALSAMI-JONES25, C.R. TYLER4 AND T.S. GALLOWAY4

1Department of Earth Science & Engineering, Imperial College London, London SW7 2AZ, UK
2Life Sciences, Natural History Museum, London SW7 5BD, UK
3Earth Sciences, Univ of Oxford, Oxford OX1 3AN, UK
4Biosciences, University of Exeter, Exeter EX4 4QL, UK
5School of Geography, Earth & Environmental Sciences, University of Birmingham, Birmingham B15 2TT, UK
6Centre for Ecology and Hydrology, Wallingford OX10 8BB, UK
7Center for Environmental Nanoscience and Risk, University of South Carolina, USA

Studies of biological uptake and environmental fate of manufactured nanoparticles (NPs) are often hampered by the difficulty of distinguishing these materials from the normal background levels of elements and natural NPs in environmental samples. Needed are methods for tracking engineered NPs in bulk samples from exposures that are carried out at realistic particle concentrations rather than the much higher levels that are often dictated by the lack of suitable analytical protocols. For metal and metal oxide NPs, this can be achieved by stable isotope tracing, employing NPs that are prepared from a single isotope of the target element.

We are currently investigating stable isotope labeling and tracing for ZnO, CeO2 and Ag NPs, all materials that have a wide range of applications in industrial and consumer products. Using suitable isotopes and NP preparation methods, stable isotope labeling is cost-effective for these elements. When combined with high precision mass spectrometry for detection, the methodology provides unprecedented sensitivity for NP tracking. For example, biological uptake of ZnO NPs can be detected even at Zn background levels, which exceed the NP concentrations by more than a factor of 10,000.

The application of such methods enables accurate tracing of NP fate and transfer in a wide range of exposure systems and biota. Importantly, the results are able to directly address the key question of whether organisms take up nanoparticles directly or whether the elements are taken up only after particle dissolution.
Quality control for novel isotope analyses

M REHKÄMPER1, F WOMBACHER2, S NIELSEN3, M SCHÖNBÄCHLER4, M FEHR5, T GOLDBERG1, F LARNER6, A LAYCOCK1, M PAUL1 AND T VAN DE FLIERDT4

1Dept of Earth Science & Engineering, Imperial College London, London SW7 2AZ, UK
2Institut für Geologie und Mineralogie, Universität zu Köln, D-50674 Köln, Germany
3Dept of Geology and Geophysics, WHOI, Woods Hole, MA 02543, USA
4Institut für Geochemie und Petrologie, ETH Zürich, CH-8092 Zürich, Switzerland
5Dept of Environment, Earth and Ecosystems, The Open University, Milton Keynes MK7 6AA, UK
6Dept of Earth Sciences, University of Oxford, Oxford OX1 3AN, UK

Research in isotope geo- and cosmochemistry is often driven ahead by investigations that interrogate novel isotope systems or particularly ‘difficult’ sample types, whereby analytical challenges are frequently addressed by the use of advanced instrumentation and/or new techniques of sample preparation and data acquisition. Testament to this are the numerous isotopic ‘methods’ articles that are published by geochemists and the even more frequent contributions that present and discuss novel data from, prominently, studies of (still) ‘non-traditional’ stable isotope systems, extinct radionuclides and nucleosynthetic isotope anomalies.

Such leading edge work faces similar but distinct analytical difficulties and additional metrological challenges. In particular, it cannot rely on well-characterized pure-element isotope standards and geological or environmental reference materials (RMs), for evaluation and documentation of data quality. The geochemical community has, however, been very adept in finding pragmatic solutions to such challenges in quality control, through innovative work of individual laboratories, critical peer review of journal articles and, most importantly, generally good-natured competition and extensive collaboration, both formal and informal, between research groups.

With regard to reference materials and method validation, geochemists and metrologists share a common interest in improving data quality and intercalibration but communication and collaboration between these communities on isotopic research is often limited. This is unfortunate because both sides could readily profit from improved interaction, for example in the preparation, characterization and distribution of RMs.

Field Sampling for Porewater Mercury and Methylmercury using DGT

DANNY REIBLE1*, PAUL BIRETA2, ARIETTE SCHIERZ1, JAMES GRUNDY2 AND RICH LANDIS3

1Center for Research in Water Resources, University of Texas at Austin, Austin, TX, USA, reible@mail.utexas.edu (*presenting author)
2Civil, Architectural and Environmental Engineering Department – EWRE, University of Texas at Austin, Austin, TX, USA
3DuPont, 974 Centre Road, Wilmington, DE, USA

Dissolved porewater concentrations have the potential to better relate to mercury methylation rates than bulk mercury sediment loadings. The diffusive gradient in thin film (DGT) technique is applied to determine aqueous mercury and methyl mercury vertical porewater concentration profiles. DGT probes were deployed in the South River (Virginia, USA) where previous industrial activities had led to mercury contamination. The river is primarily a sand and gravel stream with limited microbial productivity. The DGTs were used to evaluate methylation rates and extent and identify locations contributing significantly to methyl mercury. A potential remedial option of biochar amendment was evaluated in a small floodplain pond. The DGTs were used to measure the performance of the sediment amendment including changes to available mercury and methyl mercury. Sampling of bulk sediment, surface water, porewater, and biota was carried out in parallel. Specific redox couples were also measured over depth using cyclic voltammetry. Conclusions were drawn as to the sources of significant methylation and relationship to sediment geochemistry.
The microstructure and trace metal geochemistry of pyrite from porphyry Cu deposits

M. REICH1*, A. DEDITIUS3 AND F. BARRA12

1Dept. of Geology, University of Chile, Santiago, Chile (*email: mreich@ing.uchile.cl)
2Andean Geothermal Center of Excellence (CEGA), University of Chile, Santiago, Chile
3Graz University of Technology, Graz, Austria

Porphyry copper deposits (PCDs) are currently the world’s largest source of copper and molybdenum, and are also among the largest reservoirs of gold in the upper crust. Despite the fact that pyrite is a ubiquitous mineral phase in these deposits, the major and trace element chemistry of pyrite from PCDs remains poorly understood.

Here we report the first comprehensive trace element database of pyrite from the Dexing deposit, China’s largest porphyry Cu deposit, determined using a combination of electron microprobe analysis (EMPA) and secondary-ion mass spectrometry (SIMS). Results show that the concentrations of precious metals (e.g., Au, Ag), metalloids/chalcogens (e.g., As, Sb, Se, Te), and base/ heavy metals (e.g., Cu, Co, Ni, Zn, Hg) in pyrite from a PCD are more significant than previously thought (e.g. ~6 wt.% Cu, ~3 wt.% As, ~0.25 wt.% Au, and ~0.2 wt.% Ni).

EMPA-WDS elemental mapping and SIMS depth profiling reveal that some of these metals occur exclusively in solid solution in the pyrite structure (e.g., As, Ni) or are present in solid solution and also in micro- to nano-sized inclusions (e.g. Cu and Au). The mineralogical occurrences are associated with complex textural and chemical features such as oscillatory growth zoning and sector zoning with variable porosity, where Cu-rich, As-(precious metals)-poor zones alternate with As-(precious metals rich)-rich, Cu-poor zones, and with barren pyrite zones.

These observations point toward a decoupled behavior of Cu and As in this porphyry system, strongly suggesting that selective partitioning of metals into pyrite is most likely the result of changes in fluid composition, probably caused by fluid mixing and repeated and intermittent pulses of Cu and As-bearing fluids of magmatic/ hydrothermal origin. Despite the fact that more studies are needed to increase our knowledge about metal partitioning in sulfides during the hydrothermal stages of PCDs formation, the observations and data presented here support an important role of pyrite as a record of fluid variations, and as a host of precious and base metals, metalloids/chalcogens and potentially PGEs.

The disparate crystal records of the Youngest Toba Tuff, Indonesia

M.R. REID1* AND J.A.VAZQUEZ2

1Northern Arizona University, Flagstaff, Arizona 86011, USA (*correspondence: Mary.Reid@nau.edu)
2U.S. Geological Survey, Menlo Park, California 94025, USA

The 74 ka Youngest Toba Tuff (YTT) is the product of a giant eruption (>2800 km3) from the Toba Caldera Complex of Sumatra, Indonesia. The YTT sample suite spans the compositional range of 63-75 wt.% SiO2, with most >68.8 wt.% SiO2. The narrower compositional range of quartz-hosted melt inclusions suggests that YTT compositional heterogeneity may reflect a spectrum of crystal-liquid mixtures [1]. Quartz from high silica rhyolites are relatively unzoned whereas those from low silica rhyolites have Ti, and therefore temperature, reversals late in their crystallization history. Limited diffusional relaxation across these bands suggests rim crystallization within a few ka of eruption [2]. In contrast, allanite from a high silica rhyolite grew extensively over >35 ka and are not reversely zoned at the rims [3]. 263U-238Th-206Pb zircon crystallization dates range to even older ages but mainly predate eruption by <400 ka. Despite the strong crustal signature of the YTT (87Sr/86Sr ~ 0.714), bonafide xenocrysts are relatively rare. Growth on individual zircon grains occurred over a protracted time interval (>100-500 ka), and was likely episodic. Zircon ages in high silicic rhyolites may span a more limited range. Zircon from individual rocks exhibit a significant Th/U compositional range and evidently crystallized from a plumbing system with a wider range in thermochemical conditions than those characterized by YTT matrix glasses. Cores nucleated over at least a 300 ka interval, often from relatively unevolved magmas. Zircon rims grew from host melts and yield ages that range from ~80 ka to ~115 ka. Compositional reversals are recorded by rims in zircon from low silica rhyolite but not high silica rhyolite. Considered collectively, ages and age ranges obtained from YTT phases decrease in the order zircon > allanite > quartz, a sequence that parallels that for attainment of phase saturation conditions. Minerals stable in more diverse magmatic compositions apparently persisted longer. Crystals were apparently remobilized intermittently by magmatic rejuvenation rather than being incorporated by foundering of roof rocks at the time of eruption. Domains that ultimately erupt as low silica rhyolites were remobilized beginning 40 ka before eruption – based on the zircon/allanite ages – with the most recent reheating occurring within a few thousands years of eruption [2].


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Assessment of a gold absorbing resin in natural groundwaters for mineral exploration

N. REID¹*, D.J. GRAY¹ AND A. LUCAS²

¹ Deep Exploration Technologies Cooperative Research Centre, CSIRO Earth Science and Resource Engineering, Kensington, Western Australia, Australia

¹School of Earth and Environment, University of Western Australia, 35 Stirling Highway, Crawley 6009, Western Australia

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

One of the most important elements for mineral exploration is gold, and yet it is one of the hardest to accurately measure in groundwater. Recent successes in regional hydrogeochemistry in Australia [1] has highlighted the potential of using activated carbon via both grab sampling and a newly modified Diffusive Gradients in Thin films (DGT) technique [2] to gain low level detection of Au (and other elements) as increasing concentrations of Au can vector to large mineral systems. A question we are addressing is whether the Au signal can be concentrated and/or improved by the use of specific Au absorbing resins.

We used Micro-CT tomography to determine how a specific resin, Purolite A100, absorbs both ionic and metallic Au from solutions, and precipitates it both on and within the resin structure.

Preliminary results show that Purolite A100 absorbs more Au (and also Ag, Bi, Pt and Pd) than activated carbon and gives more consistent results at higher concentrations.

Further research is still required for improving the absorbance of Au at lower Au concentrations.


Investigating the physicochemical gradients in oil sands wastes

THOMAS REID³*, RYAN BOUDENS¹ AND CHRIS WEISENER¹

¹GLIER - University of Windsor, Windsor, Ontario, Canada

³(reid11c@uwindsor.ca)

The Athabasca Oil Sands contain one of the world’s largest oil reserves consisting of approximately 178 billion barrels of oil[1]. With 20% recoverable through open pit mining methods, this extraction process produces a considerable amount of fluid fine tailings (FFT) waste material, which must be deposited on site in tailings ponds. These ponds allow the waste sands, clays, residual bitumen and water to settle out, allowing for the water to be recycled for use again in the extraction process. It is vital to understand the physicochemical gradients which form in these tailings ponds over time, with the goal of remediation once the ponds are no longer needed.

To study the influences of biotic and abiotic processes on fresh and mature FFT, sensitive microsensor profiling techniques are being used to measure hydrogen sulphide (figure 1), oxygen, Eh, and pH profiles over a 1 year period. These profiles are accompanied by pore water extraction methods to analyse cation, anion and pore water gas expression. To compliment these static experiments, dynamic simulations will investigate shear forces (wave action and turbulence) on the water-sediment interface in each of the biotic and abiotic microcosms, under controlled atmospheric conditions.

This holistic study provides insight regarding biotransformation and physicochemical controls effecting sediment oxygen demand associated with remediated wetlands & end pit lake development.

Figure 1: HS concentration profiles of mature FFT at 2, 4, and 8 weeks, extending from cap water down into the FFT sediment; dashed line is the sediment-water interface

Adsorption of Eu(III) onto minerals in the presence of humic acids: effects of various solution parameters and sorptive fractionation on modelling and spectroscopy

P.E. REILLER, N. JANOT AND M.F. BENEDETTI

1CEA/DEN/DANS/SEARS/LANIE, Gif-sur-Yvette, France
2Institut de Physique du Globe de Paris, Université Denis Diderot, Paris, France
pascal.reiller(at)cea.fr

Adsorption of metals on minerals with humic acids is always under predicted [1]. The case of Eu(III) in ternary system including purified Aldrich humic acid (PAHA) and α-Al₂O₃ was measured, modelled and probed using time-resolved laser-induced luminescence spectroscopy (TRLS). Each binary system was studied independently [2,3,4], and the luminescence properties of Eu(III), luminescence spectra and decay times (τ₁), were acquired and compared [5]. Influence of ionic strength and PAHA concentration was also evaluated.

The typical luminescence behaviour of Eu(III)-HA system, showing a bi-exponential decay, was also found in the ternary system Eu(III)/PAHA/α-Al₂O₃, but with marked differences. Luminescence spectra and faster decay τ₁ are the same in both system at pH < 6, but with higher τ₁ indicating a rigid environment for Eu(III). For pH > 6, modifications of Eu(III) luminescence spectra and decrease of τ₁ are showing a progressive influence of α-Al₂O₃. The non-variation of τ₁ suggests the on-going influence of PAHA, notwithstanding its progressive desorption.

Comparing with previous data on sorptive fractionation of PAHA [2,3,6], and with the TRLS evolution of the system [5], an operational modelling was proposed [4], which implies that alumina-sorbed PAHA is showing a stronger interaction towards Eu(III) compared with non-sorbed PAHA even at pH > 7. This stronger interaction is due to the sorptive fractionation which reveals stronger binding sites [1,4,7].


Geochemistry of European bottled water

CLEMENS REIMANN1, MANFRED BIRKE2 AND ALECOS DEMETRIADES3

1Geological Survey of Norway, P.O. Box 6315, Sluppen, 7491 Trondheim, Norway
2Federal Institute for Geosciences and Natural Resources, Wilhelmstrasse 25 – 30, 13593 Berlin, Germany
3IGME, 1 Spirou Louis Street, Entrance C, Olympic Village, 136 77 Acharnae, Athens, Hellas

To obtain a first impression of the geochemistry and quality of ground water at the European scale bottled mineral water was used as a sampling medium. In total, 1785 bottled waters were purchased from supermarkets of forty European countries, representing 1247 wells/drift holes/springs at 884 locations. All bottled waters were analysed for 72 parameters at the laboratories of the Federal Institute for Geosciences and Natural Resources (BGR) in Germany. The result provide a first impression of the natural variation of chemical elements in ground water at the European scale. Maps demonstrate that geology is one of the key factors influencing the observed element concentrations for a significant number of elements. Examples include high values of (i) Cr clearly related to the occurrence of ophiolites; (ii) Li (Be, Cs) associated with areas underlain by Hercynian granites; (iii) F (K, Si) related to the occurrence of alkaline rocks, especially near the volcanic centres in Italy, and (iv) V indicating the presence of active volcanism and basaltic rocks. The natural variation of element concentrations in the bottled water covers usually between three to four orders of magnitude and reaches up to 7 orders of magnitude for a few elements (e.g., Li, U). A comparaison with the chemistry of European tap water, surface water and Norwegian ground water shows surprising similarities in terms of median and variation. This proves that bottled water can be taken as a proxy for European ground water quality for the majority of elements/parameters. The bottled water samples showed, however, exceptionally high concentrations for a few elements typical for deep, hydrothermal sources (e.g., B, Be, Br, Cs, F, Ge, Li, Rb, Te and Zr).

Fortunately less than one percent of all samples returned values that were above the currently valid European maximum admissible concentrations (MACs) for drinking and/or bottled water (e.g., for As, Ba, F, Se, NO₃ and NO₂). It is, however, an important observation that currently there exist no water action levels for some of the elements that show an exceptionally high natural variation (e.g., Li and U).

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Chemistry of Europe's agricultural soils - the GEMAS project

Clemens Reimann¹, Alecos Demetriades² and Manfred Birke³

¹Geological Survey of Norway, P.O. Box 6315, Sluppen, 7491 Trondheim, Norway
²IGME, 1 Spirou Louis Street, Entrance C, Olympic Village, 136 77 Acharnae, Athens, Hellas
³Federal Institute for Geosciences and Natural Resources, Wilhelmstrasse 25 – 30, 13593 Berlin, Germany

Geochemical Mapping of Agricultural and Grazing land Soil (GEMAS) is a cooperative project between the Geochemistry Expert Group of EuroGeoSurveys and Eurometaux. During 2008 and until early 2009, a total of 2108 samples of agricultural (ploughed land, 0-20 cm) and 2023 samples of grazing land (0-10 cm) soil were collected at a density of 1 site/2500 km² each from 33 European countries, covering an area of 5,600,000 km². All samples were analysed for 52 chemical elements following an aqua regia extraction, 41 elements by XRF (total), and soil properties, like CEC, TOC, pH (CaCl₂), following tight external quality control procedures. In addition, the agricultural soil samples were analysed for 57 elements in a mobile metal ion (MMI) extraction, Pb isotopes and magnetic susceptibility. The GEMAS project thus provides for the first time fully harmonised data for element concentrations and soil properties known to influence the bioavailability and toxicity of the elements at the continental (European) scale. The provided database is fully in compliance with the requirements of the European REACH Regulation (Registration, Evaluation, Authorisation and Restriction of Chemicals). It also provides valuable information for other European pieces of legislation related to metals in soil.

The results demonstrate that robust geochemical maps of Europe can be constructed based on low density sampling. At the European scale element distribution patterns are still governed by natural processes, most often a combination of geology and climate.

An Iceland-like Setting for Generation of Earth’s Earliest Known Crust

Reimink, J.R.,¹* Chacko, T.,¹ Stern R.A.,¹² and Heaman, L.M.¹

¹Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton T6G 2E3, Canada (reimink@ualberta.ca)
²Canadian Centre for Isotopic Microanalysis, University of Alberta, Edmonton T6G 2E3, Canada

The Acasta Gneiss Complex (AGC) contains the oldest rocks on Earth with U-Pb zircon ages indicating crust formation between 3.6-4.03 Ga [1-3]. Here we report whole rock geochemistry along with SIMS U-Pb, trace element, and O-isotope compositions of zircon from a >4.0 Ga tonalite unit identified during detailed mapping of the AGC.

Unlike typical Archean TTGs [4], this unit is characterized by moderate silica contents (58-62 wt % SiO₂), strong Fe-enrichment (12-15 wt% FeO), and low Mg numbers (13-18). REE patterns are relatively unfractionated (La/YbN ~2.5) and contain a significant negative Eu anomaly. These features strongly suggest that, unlike deep-seated Archean TTG magmas [4], the evolution of this AGC tonalite was dominated by shallow-level fractionation processes involving plagioclase.

Zircons from this well preserved unit document complex morphological patterns, very similar to previously described pre-4.0 Ga zircons from the AGC [1]. Two phases of igneous zircon growth, centers and mantles, are compositionally distinct but record indistinguishable U-Pb ages >4.01 Ga. Oxygen isotopic compositions from zircon centers and mantles document a decrease in δ¹⁸O from a mean of 5.6±0.1‰ to a mean of 4.7±0.1‰. This center to mantle decrease in δ¹⁸O can be explained by late-stage assimilation of hydrothermally altered crust.

Collectively, these data for the >4.0 Ga AGC tonalite are strikingly similar to those reported for intermediate rocks from Iceland (e.g., icelandites), which are thought to have formed by a combination of shallow-level basaltic magma fractionation and assimilation of surface-water altered crust [e.g., 5]. Thus, Iceland may serve as a suitable analogue for the generation of Earth’s earliest proto-continental crust.

Toward an in-situ bioremediation strategy for acidic in-situ leach uranium mining

B.C. REINSCH1*, M. DESCOSTES2, R. BERNIER-LATMANI1 AND P. ROSSI1

1École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland,
(*correspondence: brian.reinsch@epfl.ch)
2AREVA, Paris, France

In Kazakhstan, in-situ leach (ISL) mining of uranium utilizes the oxidizing power of pH < 2 sulfuric acid solutions to liberate and mobilize uranium from the ore’s naturally reducing conditions. Although ISL has the potential to be less environmentally impactful than physical mining techniques, it includes the risk of groundwater contamination. A detailed geochemical and microbiological analysis and comparison of pre-, mid-, and post-mining conditions is warranted in order to assess and potentially mitigate that risk.

A theoretically ideal remediation strategy for ISL would be one that re-equilibrates the pH, immobilizes uranium as U(IV) precipitates, and does not require physical disruption of the surface. The strategy proposed here is in-situ biostimulation. The injection of carbon-based electron donors into the subsurface would, in theory, promote the growth of indigenous bacterial communities able to reclaim the subsurface. The proposed mechanism is that stimulated sulfate reducing and/or iron reducing bacteria can return the pH to its original value and re-establish reducing conditions more rapidly than the commonly practiced strategy of natural attenuation. Biostimulation could also utilize the existing configuration of pumps and pipes, originally used to inject acid.

The objectives of this study are: 1) to characterize the impact of the injection of sulfuric acid on the subsurface geochemistry, 2) to probe changes in the subsurface microbial communities as a result of mining operations, 3) to identify through laboratory-based studies which electron donors may promote Fe- and/or sulfate-reducing microbia communities post-mining, and 4) to ascertain the composition of the microbial community post-remediation. The results presented here represent the initial stages of a pioneering study to understand the effects of uranium ISL on the environment and to design and implement an in-situ bioremediation strategy in Southern Kazakhstan.

Geochemistry of Biotite of The Vila Nova Pluronite (Central Portugal)

A.I.M. REIS1

1Department of Earth Sciences, University of Coimbra, 3000-272 Coimbra, Portugal (aimreis@gmail.com)

The Vila Nova plutonite intruded phyllites and metagraywackes of Neoproterozoic-Cambrian Beiras Group in Central Iberian Zone of Iberian Massif which is the SW segment of the European Variscan Belt and occurs in a group of seven plutonites of similar age and particular features related to a major strike slip shear zone. The Vila Nova plutonite has a compositional variability of tonalite-granodiorite-granite. Its a rock of fine to medium grained, muscovite biotite. The δ18O values are 11.09 ‰ - 11.5, 12.65 ‰. The plagioclase An(%) contents are 13.2 - 13.6, 14.6 and feldspar Or(%) contents are 86.2 - 93.2 ‰. The tonalitic lithotype do not contain feldspar. Biotite is often altered to chlorite associated with acicular rutile and opaque minerals such as pyrite and is absent in granitic composition with tourmaline. They are magmatic except in microgranular enclaves where they are reequilibrated, the XeO is 0.74 - 0.71 and are ferriferous biotites with aluminopotassic trends evidence of peraluminous magma.

The biotite in surmicaceous xenoliths, stretched on alternated reeds with muscovite, occur in the granodiorite composition and have less content of Si, Ca, Na and higher content of AlIV and Zn and, in the microgranular enclaves in the granodioritic composition the dispersed and subhedral biotite have less content of Ti, Zn, K and higher contents of Fe3+, Ca and Na than others biotites. In these textural heterogenities some elements have opposite behavior from center to rim. The biotites in the evolutionary trend have a decrease of Fe2+, Fe3+, Mn, Li, Ca, Rh, OH, Li/Mg, Rb/Mg and an increase of Mg, Na, Cs, F, Si/Ca.

Chromitites from the Andriamena greenstone belt, Madagascar: Hints of a mid-Archean ophiolite?

LAURIE REISBERG*1, MARYSE OHNENSTETTER2 AND CATHERINE ZIMMERMANN3

1Centre de Recherches Pétrographiques et Géochimiques, UMR 7358, CNRS, Université de Lorraine, BP 20, 54501 Vandoeuvre-lès-Nancy, France. (*correspondence: reisberg@crpg.cnrs-nancy.fr)
2GéoRessources, UMR 7359, CNRS, Université de Lorraine, BP 70239, 54506 Vandoeuvre-lès-Nancy, France

The Andriamena greenstone belt of Madagascar contains massive chromitite bodies of likely ophiolitic affinity, composed of about 90% chromite and 10%, mostly secondary, gangue minerals (talc, green amphibole, orthopyroxene, Ca and Mg carbonate). Arguments in favor of an ophiolitic origin for the chromitite include the high Cr# (0.67 -0.74), coupled and Mg carbonate). Arguments in favor of an ophiolitic origin for the chromitite include the high Cr# (0.67 -0.74), coupled with relatively high Mg# (0.6- 0.78) of the constituent phases display very low TiO₂ and Mg#. In addition, these phases display very low TiO₂ with relatively high Mg# (0.6- 0.78) of the constituent phases. Arguments in favor of an ophiolitic origin for the chromitite include the high Cr# (0.67 -0.74), coupled with relatively high Mg# (0.6- 0.78) of the constituent chromite. The very high Fo content of the olivine in the dunite, as high as 0.95, also attests to an ophiolitic provenance.

Platinum group element (PGE) and Os isotopic analyses were performed on several chromitite samples. Chondrite normalized PGE spectra display marked depletions in PGE relative to IPGE, with (Pt/Ir), ranging from ~0 to 0.09, though Pd contents are somewhat less depleted than those of Pt. The observed PGE depletion is another feature characteristic of ophiolitic chromitites. The IPGE enrichment is consistent with the presence of laurite microinclusions in the chromite revealed by SEM. Os isotopic compositions are tightly clustered, with 187Os/188Os ranging from 1.057 to 1.059, corresponding to T ⁸⁷⁶⁹ model ages of ~ 3.2 Ga, assuming primitive upper mantle parameters [1]. ¹⁸⁸Os/¹⁸⁷Os measurements are in progress.

If the ophiolitic nature of the chromitites is confirmed, our results might imply that mechanisms similar to present-day tectonic processes may already have been active in the mid-Archean.


Biogeochemical cycling of Au and Pt - Integrating field studies, micro-analyses and molecular biology

FRANK REITH*, CARLA ZAMMIT1, DIETRICH H. NIES, GORDON SOUTHAM2 AND JOEL BRUGGER1

1The University of Adelaide, School of Earth and Environmental Sciences, Adelaide SA5005, Australia (*correspondence: frank.reith@csiro.au)
2Martin-Luther University Halle-Wittenberg, Institute of Biology/Microbiology, Halle, Germany.
3The University of Queensland, School of Earth Sciences, Brisbane, QLD 4072, Australia

The biosphere catalyzes a variety of biogeochemical reactions that transform Au and Pt. Studying these interactions from the nano- to the macro-scale requires a well-integrated set of tools ranging from field studies to micro-analytical, synchrotron- and omic approaches. Gold and Pt grains are rare, hard to find and getting access to prospecting sites often requires a great deal of ‘field diplomacy’. To study biofilms living on grain surfaces, Au and Pt grains need to be collected under field-sterile conditions and frozen, refrigerated or fixed immediately after collection for genomic-, culturing- or electron microscopic studies, respectively. In particular, FIB-SEM-ESEM-ED3A has been useful in understanding the distribution and structure of biominerals and biofilms, as well as their effect on the (trans)formation of Au and Pt grains. In addition, FIB-SEM has been used to study analogue Au and Pt biominerals formed in laboratory experiments by organisms (i.e., Cupriavidus metallidurans) identified on Au grains. Synchrotron spectroscopy techniques (µXRF, µXANES and µEXAFS) allow us to map the distribution and speciation of Au and Pt in individual C. metallidurans cells. This has led to an understanding of the fate of environmentally important mobile Au- and Pt-complexes (identified with HPLC-ICP-MS), upon contact with cells. To understand the reaction of cells to the toxic complexes transcriptome microarrays and 2-D SDS-PAGE was used. Important determinants of Au and Pt resistance and sensitivity were studied using deletion mutagenesis and (LA)-ICP-MS analyses of cells and proteins enriched in Au. Specific Au-binding proteins have been identified with MALDI-TOF-TOF, and can be used as biosensors for in field quantification of Au. To investigate the distribution of these important determinants in surface to depth environments high-density phylogenetic and functional microarrays (e.g., PhyloChip, GeoChip) are used. Understanding the determinants of biogeochemical cycling of Au and Pt may explain the formation of large supergene deposits have formed, and provide the basis for novel approaches in exploration, bio-hydrometallurgy and bio-remediation.
Quantifying the relative contribution of natural gas fugitive emissions to total methane emissions in Colorado, Utah, and Texas using mobile $\delta^{13}CH_4$ analysis

CHRIS W. RELLA1, RENATO WINKLE1, ERIC CROSSON1, GLORIA JACOBSON1, ANNA KARION23, GABRIELLE PETRON23 AND COLM SWEENEY23

1Picarro Inc., 3105 Patrick Henry Drive, Santa Clara, California 95054 USA. *correspondence: rella@picarro.com
2National Oceanic and Atmospheric Administration, Earth System Research Laboratory, Global Monitoring Division, Boulder, CO, USA
3University of Colorado, Cooperative Institute for Research in Environmental Sciences, Boulder, Colorado

Fugitive emissions of methane into the atmosphere are a major concern facing the natural gas production industry. Because methane is more energy-rich than coal per kg of CO$_2$ emitted into the atmosphere, it represents an attractive alternative to coal for electricity generation, provided that the fugitive emissions of methane are kept under control. A key step in assessing these emissions is partitioning the observed methane emissions between natural gas fugitive emissions and other sources of methane, such as from landfills or agricultural activities. One effective method for assessing the contribution of these different sources is stable isotope analysis, using the $\delta^{13}CH_4$ signature to distinguish between natural gas and landfills or ruminants. We present measurements of mobile field $\delta^{13}CH_4$ using a spectroscopic stable isotope analyzer based on cavity ringdown spectroscopy, in three intense natural gas producing regions of the United States: the Denver-Julesburg basin in Colorado, the Uinta basin in Utah, and the Barnett Shale in Texas. Mobile isotope measurements of individual sources and in the nocturnal boundary layer have been combined to establish the fraction of the observed methane emissions that can be attributed to natural gas activities. The fraction of total methane emissions in the Denver-Julesburg basin attributed to natural gas emissions is 78 +/- 13%. In the Uinta basin, which has no other significant sources of methane, the fraction is 96% +/- 15%. In addition, preliminary results in the Barnett shale, which includes a major urban center (Dallas), are presented.

Experimental characterization of replacement symplectites: The influence of temperature and small amounts of water on microstructure evolution

PATRICK REMMERT1*, BERND WUNDER1, LUIZ MORALES1, WILHELM HEINRICH1 AND RAINTER ABART2
1GFZ Potsdam, Telegrafenberg, 14473 Potsdam, Germany (*patrick.remmert@gfz-potsdam.de)
2University of Vienna, Althanstrasse, 1090 Wien, Austria

Symplectite microstructures are a widespread phenomenon in a multitude of different parageneses in metamorphic rocks. The aim of this study is to characterize the formation of symplectites and to investigate experimentally the influence of temperature and water content on the evolution of symplectite microstructures. Synthetic monticellite (Mtc) crystals with an excess forsterite (Fo) component of about 8 mole% were annealed in a piston-cylinder apparatus at 1.2 GPa, 950 - 1200°C, run durations of 5min - 24h and water contents of 0 - 1.0 wt.% H$_2$O using Al$_2$O$_3$ as a pressure medium. At these conditions Mtc breaks down into two types of fine-grained symplectite microstructures.

The two symplectite microstructures can be explained by two types of cellular segregation reactions: (a) The Mtc precursor phase (Mtc I) is replaced by a symplectite (type I) consisting of Fo rods in a Mtc matrix without excess Fo component (Mtc II). (b) A symplectite (type II) consisting of a lamellar intergrowth of merwinite (Mw) and Fo is formed. In both cases replacement of the Mtc precursor phase by the symplectite implies chemical diffusion within the advancing reaction front.

The lamellar spacing of both symplectites shows a strong temperature dependence. At identical run durations the spacing of Sy I increases from 450 nm at 1000°C to 1200 nm at 1100°C, whereas the Sy II spacing increases from 250 to 400 nm. Both symplectite microstructures could only be produced in experiments with at least minute amounts of water. Adding H$_2$O to the experiment strongly increases the reaction rate of the symplectite formation.

Applying the formalism introduced by Degi et al. [1] yields a diffusion coefficient for MgO and CaO within the reaction front of around 7*10$^{-13}$ m$^2$/s for the formation of the Sy II indicating very fast diffusion inside the reaction front.

The vapour-brine partitioning of uranium in boiling ore systems

KIRSTEN U. REMPEL 1*, WILHELM HEINRICH 2, AXEL LIEBSCHER 3 AND PETER DULSKI 4

1Dept. of Applied Geology, Curtin University, Australia
(*correspondence: kirsten.rempel@curtin.edu.au)
2GFZ GeoForschungsZentrum, Potsdam, Germany
3(whsati@gfz-potsdam.de); 4 (alieb@gfz-potsdam.de)
4(dulski@gfz-potsdam.de)

Uranium is found in ore systems associated with high-temperature H2O-CO2 fluids of probable magmatic origin, such as skarns and iron oxide-Cu-Au-U deposits. At P-T-X conditions of vapour-liquid (V-L) coexistence, the exsolved magmatic fluids undergo boiling, so uranium mobility in the ore fluid is dependent on its partitioning between V and L. In an experiment using a pressure vessel equipped with dual sampling lines, we have determined the partition coefficients (DV/L) for U at 400°C between coexisting CO2-rich vapour and NaCl brine. DV/L increases linearly from 1.5x10⁻⁴ to 2.0x10⁻¹, with increasing P from 263-356 bar.

Figure: Uranium concentrations in vapour and liquid sample pairs taken at equivalent P, from a starting P-T-X of 356 bar, 400°C, and bulk composition of 4.2x10⁻⁴ m (100 ppm) U, 2.3 m CO2 and 0.5 m NaCl (filled square).

The results of this study suggest that boiling may be instrumental to the production of zoned uranium orebodies, as the majority of U is carried in the denser brine rather than in the coexisting CO2-rich vapour. However, at conditions approaching the critical curve, increasing concentrations of U are partitioned into the vapour (e.g., 1% of the total U at 325 bar, rising to 20% at 357 bar). This study presents the first experimental data on the V-L partitioning of U and its mobility in H2O-CO2 vapour.

Different D-rich organic reservoirs in unequilibrated ordinary and carbonaceous chondrites

LAURENT REMUSAT 1, SYLVAIN BERNARD 1, LAURETTE PIANI 2, JEAN-YVES BONNET 3 AND ERIC QUIRICO 3

1LMCM, UMR CNRS 7202, MNHN, Paris, France
2CRPG, UMR CNRS 7358, Université de Lorraine, France
3IPAG, UMR CNRS 5274, UJF, Grenoble, France

Insoluble organic matter (IOM) contained in chondrites is known to host large D-enrichments [1]. The distribution of D in carbonaceous chondrites (CC) appears to be heterogeneous at the sample, micrometer and molecular scales [1-3]. The isotopic signature is influenced by primary (pre-accretional) processes, including low temperature chemistry occurring in the outer protosolar nebula or in the parent molecular cloud [4] and secondary processes during the evolution of the parent body [1]. On the other hand, the distribution of D in the IOM of ordinary chondrites (OC) remains cryptic. Most of the OC have been subjected to thermal metamorphism. Surprisingly, the D-content of IOM in OC and CC exhibit an opposite evolution with increasing temperature of the parent body [1]. While more high temperature CC have a lower D/H compared to pristine or hydrated CC, the D/H ratio of OC IOM increases with increasing temperature.

To better understand this striking observation, we have subjected the IOM of Orgueil (CC) and GRO 95502 (OC) to thermal heating without oxygen (pyrolysis). Then, we have evaluated the evolution of each IOM upon heating by NanoSIMS (to assess the D/H distribution), STXM (molecular structure) and Raman (organization degree). In CC, the D-content decreases, while in the meantime the IOM undergoes the carbonization process (loss of heteroatoms and formation of larger aromatic structures). In OC, the D/H ratio increases likely due to the loss of a D-depleted organic component.

We conclude that in CC the D-rich organic component is thermally sensitive whereas in OC it is thermally refractory. This clearly indicates different organic moieties that may have distinct origins. Organic radicals were suggested to be the carrier of the D-excess in CC [3]. In OC, another organic component, yet unidentified has to be invoked. It might have been formed in the interstellar medium [4]. The opposite behavior of the organic D-rich component in CC and OC may induce distinct evolutions of the D/H of their IOM upon thermal metamorphism.

Groundtruthing the nitrogen isotopic composition of planktonic foraminifera as a paleobiogeochemical proxy

H. REN1*, D.M. SIGMAN2, K.K. ELLIS2, M.A. WEIGAND2, R.F. ANDERSON3, A.C. RAVELO4, M.A. ALTABET5, S.E. FAWCETT6 and P.A. RAFTER7

1RCEC, Academia Sinica, Taipei 115, Taiwan
2Dept. of Geosciences, Princeton Uni., Princeton, NJ 08544, USA (sigman@princeton.edu)
3LDEO, Columbia Uni., Palisades, NY 10968, USA (boba@ldeo.columbia.edu)
4EPS, Univ. of California, Santa Cruz, CA 95064, USA (acr@es.ucsc.edu)
5DEOS, Uni. Of Massachusetts, Dartmouth, New Bedford, MA 02744-1221 (mal2abert@umassd.edu)

The nitrogen isotopic composition of the organic matter trapped within the calcite shells of planktonic foraminifera (FB-δ15N) has been explored as a new proxy in ocean sediment records to reconstruct past changes in the marine nitrogen cycle, but information on its generation and preservation is so far minimal. In this study, we report measurements of the δ15N of foraminiferal biomass from Sargasso Sea net tow material and shell-bound N from shallow sediments collected in different open ocean regions. The annual average biomass δ15N of G. ruber, G. sacculifer, and O. universa in the Sargasso Sea surface is around 2‰, similar to but slightly lower than the thermocline nitrate δ15N, as well as their shell-bound δ15N in the surface sediment. We observe large seasonal variations in the biomass δ15N of three eutrophic zone dwelling species, G. ruber, G. sacculifer, and O. universa in the Sargasso Sea surface is around 2‰, similar to but slightly lower than the thermocline nitrate δ15N, as well as their shell-bound δ15N in the surface sediment. We observe large seasonal variations in the biomass δ15N of three eutrophic zone dwelling species, G. ruber, G. sacculifer, and O. universa in the Sargasso Sea surface is around 2‰, similar to but slightly lower than the thermocline nitrate δ15N, as well as their shell-bound δ15N in the surface sediment. We observe large seasonal variations in the biomass δ15N of three eutrophic zone dwelling species, G. ruber, G. sacculifer, and O. universa in the Sargasso Sea surface is around 2‰, similar to but slightly lower than the thermocline nitrate δ15N, as well as their shell-bound δ15N in the surface sediment. We observe large seasonal variations in the biomass δ15N of three eutrophic zone dwelling species, G. ruber, G. sacculifer, and O. universa in the Sargasso Sea surface is around 2‰, similar to but slightly lower than the thermocline nitrate δ15N, as well as their shell-bound δ15N in the surface sediment.

Heavy metal availability in contaminated soils: complementary insights from isotopic exchange, DMT, and sequential extractions

Z.L. REN1,2, J. DA1, Y. SIVRY1 AND M. F. BENEDETTI1*

1Université Paris Diderot- Sorbonne Paris Cité - IPGP, UMR CNRS 7154, Paris, France 75205 (*correspondence: benedetti@ipgp.fr)
2College of Resources and Environment, South China Agricultural University, Guangzhou, China 510642

Contaminated calcareous topsoils were sampled from paddy fields around a lead/zinc mine in Lechang, Guangdong Province, South China. The soil pH was 7.8, total heavy metal contents were 768 mg Pb kg⁻¹, 715 mg Zn kg⁻¹, 58.7 mg Cu kg⁻¹ and 22.6 mg Ni kg⁻¹.

Donnan membrane technique (DMT) and stable isotopic exchange kinetic (SIEK) technique were performed to determine the concentration of free metal ion (FMI) in soil solution and the available metal pool (isotopically exchangeable metal, E value) in soil. Traditional sequential extractions were also used to assess the metal distribution among the geochemical compartments of soil solid phase.

DMT results showed that quite few FMIs were presented in the soil solutions. At soil:solution ratio = 100 g L⁻¹, the total dissolved Pb, Zn, Cu, Ni were only 0.91, 3.29, 3.34, 0.07 μg L⁻¹, while large proportion of Pb, Cu and Ni were complexed. A good agreement was found between the FMI concentrations measured by experiments and calculated by NICA-Donnan model.

However, multi-SIEK results indicated that the isotopically exchangeable pool of Pb, Cu and Zn were large. After 12-day equilibrium, Eₚb, Eₜₕ, and Eₜ₎ value were 302, 13, and 106 mg kg⁻¹, which were up to 39%, 22% and 15% of metal total content, respectively. In contrary, Eₑₕ value was only 1 mg kg⁻¹ (i.e. 1.5% of total Ni).

Combined with the metal distribution in solid phases given by sequential extractions, the larger Pb available pool may be attributed to the high carbonate-bound and Mn oxides-bound fractions. A large proportion of Ni in the so-called residual fraction (i.e. 75% of total Ni) may explain the lower Eₑₕ.

Therefore, such combination of different techniques can give a more comprehensive insight into the heavy metal availability, thus it can provide implications to risk assessment and long term remediation.
Broader impacts of geochronology
PAUL R. RENNE*1,2
1Berkeley Geochronology Center, 2455 Ridge Rd., Berkeley, CA 94709, USA (*correspondence: prenne@bgc.org)
2Dept. Earth and Planetary Science, Univ. California, Berkeley, CA 94720, USA

Few Earth and/or planetary scientists need convincing that geochronology is fundamentally important to quantitative knowledge of planetary and biotic evolution. However, to non-scientists or even scientists from other disciplines, geochronology may be perceived as an esoteric or arcane pursuit with little “practical” value. On the contrary, geochronology plays a vital role in mineral and petroleum resource exploration. Perhaps less well-known outside the Earth science community are applications to natural hazard evaluation, particularly those due to volcanism and seismicity. In validating the cyclic orbital forcing of earth’s climate, geochronology facilitates the discrimination of anthropogenic versus endogenous climate change, and permits quantification of the rate of change. Geochronology has even played a critical role in nuclear forensics. It is fair to anticipate that technological innovations will continue to improve the precision and scope of various geochronometric techniques in the future. Consequently, geochronology will likely have increasing importance to societal issues in addition to underpinning new discoveries about how the Earth works and interacts with the rest of our Solar System.

Stepwise calibration of the Alder Creek sanidine $^{40}$Ar/$^{39}$Ar dating standard to the historical 79 CE eruption of Vesuvius
RENNE*1,2, PAUL R. AND DEINO2, ALAN D.
1Berkeley Geochronology Center, 2455 Ridge Rd., Berkeley, CA 94709, USA (*correspondence: prenne@bgc.org)
2Dept. Earth and Planetary Science, Univ. California, Berkeley, CA 94720, USA

Interlaboratory variations in argon isotope data for standards remains a significant problem for $^{40}$Ar/$^{39}$Ar geochronology. A bellweather for the problem is the ca. 1.2 Ma Alder Creek sanidine (ACs) standard, for which a range of ca. 2 % in $^{40}$Ar*/$^{39}$ArK has been reported by various laboratories. To address this problem we are calibrating ACs against sanidine (79Vs) from the 79 CE eruption of Vesuvius, whose age is known from analysis of the writings of Pliny the Younger and other sources to within 3 months [1] in 1934 years, i.e., a relative uncertainty of ±0.013%. Direct calibration of ACs against 79Vs involves measuring a ratio of $^{40}$Ar/$^{39}$Ar (R’-ACs/79Vs) between the two samples of ca. 600, which admits the possibility of bias from detector non-linearity and differential sensitivity to memory. Hence we use a third sample (X) of intermediate age to provide a stepping stone between ACs and 79Vs and make use of the fact that (R’-ACs/79Vs) = (R’-ACs/X) x (R’-X/79Vs). Neglecting atmospheric $^{40}$Ar, the optimal values of (R’-ACs/X) = (R’-X/79Vs) = 24, corresponding to an age of ca. 46 ka. Accordingly, we have selected sanidine from the ca. 40 ka Campanian ignimbrite (CIs) in the Campi Flegrei as the stepping stone. Previous studies of CIs have yielded satisfactory reproducibility and no evidence of extraneous argon. Preliminary data suggest that this approach will yield a value of (R’-ACs/79Vs) with <2% relative uncertainty, hence will contribute to clarifying the absolute age of ACs.

A new Cenozoic Record of Sulfur Isotopes from Foraminiferal Calcite.

VICTORIA RENNIE1*, GUILLAUME PARIS2, JESS F. ADKINS2 AND ALEXANDRA V. TURCHYN1

1Department of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, UK, vcr22@cam.ac.uk (*presenting author)
2Dept. of Geology and Planetary Sciences, Caltech, Pasadena, CA, USA

The sulfur isotope composition of marine sulfate ($\delta^{34}S_{SO_4}$) reflects the balance between the weathering and burial fluxes of both evaporite minerals and pyrite, and their isotopic composition. These are the dominant fluxes into and out of the marine sulfur cycle, and thus a change in the seawater $\delta^{34}S_{SO_4}$ would reflect a change in the global sulfur cycle. The importance of the sulfur cycle lies in its potential to help elucidate the subsurface remineralization of organic carbon and, indirectly, the oxidation state of Earth’s surface environment.

We present CAS $\delta^{34}S_{SO_4}$ results from single species foraminifera, using a new sulfur isotope analytical technique optimised for mass limited samples [1]. We report an interspecies variability of up to 1‰ in planktonic forams and a large decrease in $\delta^{34}S_{SO_4}$ variability upon the choice of shell cleaning. This method also allows us to identify contaminant phases with greater ease than in bulk studies. Our $\delta^{34}S_{SO_4}$ record for the Cenozoic, using a species-specific approach, is in agreement with the coeval barite $\delta^{34}S_{SO_4}$ record, engendering confidence in CAS as a proxy for $\delta^{34}S_{SO_4}$.


Past and present impact of mining activity on metal and metalloid contamination in sediments of the Gardon River watershed (France)

ELEONORE RESONGLES1*, CORINNE CASIOT1, REMI FREYDIER1, LAURENT DEZILEAU2, JEROME VIERS3 AND FRANÇOISE ELBAZ-POULICHET4

1Hydrosiences UMR 5569, CNRS Universités Montpellier I and II IRD, Montpellier, France, eleonore.resongles@univ-montp2.fr (*presenting author)
2Géosciences UMR 5243, CNRS Université Montpellier II, Montpellier, France
3Géosciences Environnement Toulouse UMR 5563, CNRSUniversité Paul Sabatier IRD, Toulouse, France

Contamination of river sediments by metal(loid)s originating from mining activity is a worldwide problem. Because the transport of metals associated with sediments can represent more than 90% of the total flow of metals in rivers, identify their sources and evaluate their potential mobility are particularly important.

The purpose of this work was to assess past and present influence of mining activity on metal(loid) enrichment in sediments of a former mining watershed now industrialized and urbanized, the Gardon River watershed (France).

Samples of a sedimentary archive and current sediments of the Gardon River and its tributaries were characterized combining geochemical analyses, zinc isotopic analyses and sequential extractions.

Considering metal(loid) concentrations in sediments upstream from the mining sites and in bottom sediments of the archive, natural background values were proposed. Based on these values, enrichment factors (EF) were calculated. Several tributaries were highly impacted by old mining sites (EF values up to 250 for Pb, 160 for Cd, 60 for Zn, 70 for As and 1850 for Sb) and by industrial activity. These polluted tributaries impacted metal(loid) content of the main stream sediments. EF values increased in Gardon River sediments downstream from old Pb/Zn mines about 3-fold for Pb, Cd and 2-fold for Zn, As and downstream from old Sb mines about 5-fold for Sb. Interelement relationships were used to distinguish the main contaminant sources. Although Zn isotopic signatures differed significantly for mining impacted tributaries ($\delta^{66}Zn~0.08‰$) and for industrial impacted tributary ($\delta^{66}Zn~0.31‰$), Zn isotopic composition remained homogeneous in the main stream sediments of the Gardon River watershed ($\delta^{66}Zn$ values around 0.20‰). Finally, the percentage of metal(loid)s present in the “mobile” pool, as estimated by sequential extraction, was: Sb (1-5%) < As (1-22%) < Zn (10-65%) = Pb (15-68%).
Quantification of the role of orbital and millennial timescale processes on δ¹⁸O and ¹⁷Λ signals

Corentin Reutenauer¹, Amaëlle Landaïs², Marie-Noëlle Woillez³, Camille Risi¹, Pascale Bragonnot², Thomas Blunier¹, Véronique Mariotti³ and Masa Kageyama³

¹Centre for Ice and Climate, Niels Bohr Institute, University of Copenhagen, Juliane Maries Vej 30, DK-2100 Copenhagen Ø, Denmark (creuten@nbi.ku.dk)
²Institut Pierre-Simon Laplace/Laboratoire des Sciences du Climat et de l’Environnement, LSCE/IPSL, UMR CEA-CNRS-UVSQ 8212, CE Saclay, L’Orme des Merisiers, 91191 Gif-sur-Yvette Cedex, France
³EPHE, UMR CNRS 5805 EPOC - Université Bordeaux 1 Avenue des Facultés, 33405 Talence (France)
⁴Laboratoire de Météorologie Dynamique, Jussieu, Paris, France

The triple isotope composition of atmospheric oxygen (δ¹⁸O, ¹⁷Λ) integrates the signature of various mass dependent processes associated with hydrological cycle, biological cycle and non mass dependent photochemical reactions in the stratosphere, both on orbital and millennial timescales: changes in global seawater, hydrological cycle, relative humidity, vegetation distribution and C₃/C₄ plants partition. At the orbital timescale, tropospheric δ¹⁸O bears a strong orbital precession signal while at the millennial timescale, d¹⁸O depicts a clear decrease in phase with Greenland InterStadial events. ¹⁷Λ (ln(δ¹⁷O+1)-Λ*(δ¹⁸O+1)) is more directly related to variations in the global biospheric productivity with a main variability associated with the glacial – interglacial changes.

Here we make use of a global model integrating changes in climate, biosphere productivity, water isotopic composition to quantify the contribution of the different processes to δ¹⁴O and ¹⁷Λ signals at relevant orbital periods (snapshots of pre-industrial period, Last Glacial Maximum (LGM), Heinrich event). The model accounts for the latest fractionation ratios between ¹⁸O /¹⁶O and ¹⁷O/¹⁶O associated with oxygen respiration processes and leaf transpiration, oceanic net primary production (simulated by PISCES model), the spatial and temporal variation of vegetation distribution (simulated by ORCHIDEE model), climatic conditions and isotopic composition of meteoric water and water vapor (LMDZ global circulation model)

Bacterial diversity in Baltic Sea sediments from Skagerrak and Bothnian Bay

Carolina Reyes¹ *, Oluwatobi Oni¹ , Olaf Dellwig² , Michael E. Böttcher² and Michael W. Friedrich¹
¹Leobener Strasse, NW2, D-28359 Bremen, Germany
( * correspondence: reyes@uni-bremen.de)
²Leibniz-Institute for Baltic Sea Research, Seestrasse D-18119 Rostock, Germany

The biogeochemical cycling of iron is a key process in terrestrial and aquatic systems including marine environments. However, limited information exists about the diversity and metabolic pathways of microorganisms linked to the iron cycle in ocean sediments. The goal of this study was to determine the bacterial community diversity in sediment samples from Skagerrak (SK) and Bothnian Bay (BB) using pyrosequencing as a first step in characterizing microorganisms potentially involved in iron reduction at these two sites. DNA was extracted from various depths from sediments collected in SK and BB. Porewater profiles of relevant electron acceptors showed that sulfate was ~28 mM and ~ 2 mM in in SK and BB sediments, respectively. H₂S was below detection in both sediments, and Fe²⁺ and Mn²⁺ levels reached ~ 140-150 μM in SK sediments between 6-7 cm depth and ~300 μM within the first 2 cm in BB sediments. V1-V3 regions of the 16S rRNA gene were used for 454 titanium pyrosequencing and sequences were analyzed using QIIME (1). Proteobacteria dominated these sediments and potential iron- and manganese-reducing bacteria included Desulfurimonadaceae, Alteromonadaceae, Geobacteraceae, Pelobacteraceae, Shewanellaceae, Myxococcales, Oceanospirillales, and Campylobacteraceae. Additionally, Actinobacteria, and Bacteroidetes were also dominant. These results imply that marine systems are likely to harbor more metabolically diverse iron and manganese reducing microorganisms than the traditional Shewanella and Geobacter model systems.


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Igniting flare-up events in Sistan Suture Zone, Iran

M. REZAEI-KAHKHAEI† AND F. CORFU

†Department of Geoscience, Shahrood University, Iran
(†correspondence: Rezaei@shahroodut.ac.ir)
‡Department of Geosciences, University of Oslo, PB 1047 Blindern, N-0316 Oslo, Norway
(fernando.corfu@geo.uio.no)

Sistan Suture Zone (SSZ) was undergone a number of important short-lived tectonic events from the middle Cretaceous to recent: (i) rifting of a large continental mass in the middle Cretaceous produced the Lut and Afghan blocks with an intervening marine basin (flysch) accumulated; (ii) northeastward subduction under the Afghan block by the Maastrichtian; (iii) collision between the Lut and the Afghan blocks terminated subduction by the middle Eocene; and continued convergence between the Lut and Afghan blocks resulted in widespread conjugate strike-slip faulting [1]. Zahedan–Saravan granitoides are parts of SSZ and occurred after closure of the ocean with a northwest–southeast trend (figure). The granitoides can be separated into two groups based on detailed age, major and trace-element geochemistry and field work. They are dominated by biotite granites at about 50km away from subduction place (ophiolitic rocks) with ~43Ma in age and granodiorites at 70-90km away from subduction place with 30Ma in age. The granitoides were cut by lots of andesitic and rhyolitic dykes at ~29Ma before they completely cold. U–Pb dating and geochemical analyses reveal: (1) a shift between the ages of biotite granites near the subduction place and the granodiorites farther than biotite granites from the subduction place; (2) Relative to granodiorites, biotite granites are richer in CaO, MgO, TiO₂, Ni, Cr, Co, Zr, Yb, Cs and Lu; and (3) an apparent flare-up in the SSZ from 43 to 29Ma.

Figure: Geological map of Zahedan–Saravan granitoides.


Dependence of Sulfur Cycling and Mobility in Peat Soil on the Water Table Regime

F. REZANEZHAD†*, R-M. COUTURE‡, C. PARSONS†, R. KOVAC†, D. O’CONNELL† AND P. VAN CAPPELLEN‡

†Ecohydrology Research Group, University of Waterloo, Waterloo, Canada (†correspondence: frezanez@uwaterloo.ca)
‡Norwegian Institute for Water Research, Oslo, Norway

Water table fluctuations change the soil redox environment and hence, affect the metabolism of electron donors and acceptors by the native microbial community. To investigate the role of water table dynamics on biogeochemical transformations and fluxes in soils, an automated column system was developed to simulate the interactions between groundwater and surface waters under controlled conditions. In this system, the position of the water table is imposed using a computer-controlled, multi-channel pump connected to a hydrostatic equilibrium reservoir and a water storage reservoir. We compared two water table regimes: i.e., fast (4 days) vs. slow (16 days) water table fluctuations. The pulse of oxygen introduced by lowering the water table caused a partial and temporal oxidation of previously reduced species. As expected, draining and rewetting of the soil columns resulted in a significant re-oxidation of reduced sulfur species, changes in pore water SO₄²⁻ concentration and microbial sulfate reduction rates. However, the dual-porosity structure of the peat soil was found to strongly modulate the sulfur cycling and mobility. This study supports the importance of water table dynamics and soil texture on biogeochemical functioning of peat soil environment.
Caprock’s nanoporous structure modification by supercritical CO$_2$/water interaction: A contribution of adsorption techniques

D. RHENALS$^{1,2}$, S. LAFORTUNE$^3$, H. SOULI$^2$ AND P. DUBUJET$^2$

$^1$French National Institut for Industrial Environment and Risks, Parc Technologique Alata, BP 2, Verneuil-en-Halatte, 60550, France david-rhenals@ineris.fr

$^2$National School Engeeniers of Saint Etienne, 58 rue Jean Parot, Saint-Etienne, France

CO$_2$ storage is envisioned as a technique which reduces large quantities of CO$_2$ rejected in the atmosphere because of many human activities.

The effectiveness of this technique is mainly related to the storage capacity as well as its safety. The safety of this operation is primarily based on the conservation of petrophysical properties of the caprock, which prevents the transport of CO$_2$ through it. However when CO$_2$ reaches the reservoir/caprock interface due to buoyancy effects, the interaction between interstitial fluid and injected fluid creates a series of dissolution/precipitation reactions affecting the properties of containment of the caprock, which is generally characterized by low transport properties.

This study aims to assess the impact caused by CO$_2$/interstitial fluid interaction on the nanostructure of the caprock under geological storage conditions. In order to do this, degradation experiments in a well characterized shale have been conducted using batch reactors for two months.

Adsorption-desorption isotherms showed an increase in the sorption capacity as well as a variation on pore size distribution. BJH and Dubinin Stoeckli distributions showed an increase in porous density lower than 10 nm, which is mainly attributed to dissolution of carbonates and some aluminosilicates detected initially with XRD techniques. Chemical water analysis showed an increase in Ca,Mg,Na,K, Si concentration, which is consistent with porous structure variation determined by physical adsorption.

Composition of the shallow aqueous fluids released beneath the SE Mariana Forearc Rift

JULIA RIBEIRO$^1$, ROBERT J. STERN$^1$, KATHARINE A. KELLEY$^2$, ALISON SHAW$^3$, FERNANDO MARTINEZ$^4$ AND YASUHIKO OHARA$^5$

$^1$Geosciences, University of Texas at Dallas, USA.

$^2$GSO, University of Rhode Island, USA.

$^3$Depart. of Geology and Geophysics, WHOI, USA.

$^4$SOEST, University of Hawai‘i at Manoa, USA.

$^5$Hydrographic and Oceanographic Depart. of Japan, Japan.

Fluids released from subducted slabs are thought to be more aqueous beneath forearcs than are the fluids released beneath arc volcanoes; however, investigating their composition is challenging as the cold forearc mantle generally does not melt. Basaltic lavas of the Southeast Mariana forearc rift (SEFMR) provide an unusual opportunity to examine basalts affected by such fluids. SEMFR extends from arc volcanoes nearly to the Mariana trench and was generated by forearc seafloor spreading ~2.7–3.7 Ma ago.

SEMFR basalt compositions are similar to backarc basin basalts and contain olivines with unusually depleted basaltic melt inclusions. These OL-MI were captured by unusually refractory olivines (Fo$_{90-93}$), and we interpret them to have formed as hydrous melts trapped in the forearc mantle. Fragments of this mantle (OL xenocrysts and Cr-spinel) were entrained with SEMFR basalt magmas during their ascent. SEMFR glassy rinds and Ol-MI have variable volatile contents (mean H$_2$O=1.85±0.26 wt%, S=757±109 ppm, Cl=334±169 ppm, F=94±31 ppm, CO$_2$=144±137 ppm).

SEMFR Ol-MI and their host basaltic glassy rinds have unusually high ratios of volatiles and fluid-mobile elements (FMEs; mean H$_2$O/Ce=10096±3901, Cl/Nb=1238±516, Cs/Th=6±5, Ba/Th=523±203, Rb/Th=79±38 for the Ol-MI; and mean H$_2$O/Ce=4953, Cl/Nb=838, Cs/Th=0.84±0.66, Ba/Th=265±97, Rb/Th=27±14 for the glassy rinds) ever recorded in the Mariana intraoceanic arc (mean H$_2$O/Ce=1705±1125, Cl/Nb=429±414, Cs/Th=0.39±0.16, Ba/Th=264±150, Rb/Th=15±3), indicating that the shallow fluids have distinctive FMEs/Th and volatile/incompatible ratios. SE-NW gradient in these ratios demonstrate that the aqueous fluids and the volatile fluxes are the highest at ~50–100 km slab depth, suggesting that hydrous minerals in the subducted slab mostly break down beneath the arc.
Contact-metamorphic effects of the
Santa Eulália Plutonic Complex
(Southern Portugal): Litological and
structural constraints

RIBEIRO, M.A.1,*, SANT’OVAIA; H. 1 AND CRUZ, C. 1
1Centro Geologia, Faculdade de Ciências, Univ. Porto R.
Campos Alegre, 4169-007 Porto, Portugal
(*correspondence maribeir@fc.up.pt)

The Santa Eulália Plutonic Complex (SEPC) is a late-variscan granitic pluton in SW sector of the Iberian Orogen. This granite with 400 km² cross-cuts the regional NW-SE variscan structures, namely a major high-grade and high-strain shear zone in the contact between two axial geotectonic zones of the iberician varicin belt. The host rocks of SEPC are composed by low to high grade metamorphic rocks from Upper Proterozoic to Lower Paleozoic. In the NE-sector of the shear zone a low grade metasedimentary Ediacaran unit (Série Negra) composed by siliciclastic rocks, including black cherts, is located adjacent to a high grade unit (migmatites and gneiss). In the SW-sector of the shear zone, a low-grade metasedimentary and metavolcanic Cambrian sequence has quartz-pelitic, carbonate and volcanic rocks. The lithostratigraphic units are also tectonic units bounded by major high-strain transient faults placing side by side different rock types and different metamorphic grades, but always characterized by a well-developed vertical foliation. Both at east or at west, the host rocks are phyllite and quartz-phylite, in chlorite zone conditions, without any thermal effects even at short metric distance from the contact. The metapelitic rocks show millimetric veins (2mm thick) with biotite, quartz, chlorite and apatite, concordant with foliation, without exhibiting any thermal effects on the walls. The Cambrian carbonate rocks outcropping in narrow bands near the ESE border of SEPC did not show any post-kinematic thermal effect. Unlike, in the western sector of SEPC the thermal effect is marked in the metasedimentary roof pendants, by metamorphic and metasomatic paragenesies in pelitic and carbonate hornfels, the later with large wollastonite crystals.

Our results highlight that the thermal effects of the SEPC in the host rocks are restricted to the roof pendants and the metasomatic effects are constrained by the carbonate rocks. The shape of the pluton, the absence of lateral thermal effects, the smooth bend of the vertical host rocks around the pluton in eastern border suggest a small thickness of the massif in the western border, and a deep rooting in the major vertical shear zone at the eastern border.

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Diverse capacity for
2-methylhopanoid production correlates with specific niches

JESSICA N. RICCI1, MAUREEN L. COLEMAN1, PAULA V. WELANDER2, ALEX L. SESSIONS1, ROGER E. SUMMONS2, JOHN R. SPEAR3 AND DIANNE K. NEWMAN1,4*
1California Institute of Technology, Pasadena, CA 91125, USA (jricci@caltech.edu, mcoleman@uchicago.edu, als@gps.caltech.edu, correspondance: dkn@caltech.edu)
2Massachusetts Institute of Technology, Cambridge, MA 02139, USA (welander@stanford.edu, rsummons@mit.edu)
3Colorado School of Mines, Golden, CO 80401, USA (jspear@mines.edu)
4Howard Hughes Medical Institute, Pasadena, CA 91125, USA

Molecular fossils of 2-methylhopanoids (2-MeBHPs) are important geological biomarkers and have often been interpreted as proxies for cyanobacteria and their main metabolism oxygenic photosynthesis [1]. However, substantial culture and genomic-based evidence indicates that organisms other than cyanobacteria can make 2-MeBHPs [2, 3]. Yet, these lines of evidence do not address which organisms produce 2-MeBHPs in the environment. In this study, we use metagenomic and clone library methods to address the environmental diversity of hpnP, the gene encoding the C-2 hopanoid methylase. We show that hpnP copies from alphaproteobacteria and unknown origin are found in diverse modern environments, including some representative of those preserved in the rock record, while cyanobacterial hpnP genes are more rare and localized to specific habitats. Moreover, hpnP diversity in any given locale can be spatially and temporally heterogeneous, stressing the need to sample environments rigorously before drawing general conclusions. Additionally, we asked if hpnP is overrepresented in organisms or environments with a specific metabolism or associated with a particular niche. We found the presence of hpnP to be significantly correlated with organisms and environments known to support plant-microbe interactions. Our results indicate that 2-MeBHPs can no longer be used as unambiguous biomarkers for cyanobacteria and hints at a potential interpretation for 2-MeBHPs separate from oxygenic photosynthesis that underpins the observed enrichment of hpnP in these contexts.


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Thermodynamic analysis of water-rock-hydrocarbon interactions in petroleum systems

LAURENT RICHARD

Geoquímics dels Àngels, Carrer dels Àngels 4-2-1, 08001 Barcelona, Spain

Throughout their evolution across the crust of the Earth, minerals and organic compounds interact in many geological processes ranging from the low-temperature early diagenesis of marine sediments to the metamorphism of pelitic schists. The geochemical cycles of iron, sulfur or nitrogen (among other elements) are governed by such interactions, which correspond to oxidation-reduction reactions. Well-documented examples include the decarbonation of siderite in the presence of carbonaceous matter [1], the formation of sulfur-rich organic matter in carbonate sediments [2], or the exchange of nitrogen isotopes among petroleum and clays in clastic reservoirs [3].

It is the purpose of the present communication to illustrate how thermodynamic properties published for solid and liquid hydrocarbons and sulfur- and nitrogen-bearing compounds of geochemical interest [4,5] can be used to develop quantitative models for the evolution of water-rock-hydrocarbon systems, as well as to make reasonable estimates regarding the composition of petroleum fluids as a function of temperature, pressure, the fugacities of CO₂, H₂S, NH₃ and H₂, and their mineralogical and aqueous environment. Conversely, I will show how compositional data for crude oils can in some instances be used to evaluate or retrieve thermodynamic data.


The role of arc magmas and subduction-modified lithosphere in ore formation

JEREMY P. RICHARDS

Dept. Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta, Canada, T6G 2E3
Jeremy.Richards@ualberta.ca

Arc magmas are a unique source of subduction-derived volatiles (water, sulfur, and chlorine: mostly derived from seawater-altered oceanic lithosphere), plus water-soluble elements (alkalis and large-ion lithophile elements) and chalcophile and siderophile metals. Upon emplacement in volume in the upper crust, these magmas may generate porphyry Cu±Mo±Au and epithermal Au±Cu deposits. However, during their ascent through the upper plate lithosphere, they interact with these rocks to form hybrid calc-alkaline magmas, and fractionate to leave ultramafic to mafic, amphibolitic cumulate residues at the base of the crust (MASH process of Hildreth and Moorbath, 1988).

Over the life of an arc (typically ∼10–15 m.y.), the mantle wedge above the subduction zone becomes increasingly hydrated and oxidized as slab fluids cause progressive metasomatism, leading to partial melts that also increase in water content and oxidation state over time. Early primitive magmatic fluxes entering the upper plate lithosphere may leave considerable amounts of metals behind in cumulate zones as sulfides separated from relatively reduced (∆FMQ < 0) magmas (Lee et al., 2012). However, increasing oxidation state in later magmas (∆FMQ = 1–2) suppresses sulfide-saturation, and leads to efficient transport of metals in magma fluxes reaching the upper crust (Botcharnikov et al., 2011). Consequently, major porphyry-forming events are commonly relatively late in the evolution of a given arc.

The deep crustal residues of arc magmatism are relatively fusible (amphibole-rich) and likely contain small amounts of metal sulfides. Re-melting of these residues during later tectonic events, such as collision or rifting, may generate metalliferous magmas with similar chemical and isotopic characteristics to normal arc magmas, which may go on to form post-subduction porphyry Cu±Mo±Au deposits. Their derivation from partial melting of deep crustal garnet-amphibolites gives these magmas adakite-like high Sr/Y and La/Yb ratios, but they are not formed by slab melting.

Rhizogenic C-Fe Redox Cycling: Sleeping Couple No Longer

D. DEB. RICHTER1*, A.R. BACON3, M.L. MOBLEY2, M. OELZE3 AND F. VON BLANKENBURG3

1Duke University, Durham, NC 27708 USA
2University of Wyoming, Laramie, WY 82072 USA
3German Research Center for Geosciences, D-14473, Potsdam, Germany

Nearly all soil data derive from bulked collections that homogenize soil heterogeneity [1, 2]. We therefore have limited understanding of biogeochemical processes, properties, and gradients that may contrast greatly amongst the many micro-environments that exist within soil profiles. Rooting can affect the upper several meters of soils and especially subsoil rhizospheres are hotspots of biological and chemical activity. In upland soils, distinctive redoximorphic features often visually illustrate microenvironments that contrast not only in color, but in chemistry, physics, and biology. Such redoximorphic features are often interpreted as being relic features of past ecosystems [3]. We hypothesize that mottles are both relic and active microsites in which organic-reductant enriched rhizospheres are periodically reduced when saturated, when the C-Fe redox cycle is associated with carbon stabilization, FeIII reduction, mineral dissolution reactions, and colloidal translocation.

Depth-dependent sampling of redoximorphic microsites in three upland soils was combined with chemical and physical analyses to investigate processes, properties, and time scales on which these rhizogenic microsites operate. In all three soils, we attribute C enrichment and Fe depletion in rhizospheres to result from electron acceptors periodically switching from O2 to FeIII and other redox-active species, when subsols become periodically saturated due to wet conditions and low hydraulic conductivity. Both \( \Delta^{13}C \) and \( \Delta^{56}Fe \) [4] data indicate that the rhizogenic C-Fe redox cycle operates in the contemporary forest ecosystem, thus redoximorphic features are both relic and active. Large contrasts in clay and crystalline Fe concentrations among these microsites demonstrate large but local-scale mobility of Fe and colloidal materials. The significance of the upland rhizogenic C-Fe redox cycle is underscored by the deep and extensive rooting and mottling of many upland soils across a range of plant communities, lithologies, and climatic regimes.


Kinetic isotope fractionation at the frontier of modern geochemistry

FRANK RICHTER

The Univ. of Chicago, Chicago, IL USA
[richter@geosci.uchicago.edu]

Geochemistry can claim a special place in the Earth sciences because it provides distinctive insight into both processes and the time scale over which they operated. I will review recent developments both from experiments and natural settings that illustrate how stable isotope fractionations are being used to identify the process responsible for chemical zoning, and that when the zoning is unambiguously shown to be due to diffusion, can it be used to provide a measure of time. To make this case for the role of stable isotopes the first thing one needs to demonstrate is that mass transport by diffusion in silicate systems is easily recognized by the fact that it produces isotopic fractionations that are large compared to modern analytical methods. The state of affairs in terms of the results of laboratory experiments involving chemical diffusion in melts [1-4], minerals [5], and metal alloys [6] is that in every case so far studied large kinetic isotope fractionations were found and thus they do provide a “fingerprint” with which to distinguish mass transport by diffusion from other mechanisms. What makes this especially relevant is that what has been found in the laboratory experiments has also been found in numerous natural settings ranging from quenched contacts between mafic and silicic melts [7], minerals from mantle xenoliths [8], from lava flows both on Earth and from Mars [9,10] and from a lava lake [11]. A corollary to the above arguments is that when one finds chemical zoning that does not have correlated stable isotope fractionations, one should avoid any temptation to interpret these as providing a measure of time. Thus kinetic isotope fractionations can both give special insight into the causes of chemical zoning, but equally importantly, spare us from the embarrassment of using diffusion kinetics to infer cooling rates from chemical zoning caused by some process other than diffusion.

A history of inhibition: thresholds and echinoderm Mg/Ca

R. E. M. Rickaby¹, M. Vickers¹, H. C Jenkyns¹, A. S. Gale², P. Bots³ and S. Shaw³

¹Department of Earth Sciences, University of Oxford, South Parks Road, Oxford, OX1 3AN; rosr@earth.ox.ac.uk
²School of Earth and Environmental Sciences, University of Portsmouth Burnaby Building Burnaby Road Portsmouth PO1 3QL
³SEAES, University of Manchester, Oxford Rd, Manchester, M13 9PL

Oscillations between an ocean which generates a primary abiogenic precipitate of calcite or aragonite have been identified throughout the Phanerozoic and attributed to variability in the major ion chemistry of the ocean (magnesium, calcium and sulphate concentrations as lead candidates). Such variability represents fundamental changes to Earth surface processes, notably the balance among continental weathering, sedimentation, and volcanic activity. These cycles in seawater chemistry and primary mineralogy of marine carbonates have implications for reconstructing the drivers of changes in chemistry and primary mineralogy of marine sedimentation, and volcanic activity. These cycles in seawater chemistry notably the balance among continental weathering, represents fundamental changes to Earth surface processes, and a quantitative reconstruction and mechanistic understanding of the drivers of these fundamental ocean chemistry changes remains elusive.

First we shall explore how the combined effects of chemical inhibitors can alter the potential thresholds for a change in primary marine carbonate precipitate (Bots et al., 2011). We then employ an established method (Dickson, 2002) to provide insight into refining the Meso-Cenozoic history of the dominant kinetic inhibitor of calcite precipitation, namely magnesium. We demonstrate the utility of a uniquely pristine sample compilation of echinoderm fragments collected from clay hosted sediments to preserve a history of seawater Mg/Ca. Our reconstructed history of seawater Mg/Ca is largely concordant with existing results except for a part of the middle Jurassic which appears to be characterised by much lower Mg/Ca ratios than predicted by most models.


Boundary addition of Hf and Nd in the Southern Ocean

J. Rickli¹, M. Gutjahr², D. Vance¹, C.D. Hillenbrand³, G. Kuhn² and M. Fischer - Götde⁵

¹ETH Zurich, Institute of Geochemistry and Petrology, Switzerland (joerg.rickli / derek.vance@erdw.ethz.ch)
²GEOMAR Helmholtz Centre for Ocean Research Kiel, Germany (mgutjahr@geomar.de)
³British Antarctic Survey, Cambridge, UK
⁴Alfred Wegener Institute, Bremerhaven, Germany
⁵Westfälische Wilhelms Universität, Münster, Germany

Hf and especially Nd isotopes are increasingly used to reconstruct past ocean circulation. Many of these applications rely on their quasi-conservative behaviour implying that the key process that governs their distribution is circulation. Here, we report new elemental (Hf, Zr, Nd) and isotope data (εHf, εNd) from the Pacific sector of the Southern Ocean, which document the relative significance of circulation vs boundary processes on the Hf and Nd distribution adjacent to Antarctica. Seawater depth profiles were sampled in the Ross Sea, along the West Antarctic continental rise and in the vicinity of the Marie Byrd Seamounts offshore the Amundson Sea Embayment (ASE). In addition, several samples were taken within 1.5 m to the seabed in the ASE. The samples were not filtered, which implies that some of the observations may be accentuated by contributions from the leaching of particulates during sample acidification.

The key observations for Nd include (a) the shift to radiogenic εNd and elevated Nd concentrations in the ASE (εNd up to -5.4), (b) a gradual increase in εNd with depth from 1000 m to 3000 m water depth in the open ocean (-9 to -7.8) along the entire West Antarctic margin and (c) distinctly more radiogenic deep waters beneath 3000 m, especially at the Haxby seamount (up to -3.1). (a) is indicative of boundary release of Nd. (b) probably reflects the mixing of freshly forming boundary affected deep waters with circumpolar deep water (CDW) upon sinking; (c) indicates that, in addition to the shelf, the deep ocean floor and basaltic seamounts act as sources of radiogenic Nd.

Hf isotopes are relatively homogenous in the data set (εHf mostly between +2 and +3.8). Boundary release is, however, evident from elevated Hf and Zr concentrations in the embayment. In addition, distinctly unradiogenic εHf of -1 are observed in deep waters at the Haxby Seamount. The data thus suggests that relatively unradiogenic Hf is released from Antarctica in the sampling area, which probably also accounts for the slight but systematic difference between measured εHf of CDW and deep waters of the eastern Pacific compared to the Atlantic sector of the Southern Ocean.
**Is this a good time to be burning fossil fuels?**  
ANDY RIDGWELL ¹  
¹University of Bristol, Bristol, UK, andy@seao2.org  

The basic for any sane analysis and discussion of the biotic response to past ocean acidification is, of course, identifying that there has been ocean acidification in the first place. But outside of the relatively recent geological past, the measurement and interpretation of direct proxies for the key parameters involved – pH and carbonate ion concentration (saturation state) becomes increasingly challenging. This is important as only the closely coupled decline in both these parameters together constitutes a future-relevant marine environmental change. One can resort to analysis of the size and duration of carbon isotopic changes and if really desperate … models, in order to make estimates of the magnitude of carbon release and perturbation, but often such thinking takes place in a conceptual framework delineated by observations of how the modern carbon cycle works.

What I would like to explore here is whether the sensitivity of ocean chemistry to perturbation could have been much greater earlier in the Phanerozoic compared to today. For instance, following the advent and proliferation of planktic (carbonate) biomineralization during the Mesozoic: did the emergent deep sea carbonate ‘buffer’ preclude ocean acidification driven mass extinction? And what would it take in terms of fossil fuel CO₂ emissions to overwhelm it today?

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**Evolution of the oceans biological pump**  
ANDY RIDGWELL ¹  
¹University of Bristol, Bristol, UK, andy@seao2.org  

Earth history is punctuated by a huge variety of transitions and perturbations in climate and global biogeochemical cycling. These may be linked to major extinctions or evolutionary innovations, and may exhibit evidence for greenhouse warming and CO₂ release and hence potentially hold direct future-relevant information. In interpreting the geological record it is common to assume the presence in the ocean of a strong vertical ‘pump’ of carbon and associated trace elements and isotopic properties. Proxies for past environments and perturbations are duly interpreted on this basis. However, evolutionary innovations have the potential to change the ground rules and give rise to non uniformitarian behaviors of the global carbon cycle in deeper time. For instance, the cycle and reservoir of dissolved organic in the ocean may have been dominant in the past and has been invoked to explain a number of prominent features of the geological record. But is even this thinking too constrained by our familiarity with the modern? Just how radically different might the biological pump have been at different times since the the advent of photosynthesis? When was a biological pump of any sort first developed?

In this talk I’ll start by summerizing the known knowns and known unknowns surrounding the marine carbon cycle as it exists today, as we need to be clear at the outset about what key processes are incompletely understood. I will then piece together a potted history of how today’s carbon cycle might have arisen in relation to the various evolutionary developments and transitions over the past ~2 Ga and discuss the implications for how we interpret the geological record.
Surface Complexation Modeling of cation adsorption by TiO₂ nanoparticles

MOIRA K. RIDLEY*, MICHAEL L. MACHESKY and JAMES D. KUBICKI

1Texas Tech University, Dept. of Geosciences, Lubbock, TX, USA, moira.ridley@ttu.edu (* presenting author
2University of Illinois, Illinois State Water Survey, Champaign, IL, USA, machesky@illinois.edu
3The Pennsylvania State University, University Park, PA, USA jdk7@psu.edu

Surface Complexation Models (SCM) provide a means to quantify the specific adsorption of ions, the interaction of electrolyte ions, and the pH-dependent charging at mineral-aqueous solution interfaces. Additionally, SCMs provide a thermodynamic framework for predicting surface protonation equilibria. The charge distribution (CD) and MUSIC model facilitates the integration of molecular-scale information with macroscopic data to describe the interface behavior of ion-mineral systems.

In this presentation, we will discuss the application of the CD and MUSIC model to provide a thermodynamic description of the primary charging behavior of a suite of monodisperse, nanocrystalline anatase particles in NaCl media. Additionally, the CD-MUSIC model has been used to evaluate the interaction of Sr²⁺ and Ca²⁺ ions with the same suite of nano-anatase samples.

The adsorption of cations onto nano-anatase was evaluated over a wide range of pH, surface loading, and ionic strength. Complementary DFT-MD molecular simulations were also completed to evaluate the bonding geometries of all cations on the predominant (101) anatase surface. The adsorption behavior for the two divalent cations onto the anatase surface are broadly similar; although, Ca²⁺ first adsorbs at slightly low pH values and has slightly steeper charging curves than Sr²⁺. The variations in the macroscopic charging curves for the interaction of Sr²⁺ and Ca²⁺ with anatase reflect the differences in binding geometries identified at the molecular-level. The DFT-MD optimizations show inner-sphere binding for all cations; however, the most stable binding geometries are different for each ion. The Na⁺ and Sr²⁺ ions have bidentate coordination geometries, with Na⁺ ions coordinated to two bridging oxygen (BO) surface sites and Sr²⁺ coordinated to two terminal oxygen surface sites. Conversely, Ca²⁺ ions are coordinated to three BO sites. This molecular-scale information was used explicitly to constrain all CD-MUSIC model fits.

Organic carbon and trace element mobilization from a biochar amended arable soil: A soil column study

THOMAS RIEDEL, JENNIFER GEILICH and S ASCHA IDEN

1Technische Universität Braunschweig, Institut für Geökologie

The addition of charred biomass (biochar) to agricultural soils is currently attracting attention as a means for sequestering carbon and as a potentially valuable method to improve soil fertility. Because some uncertainty remains about the possible impacts of biochar additions on organic carbon and trace element cycling in arable soils we conducted a soil column study to investigate the mobilization of trace elements (Mn, Fe, Cu, Zn) and organic carbon.

Amendments of 1% (w/w) of grounded and finely dispersed biochar resulted in a net reduction of organic carbon, Cu and Zn leaching from the saturated soil columns. The organic carbon leaching from the amended soil was less phenolic indicating that sorption to biochar was compound specific. A more detailed characterization of the organic matter with ultra-high resolution mass spectrometry revealed that the most non-polar compounds detectable with this method were retained by the biochar likely because of hydrophobic interactions.

Cu and (to a lesser extend) Zn were associated with the organic matter retained by the biochar as revealed by gel-permeation liquid chromatography hyphenated with inductively coupled plasma mass spectrometry. Complexation with organic matter may therefore play an important role in the interactions of some metals with biochar in soils. The elution behavior of Fe and Mn was almost unaffected.

After two weeks of flow interruption the waterlogged soil columns had turned anoxic. Under these conditions the elution behavior of the trace elements changed markedly. Mobilization of Fe and Mn increased strongly, but the increase was less pronounced for the biochar amended soil indicating that sorption of Fe(II) and Mn(II) to the biochar had occurred. Zn and organic carbon on the other hand showed almost no difference to the oxic elution indicating no redox sensitivity.

Our results show that charred biomass affects the quantity and quality of organic matter as well as the quantity and speciation of trace elements leaching from agricultural soils.

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**Tectonically enhanced deep subsurface microbial carbon cycling in the Nankai Trough, Japan**

N. RIEDINGER1*, M. STRASSER2 AND T.W. LYONS1

1Dept. of Earth Sciences, Univ. of California, Riverside, CA 92521 USA (*correspond.: natascha.riedinger@ucr.edu)

2Geological Institute, ETH Zurich, 8092 Zurich, Switzerland

The occurrence and activity of microbial communities in deep subsurface environments are highly investigated. However, the abundance of microbial life and the source of energy necessary for these microorganisms remain controversial and under explored.

Here we investigate the impact of depositional and tectonic events on those deep microbial processes in sediments at IODP (Integrated Ocean Drilling Program) Site C0006, drilled and sampled during IODP Expedition 316 at the Nankai Trough, Japan. The observed methane isotope profiles indicate that active microbially mediated methane production occurs in sediments below 450 mbsf. This observation is supported by alkalinity measurements, indicating a source of inorganic carbon into the pore water as a by-product of deep in situ methane production. Thus, our data provide evidence for carbon cycling in these deep subsurface sediments. This is likely related to the highly dynamic tectonic regime at Nankai Trough, where tectonically induced temporary temperature increase can re-stimulate organic matter at distinct depths.

While tectonic activity can lead to the reactivation of recalcitrant organic matter, the variable sedimentary system provides niches for microbial abundance. The newly available/accessible organic carbon compounds fuel the microbial community – resulting in an onset of microbial methane production several hundred meters below the seafloor. This process is also captured in the isotope signal of methane, and thus methane isotopes can help us pin down locations of active microbial processes in deeply buried sediments.

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**Accurate isotope composition measurements by a miniature LMS system designed for in situ space research**

A RIEDO1*, M. NEULAND1, S. MEYER1, M. TULEJ1 AND P. WURZ1

1Physics Institute, Space Research and Planetary Sciences, Sidlerstrasse 5, 3012 Bern, Switzerland (*correspondence: andreas.riedo@space.unibe.ch)

A miniature laser ablation reflectron time-of-flight mass spectrometer designed for in situ space research for sensitive and accurate measurements of the elemental and isotopic composition of extraterrestrial material is described and its performance for accurate in situ measurements of isotope composition is demonstrated [1-4]. A ns- (266 nm, 5 ns, 20 Hz) [1-2] and a fs-laser ablation ion source (775 nm, 190 fs, 1kHz) [3] were used to investigate figure of merits (mass resolution, dynamic range, detection sensitivity and accuracy of measurements). The studies are performed with a high spatial resolution by focusing the pulsed laser radiation to spot of about Ø20 and 40 µm, respectively on the sample surface. The measurements are conducted with high dynamic range of at least 10^8 and a mass resolution (m/m) of up to 800-900, as measured at ^56Fe [1]. High detection sensitivity is achieved in measurements of both, metallic and non-metallic elements (tens of ppb) [1]. While ns-laser ablation ion source have to be calibrated with appropriate NIST standard reference materials (SRM), the relative sensitivity coefficients (RSC) were determined to be close to one when the fs-laser ablation ion source was applied [3]. Hence, the coupling of LMS with a fs laser system is preferable and is of considerable interest for the development of standard-less instruments. We developed a measurement procedure, which will be discussed in detail, that allows LMS to measure isotope composition of elements, e.g. Ti, Cr, Pb, etc., with a measurement accuracy and precision in the per mille and sub per mille level for the first time and is comparable to the performance of other well-known and accepted measurement techniques (TIMS, SIMS and LA-ICP-MS) [2-3]. High performance of the LMS instrument offers versatile applications regarding in situ investigations of the chemical composition (elemental and isotopic) of extraterrestrial surface material [1-4].


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Insight into biotite weathering rate using U-series isotopes

S. RIHS*1, A. GONTIER1, M.P. TURPAULT2, D. LEMARCHEAND1, A. VOINOT1 AND F. CHABAUX1

1LHyGeS/Université de Strasbourg (UMR 7517), Strasbourg, France (* correspondence: rihs@unistra.fr)
2Lab. Biogéochimie des Ecosystèmes Forestiers, (UR INRA 1138), Champenoux, France (turpault@nancy.inra.fr)

While the chemical weathering rate of silicates is a key parameter for several geochemical processes, field measurement of these rates remains challenging. Uranium- and Th-series nuclides were used to investigate biotite weathering in a soil profile. Some crystal-habits of biotites (including the alteration products) were hand-picked from five horizons (20 to 140 cm) of a soil profile from the experimental Breuil-Chenue site (France). Additionally, biotites from a seemingly ‘fresh’ block of the granitic bedrock were also recovered. Chemical analyses and XRD data allow quantifying the fraction of biotite remaining in these crystal-habits (91% to 9%). The extraction of the ‘fresh’ biotite interlayer demonstrates the lack of U and Th in this interlayer.

Unexpected behaviour of U and Th nuclides was recorded in these biotites An unambiguous loss of 232Th occurs during the transformation of the biotite to its alteration products, whereas little U loss (similar to Fe) was observed, implying an efficient redistribution of U between the primary mineral and the alteration products (mainly kaolinite and vermiculite) within the crystal-habit. The measured U-series activity ratios show a ordered evolution, consistent with an increased weathered stage in these samples. However, this "U-series-derived-weathered-stage" is not always coherent with the location of the sample within the soil profile, i.e.: the ‘fresh’ biotite from the granite bedrock actually displays some U-series activity ratios typical of significantly weathered samples, suggesting an incongruent leaching of U and Th isotopes. These results highlight that the U- and Th-series nuclides are probing some water-mineral interactions occurring before macroscopic mineral transformation.

Using an open-system leaching model, the coupled (234U/238U), (234U/230Th), and (226Ra/230Th) disequilibria measured in the samples permit to calculate a weathering duration ranging from 12 to 50 ka for the most altered biotite of this soil profile. The biotite weathering rates deduced from these data are consistent with the range of field rates previously reported [1], suggesting a valuable use of U-series isotopes for mineral-weathering field rate determination.

Regional scale OA oxidation observed over the Po Valley basin (Italy), at Mt. Cimone (2165 m asl)

M. Rinaldi¹, S. Gilardoni¹, S. Decesari¹, S. Fuzzi¹, P. Cristofanelli¹, S. Bonasoni¹, S. Ferrari², V. Poluzzi¹ and M.C. Facchini¹

¹Istituto di Scienze dell’Atmosfera e del Clima, Consiglio Nazionale delle Ricerche, Bologna, 40129, Italy
²Centro Tematico Regionale Aree Urbane, Arpa Emilia-Romagna, Bologna, 40138, Italy

High resolution time of flight aerosol mass spectrometer (HR-ToF-AMS) measurements have been performed, for the first time, at Mt. Cimone GAW station (44°12’ N, 10°42’ E, 2165 m asl) from 11 June to 9 July 2012, under the framework of the EU project PEGASOS and the Emilia-Romagna Region project SUPERSITO.

The peculiar character of the site allows the investigation of organic aerosol (OA) ageing occurring at regional scale over the Po Valley. In fact, particles sampled during the day are representative of the early stages of aerosol atmospheric oxidation, comprising processed primary OA and secondary OA formed in the Po Valley basin, being the site within the planetary boundary layer (PBL). During the night, the aerosol sampled at Mt. Cimone is representative of more processed conditions, as the site is in the free troposphere (FT), containing aerosols with an age from several hours to days.

Elemental analysis performed with high resolution mass spectra [1], revealed decreasing average H/C and increasing O/C ratio from PBL to FT samples. As a consequence, the OM/OC ratio passes from 1.83±0.05 in PBL, to 1.94±0.08 in FT samples.

These results evidence the progressive oxidation of OA over the Po Valley basin, from few hours after their emission/formation to one or more days of atmospheric processing. On a Van Krevelen space, the data produce a slope of ~ -1, suggesting that the observed regional scale oxidation processes occur mainly through the addition of carboxylic functional groups [2]. This is further confirmed by the analysis of the HR mass fragments, showing that, from PBL to FT samples, the average contribution of fragments containing carbon, hydrogen and more than one oxygen atom (CHO>1) passes from 25% to 33%, while both CH and CHO fragments decrease their contribution.


Sr²⁺ and Mn²⁺ incorporation during CaCO₃ cementation on calcitic and aragonitic shells

T. Rinder¹*, M. Dietzel² and A. Deditius²

¹GET/CNRS, 14 avenue Édouard Belin, 31400, Toulouse (*correspondence: rinder.thomas@gmx.net)
²TU Graz, Institute of Applied Geosciences, Rechbauerstr. 12, Graz, Austria

Precipitation of calcium carbonates may cause significant changes in the porosity, permeability and overall physical properties of sedimentary rocks. For instance in sandstone the loss of permeability and porosity negatively influences the potential quality of the hostrock as a hydrocarbon or groundwater reservoir [1]. In recent years more attention to cementation issues is received for the increasing efforts to reduce CO₂ emission into the atmosphere and the possibility of long term storage by means of underground fixation in carbonates [2].

In the present study flow through experiments were carried out to investigate carbonate cementation of primary unconsolidated shell material by investigation of the spatial distribution and trace element incorporation of the precipitated material. NaHCO₃ – Na₂CO₃ – CaCl₂ solutions supersaturated with respect to calcite were pumped through columns packed with shell fragments of a grain size between 0.5 and 1mm. Sr²⁺ and Mn²⁺ addition was used to trace the temporal and spatial evolution of newly formed precipitates in the pore space.

Overall distribution coefficients calculated from aqueous bulk solutions result in a D₆ of 0.68 and D₃₆ of 6.08 for the precipitated CaCO₃. These coefficients are in good agreement with literature values within the given proportions of precipitated calcite and aragonite. However, apparent measured distribution coefficients in the newly formed CaCO₃ solids derived from electron microprobe analysis are highly heterogeneous and results in a maximum D₆₆ and D₃₆₆ value of 18 and 163, respectively.

Alternating trace element rich and poor growth zones were discovered in our experiments carried out at a constant solution composition, temperature and flow rate. We suggest that the incorporation behaviour depicted by bulk ratios which serve as proxies for the reconstruction of environmental conditions during precipitation of CaCO₃ is not necessarily valid on the microscale. The actual locally occurring trace element incorporation into CaCO₃ can significantly exceed or fall below the average bulk incorporation.

Using TOF-SIMS isotope mapping for studying dissolution and precipitation processes at mineral grains in an experimental CO₂-sequestration setup

S. RINNEN¹, A. RISSE², C. OSTERTAG-HENNING² AND H.F. ARLINGHAUS¹
¹Physikalisches Institut, University of Muenster, Wilhelm-Klemm-Str. 10, 48149 Muenster, Germany (stefan.rinnen@wwu.de)
²Bundesanstalt fuer Geowissenschaften und Rohstoffe, Hannover, Germany

CCS (Carbon dioxide capture and sequestration) is a technique investigated for its possible employment in the reduction of the amount of anthropogenic CO₂ gas emitted into the atmosphere. Deep saline aquifers are one option for storing CO₂ gas streams produced e.g. by the combustion of fossil fuels at power plants. These gas streams contain different impurities depending on their origin, among them O₂, NOx, SOx in addition to the CO₂. We have used ToF-SIMS to determine the influence of these impurities on dissolution and precipitation processes at the minerals.

Experiments under in situ pressure and temperature conditions of possible geological storage sites were performed at the German Bundesanstalt fuer Geowissenschaften und Rohstoffe (BGR) in flexible Dicks on-type gold-titanium cells and small gold capsules. Minerals common in the deep saline aquifers (e.g. siderite, calcite) were placed in small reaction cells of thin gold foil in a reactor vessel and exposed to isotopically enriched water (H₂¹⁸O) or carbon dioxide (¹³CO₂) during the experiments. To facilitate the determination of the amount of dissolved ions incorporated into newly formed precipitates within the reaction chambers, a database of positive and negative ToF-SIMS spectra for a variety of rock-forming minerals were set up to identify minerals and mineral alterations. In addition, preparation techniques were developed for high-resolution measurements of the incorporation of isotope-labeled elements/ions (e.g. ¹⁸O) into mineral precipitates. The results show that ToF-SIMS can simultaneously image the elemental, isotopic, and molecular compositions of these minerals with high spatial resolution. Also, elemental and isotopical distributions as a function of depth can be monitored.

Carbonatitic Magmas? A Mineralogical and Isotopic Approach

DEBORA C. RIOS¹²* DONALD DAVIS², HERBET CONCEIÇÃO³, MARIA DE LOURDES S. ROSA³, AND CÂNDIDO A.V. MOURA⁴
¹Jack Satterly Geochronological Lab, University of Toronto, Canada, debora.rios@utoronto.ca (* presenting author)
²GPA, CPG em Geologia, UFBA, Salvador-BA, Brazil
³Núcleo de Geologia, UFS, Sao Cristovao-SE, Brazil.
⁴Para-Iso Isotopic Laboratory, UPFA, Belem-PA, Brazil.

Massive deep orange calcites are intensely colored, coarse grained rocks, in contact with silicate rocks that exhibit centimetric crystals of phlogopite, occurs at Serrinha Nucleus (SerN), Brazil. Occelli are a common feature, composed of euhedral fluorapatite, diopсидic pyroxenes and barite. Associated creamy coloured rocks are composed of >90% calcite, 3-8% green-olivine and diopside, 1-2% euhedral sulphides and well developed crystals of purple-spinel and blue-fluorapatites, as well as rounded mafic enclaves composed of amphibole, biotite and pyrite. Coarse calcite veins and/or dykes also cut the 2.1 Ga syenite-lamprophyre association and the meta-gabbros of Itapicuru Greenstone, demonstrating a clear interrelation between carbonates and silicate minerals including Fe-Mg-Mn calcite, diopside, apatite, quartz and Fe-Ni oxides. Rutile, few zircons and pyrite were described from the heavy mineral concentrates.

C and O preliminary results for δ¹³C (PDB) between +12 e +13 per mil, δ¹⁸O (PDB) of -10 per mil, and V-SMOW of +20, suggest the involvement of different magmatic or hydrothermal phases in these rocks formation. LA-ICP Pb-Pb analyses of calcites yielded model ages of ~1950 Ma and U-Pb ages from 2 zircons are (i) 2.11 Ga, close to that of SerN syenites and lamprophyres, suggesting that these rocks may be comagmatic and (ii) a clear core-border relationship showing ages of 2.7 and 2.5 Ga, respectively, similar to those reported for zircon xenocrysts in syenites and kimberlites.

Our results show that these rocks are calcite carbonatites, fairly well exposed, and that have not been metamorphosed. The occellar texture suggests liquid immiscibility, indicating silicate magma droplets. Although further work remains to be done, the isotopic data suggest an emplacement age of ~2.0-2.1Ga, coeval with emplacement of the syenites and lamprophyres and to the gold mineralization at Itapicuru Greenstone. This syenite-lamprophyre-carbonatite association is closely related to Au in many Archean cratons worldwide.
Investigation of reactive transport with closed-flow column experiments and parallel factor analysis (PARAFAC) of fluorescence data

THOMAS RITSCHEL* AND KAI UWE TOTSCHE
Institute of Geosciences, Friedrich-Schiller-University Jena
(*correspondence: Thomas.Ritschel@uni-jena.de)

The study of biogeochemical interfaces is crucial to understand soil functioning [1]. The sorption of solutes and colloids to these interfaces results in the phenomenon of retardation. Besides the interactions at the sorbent-solution-interface, the sorption rate depends also on the spatial structure of the pore network (size distribution, connectivity, topology). Column experiments allow for the consideration of the structure and thus for a quantification of possible rate limitations. We focus on column experiments run in closed-flow mode. There, a typical oscillation in the “breakthrough” of solute concentration, which conveys additional information about the flow regime (dispersivity, water content, immobile water) as well as the effective interaction kinetics, can be observed. Another major feature of the closed flow design is the conservation of tracer mass inside the column setup. Therefore, the investigation of sorption characteristics can be simplified by using mass balances.

Our objective was to study the interaction between different solutes (conservative tracers, e.g., NaCl and reactive tracers, e.g., acetate, oxalate and vanillic acid) and artificial porous media (composed of quartz, illite, goethite and charcoal in a well defined grain size distribution). The reactive tracers were chosen to probe specific reactive surfaces, which allowed for a consideration of involved sorption mechanisms and an estimation of sorbent surface coverage. The concentration-time profile of solutes was measured with non-consuming techniques (fluorescence spectroscopy or electrical conductivity measurements). PARAFAC analysis of fluorescence data was used for the quantification of aromatic compounds in complex background solutions. Since the reconstructed sorption characteristics are influenced by physical and chemical non-equilibrium and possible sorption sites were unavailable due to aggregate formation and immobile regions in the porous medium, we were able to estimate the amount of void volume and the availability of sorption sites of goethite.


Hydrogeochemical modeling and noble gas analysis of spring waters from Poços de Caldas, MG-Brazil

RITTER S.M.1, ISENBECK-SCHRÖTER M.1,*, FREUNDT F.2, AESCHBACH-HERTIG W.2 AND BONOTTO D.M.3
1Inst. of Earth Sciences, Heidelberg Univ., INF 236, 69120 Heidelberg, Germany
(*corr: Margot.Isenbeck@geo.uni-heidelberg.de)
2Inst. of Env. Physics, Heidelberg Univ., INF 229, 69120 Heidelberg, Germany (aeschbach@iup.uni-heidelberg.de)
3Instituto de Geociências e Ciências Exatas, UNESP-Campus of Rio Claro, Av 24-A, n°1515 Bela Vista 13506-900 - Rio Claro, SP - Brazil (dbonotto@rc.unesp.br)

Thermal and non-thermal spring water samples from the city of Poços de Caldas were analysed with respect to their chemical composition and dissolved noble gas contents. The objective is a better understanding of the hydrogeochemical evolution, maximum reservoir temperature, groundwater age and possible heat sources of the low-enthalpy thermal system. The genesis of the thermal alkaline waters (Na-K-(H)CO3-SO4-F-type) could be approached by an inverse model of water-rock interactions with Phreeqc. The model favours four main processes to take place in thermal water formation: (I) pyrite oxidation; (II) CaF2 or NaF dissolution; (III) calcite precipitation; (IV) Na-K-alumosilicate weathering; (V) equilibrium at depth of Na and K with Na-K-alumosilicates (e.g. orthoclase and nepheline). Thoroughly chosen chemical Geothermometers, calculated with the computer program SolGeo [1], indicate maximum equilibrium reservoir-temperatures of 105-130°C, which offer estimates on the circulation depth of 2.6-3.3 km.

Dissolved noble gas contents and their isotopic ratios in the water samples generally support previous assumptions [e.g. 2] of (i) different aquifer sources for the springs; (ii) the occurrence of mixing of thermal and non thermal water during ascent; and (iii) relatively long residence times of the circulating meteoric water in the geothermal system. Further noble gas data examination could lead to obtain age constraints derived by 4He accumulation and more information about the heat source of the geothermal system.


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Early mantle composition and evolution inferred from $^{142}$Nd and $^{182}$W variations in Isua samples

H. RIZO$^{1,2}$, M. TOUBOUL$^2$, R.W. CARLSON$^1$, M. BOYET$^3$, I.S. PUCHTEL$^1$ and R.J. WALKER$^2$

$^1$Carnegie Institution of Washington, Dept. of Terrestrial Magnetism, Washington DC 20015, USA.
$^2$University of Maryland, College Park, MD 20742, USA
$^3$Universite Blaise Pascal, 63038 Clermont-Ferrand, France

The composition and evolution of the early terrestrial mantle is largely unknown due to the sparse geological record preserved from Earth’s infancy. The short-lived $^{144}$Sm-$^{142}$Nd chronometer applied to Eoarchean Greenland rocks led to the discovery of the oldest known mantle reservoir. Samples derived from this reservoir have $^{142}$Nd excesses of 10-20 ppm compared to modern samples, which combined with $^{147}$Sm-$^{142}$Nd systematics suggest that their source was depleted in incompatible elements, and formed in the first 150 Ma of Solar System history [1-4]. Recently, $^{182}$W excesses of $\pm 13$ ppm relative to terrestrial standards were also detected in rocks from the same area [5], as well as in the mantle sources of 2.8 Ga komatiites [6]. $^{182}$W excesses could reflect imperfect mixing of late-accreted materials into the mantle during the period between 4.5 and 3.8 Ga. Given the short half-life of $^{182}$W, these excesses could instead reflect Hf/W fractionations during the first tens of Ma of the Solar System history. In this case, $^{182}$W and $^{142}$Nd signatures would indicate that early-formed mantle reservoirs were not erased during the Moon-forming giant impact. Re-mixing of early-formed Greenland reservoirs likely started during the Hadean and the obliteration of these heterogeneities with respect to $^{142}$Nd seems to have been completed by 3.3 Ga [7], whereas the $^{182}$W anomalies detected in 2.8 Ga komatiites imply that W isotopic heterogeneities persisted in the mantle until at least the late Archean [6]. We present new highly siderophile element and $^{182}$W data for 3.8 Ga to 3.3 Ga old Isua samples, previously analyzed for $^{142}$Nd. This dataset may help constrain the composition of the Archean mantle as it evolved through time, and may allow modeling the mixing rate of late accreted meteoritic material in the mantle.


Noble gases geochemistry of magma degassing at Santorini (Greece): Inferences on 2011-2012 unrest

RIZZO A.$^1$, BARBERI F.$^2$, CARAPEZZA M.L.$^3$, FRANCALANCI L.$^4$, D’ALESSANDRO W.$^1$, DI PIAZZA A.$^2$ AND SORTINO F.$^1$

$^1$Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Via Ugo La Malfa 153, 90146 Palermo, Italy
$^2$Dipartimento di Scienze, Università di Roma Tre, Largo San L. Murialdo 1, 00146 Roma, Italy
$^3$Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Roma 1, Via di Vigna Murata 605, 00143 Roma, Italy
$^4$Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Viale Pira 4, 50121 Firenze, Italy

We performed a noble gases investigation of fluid inclusions hosted in olivines and pyroxenes from mafic enclaves contained in the 1570 and 1925 A.D. dactitic magmas erupted at Nea Kameni. These enclaves are a portion of mafic magma batches that replenished the shallow chamber of the plumbing system hosting cooler and more silicic melts. Their Sr-Nd isotope ratios are quite similar to those measured in the host dactitic rocks, implying a common parental magma. Therefore, the analysed enclaves may be considered representative of the historic magma erupted at Nea Kameni which could be still present in the volcano plumbing system feeding the crater fumaroles.

Gases extracted from fluid inclusions are affected by an appreciable air contamination, as their $^{4}$He/$^{20}$Ne and $^{40}$Ar/$^{36}$Ar ratios are near to the typical atmospheric signature. The $^{3}$He/$^{4}$He ratios of olivines, once corrected for air contamination (3.1-3.6 Ra), show higher and more reliable values than the cogenetic pyroxenes. These values partially overlap those of the gases (3.5-4.0 Ra) collected from Nea Kameni fumarolic field and from bubbling springs at Palea Kameni. The range of $^{3}$He/$^{4}$He ratios (3.1-4.0 Ra) is appreciably lower than typical arc volcanoes (R/ Ra ~7-8), implying that a contamination by $^{3}$He-rich fluids occurred either directly in the mantle and/or in the plumbing system. Comparison of $^{3}$He/$^{4}$He and $^{40}$Ar/$^{36}$Ar ratios measured in enclaves with those of fumarolic gases, as well as long-term monitoring of R/Ra in the latters, coherently indicate that magma involved in the 2011-2012 unrest is likely more primitive and $^{3}$He-rich than the mafic enclaves. This would imply that the Santorini magma presently available for eruption has a lower explosive potential than in the recent historic eruption of Nea Kameni.

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F and Cl solubilities in wadsleyite and ringwoodite

M. ROBERGE1, H. BUREAU1, N. BOLFAN-CASANOVA2, D. FROST1, C. RAEPSAET4, S. SURBLE1, H. KHODJA4 AND G. FIQUET1.

1IMPMC, UPMC-CNRS, 75252, Paris, France
2LMV, UBP-CNRS, 63038, Clermont-Ferrand, France
3BGI, 95440 Bayreuth, Germany
4LEEL, SIS2M, CEA-CNRS, 91191 Gif-sur-Yvette, France

The relative distribution of volatile elements (e.g. H, C, F, Cl, S) in the different Earth’s various reservoirs provides strong constraints on the understanding of the Earth’s history. This study aims to access the mechanism and proportion of halogen that may be accomodated in minerals of Earth’s Transition Zone (TZ; 410 to 660 km depth). The storage of water in the TZ is thought to be important due to its high solubility (up to 3.3 wt% water [1,2]) in wadsleyite (Wd) and ringwoodite (Rw), the two main phases of the TZ (60% of its volume). As the halogen and water cycle are often linked (see the review after [3]), we investigate whether the TZ could be a deep reservoir for F and Cl. Therefore, we are measuring the F and Cl solubilities in Wd and Rw. F and Cl doped Wd and Rw samples were synthesized in multi-anvil press to reach the conditions of pressure and temperature of the TZ (14 to 22 GPa; 1100 to 1450°C). The obtained crystal sizes were greater than 10 µm, allowing precise measurement of halogen contents in individual crystals. The synthesis were performed under both anhydrous and hydrous conditions to study the influence of water on the F and Cl solubilities. F and Cl quantification was realized by ion beam analysis: we used µ-PIXE (µ- Particle Induced X-ray Emission) for Cl. We show that F and Cl can be incorporated in Wd and Rw in significant amounts. F solubility decreases with the presence of water. This suggests that F (possibly Cl) and water (OH) are accommodated on the same crystallographic sites in Wd and Rw. If we assume that the transition zone would store significant amounts of Cl and F, it means that (1) the TZ has been continuously supplied by Cl and F-bearing subduction materials, or (2) TZ is a hidden deep light halogen elements reservoir which never exchanges with the rest of the mantle. In both cases, F and Cl bulk silicate Earth contents may have been underestimated. If confirmed, the Earth’s accretion models may have to be revisited.


Mass independent isotope fractionation in Ozone

REINHARDT, P.1 AND ROBERT, F.2

1Laboratoire de Chimie Théorique, UMR-CNRS 7616, UPMC, 4 place Jussieu, F 75252 Paris, France
2Laboratoire de Minéralogie et Cosmochimie du Muséum, UMR CNRS 7202, MNHN, Paris 75005, France.

We propose that the average lifetime of an activated O₃⁺ complex yielding ozone and formed by collisions involving distinguishable isotopes in the reaction O + O₂, is not equal to the average lifetime of the same complex but formed by collisions involving indistinguishable isotopes. We ascribe the mass independent isotopic fractionation factor (η) [1] to the average lifetime ratio of complexes formed by reactions involving dis- and indistinguishable isotopes.

Calculated average lifetimes of the O₃⁺ complexes in a thermal gas were obtained by classical trajectories of collisions O + O₂, where all atoms have the same mass (16 amu). Simulations have been carried out in an ab-initio potential surface [2] of three oxygen atoms in a singlet ground state. We derive the mass-dependent fractionation as measured in laboratory experiments [3] by including differences in the zero-point energies of involved O₂ molecules. The numerical results account well for the measured isotopic fractionation in ozone [3, 4], as reported in the Table 1.

<table>
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Table 1: ΔZPE the difference in zero-point energies; α(MD) the calculated mass-dependent fractionation factor; α(calc.) the overall calculated isotopic fractionation factor; α(mes.) the measured isotopic fractionation factor as reported by [3]; last column: the type of reaction. R and NR for reactive and non reactive, I for Indistinguishable. The reference reaction is shown by a (*).

New insights into the evolution of a stagnant magma chamber - magma loss and liquid evolution in the Upper Zone of the Bushveld Complex

R. JAMES ROBERTS

The Upper Zone (UZ) of the Bushveld Complex is the final magma chamber to be emplaced and crystallised during the evolution of the mafic portion of Bushveld magmatism. Though isotopic evidence indicates that no magma was added to the UZ during its crystallisation history, numerous studies have postulated the loss of large volumes of magma (20-40% of the original volume[1,2]) from the magma chamber. These estimates are problematic in that volcanic material related to the Upper Zone has never been identified. This new study utilises Zr and K bulk rock data to argue that the Upper Zone has experienced little or no magma loss. Previous estimates of Zr abundance have been too low, as researchers have assumed that Zr was incompatible in the UZ; in fact, zircon is a cumulus phase in the UZ, and is especially abundant in the magnetite and nelsonite layers in the sequence. The new estimate of <5% magma missing from the original magma is conformable with global studies on intrusion/extrusion rates for mafic magmas[3], and has consequences for the evolution of the liquid line of descent (LLD) for the UZ. A new multi-part LLD for the UZ was constructed and tested using MELTS. The modelled liquid and the actual sequence of cumulus phase in the UZ, and is especially abundant in the magnetite and nelsonite layers in the sequence. The new estimate of <5% magma missing from the original magma is conformable with global studies on intrusion/extrusion rates for mafic magmas[3], and has consequences for the evolution of the liquid line of descent (LLD) for the UZ. A new multi-part LLD for the UZ was constructed and tested using MELTS. The modelled liquid and the actual sequence of minerals present in the UZ is extremely close, indicating that the UZ separated into a number of separate magma packets which then crystallised independently of one another. It is noted that despite the good correlation between the model and the actual rocks, the high Fe, low Si bulk liquid calculated for the UZ is unlikely to occur in nature, and that a portion of the UZ magmatic sequence is likely to be hidden underneath the roof rocks of the Bushveld Complex.


Distinguishing between advection and source changes recorded by Nd isotopes in the NE Atlantic

N. L. ROBERTS* AND A. M. PIOTROWSKI

Nd isotopes, measured on authigenic sediment phases, are a powerful tracer of past changes in ocean circulation [1]. Recent method developments have shown that planktonic foraminifera, which have not been chemically cleaned, preserve the Nd isotope signature of bottom water, and thus are an alternative phase to sediment leachates, avoiding possible contamination by volcanic phases [2, 3]. However, interpretation of downcore changes in Nd isotope records, in terms of past changes in water mass proportion, relies on the accurate reconstruction of the endmember composition of water mass source. Records from Fe-Mn crusts [4] and corals [5] from the NW Atlantic, and a sediment leachate record measured on core ODP 980 in the NE Atlantic [6] suggest the Nd isotope composition of the northern source endmember remained constant between the last glacial and the Holocene. However, a recent study comparing sediment leachate and uncleaned foraminifera Nd isotopes from a core close to ODP 980 indicates that sediment leachate data from this region are not reliable [7], thereby calling into question the invariant nature of the northern source endmember composition.

We present Nd isotope records, measured on unclean planktonic foraminifera, from a depth transect of cores in the northern NE Atlantic, which today are bathed by a mixture of overflow waters and Labrador Sea water. Our records sample Nd isotope composition from 1 – 4 km depth, and from 0 - 30ka. We compare our Nd isotope records with previously published benthic δ13C and B/Ca records, measured on the same cores, and used to infer past changes in ocean circulation [8]. We use the observed decoupling between these three proxies to distinguish between endmember source changes in the Nd isotope composition and circulation controlled changes, with implications for interpreting changes in the Nd isotope signatures recorded elsewhere in the N Atlantic.


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Linking Iron and Nitrogen Cycles in Lake Sediment

ELIZABETH ROBERTSON1 AND BO THAMDRUP1
1Nordic Centre for Earth Evolution, Institute of Biology, University of Southern Denmark, Odense M, Denmark

In anoxic environments, iron reduction can function as a significant pathway for organic matter oxidation, resulting in the production of ferrous iron. This Fe^{2+} can potentially be re-oxidised by nitrogen species formed in surface sediment (e.g. nitrate; NO_{3}^{-}, nitrite; NO_{2}^{-}). The fate of such oxidized nitrogen compounds is of particular importance to nitrogen availability in microbial communities – determining whether nitrogen is retained in the environment in a bioavailable form (NH_{4}^{+}) or effectively ‘lost’ as N_{2}. Although both freshwater and marine microbial strains have been isolated which are capable of coupling NO_{3}^{-} reduction to iron oxidation, the role of such processes for either iron or nitrogen cycling in natural environments is largely unknown.

The potential interactions of iron with NO_{3}^{-} reduction pathways were investigated in anoxic incubations with iron-rich sediment from a shallow, mesotrophic Danish lake. 15N tracing methods were used to determine contributions of denitrification and dissimilatory nitrate reduction to ammonium (DNRA) and how Fe^{2+} potentially influences the partitioning between these processes. DNRA was found to be the dominant nitrate reduction process and appeared to be further stimulated by addition of Fe^{2+} to incubations. These results suggest that NO_{3}^{-} reduction coupled to Fe^{2+} oxidation in this sediment yields NH_{4}^{+} as opposed to N_{2} as previously described in several culture studies; resulting in nitrogen being retained in the system as a bioavailable substrate. Whether our findings are more generally applicable to aquatic systems such as marine sediments and anoxic waters where Fe^{2+} and oxidized nitrogen species co-occur is currently being explored.

Identifying carbon pools in heterogeneous materials: Use of peak fitting and TGA-DSC-MS data

S.A. ROBERTSON1*, E. LOPEZ-CAPEL2, D.A.C.MANNING2, N. FINLAY1 AND K.L.JOHNSON1
1School of Engineering and Computing Sciences, Durham Univ, DH1 3LE, UK (*correspondence: steven.robertson@durham.ac.uk)
2School of Civil Engineering and Geosciences, Newcastle Univ, NE1 7RU (elisa.lopez-capel@newcastle.ac.uk)

Thermogravimetry-differential scanning calorimetry (TG-DSC) is an effective tool for the analysis of modelable carbon pools (including labile, recalcitrant, resistant and inorganic carbon) in soils [1,2]. Coupling of the TG-DSC instrument with a quadrupole mass spectrometer to give a TG-DSC-MS arrangement allows the temperature dependent evolution of low molecular weight species such as carbon dioxide and methane to be monitored at the same time as mass losses [2].

A TG-DSC-MS analytical run from 100 to 1000 °C in an atmosphere of 20% O_{2}, 80% He produces data that can be interpreted using GRAMS-AI software (Thermo Scientific). After ruling out potential interferences, monitoring the m/z 44 ion shows the evolution of CO_{2} at different temperatures during the TG-DSC-MS run and a semi-automated peak fitting process has been developed, whereby the proportions of labile, recalcitrant, resistant and inorganic carbon in a sample can be estimated. By defining a range of temperatures over which each carbon pool might be expected to thermally decompose, and running multiple iterations of GRAMS-AI’s peak fitting algorithm, a composite “best fit” of the four individual carbon pool peaks to the m/z 44 trace can be produced. The relative peak areas indicate the proportion of each type of carbon in the sample and parallel use of an elemental analyser allows estimation of carbon masses.

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The approach adds utility to the TG-DSC-MS approach where heterogeneous materials are under investigation and has been used to investigate man-made soils [3] and to study organic rich residuals from the drinking water industry [4]. It appears to have general applicability in cases where rapid estimation of the size of the four carbon pools is required.


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Characterization of Gas-Phase Air Pollutants and their Public Health Impact

ROBERTS-SEMPLE D
dawn_semplea@yahoo.com

Air pollution can have deleterious effects on human health. This study examines the role of meteorological factors on air pollution concentrations and their cumulative effects on public health in Hackensack Meadowlands, New Jersey. Ambient concentrations of nitrogen oxides (NO\textsubscript{x}) and ground-level ozone (O\textsubscript{3}) were measured and meteorological variables were monitored at the Meadowlands Environmental Research Institute (MERI) from June 2007 to May 2008, to characterize the temporal and seasonal variations of gas-phase air pollutants. Health records of respiratory hospital admissions were obtained from the New Jersey Department of Health and Senior Services (NJDHSS). Statistical analyses were conducted by using time series, multiple linear and principal component regression techniques. The meteorological conditions and air pollutants that may be associated with human respiratory health effects were analyzed.

The results show that ambient levels of NO\textsubscript{x} and O\textsubscript{3} are influenced by certain meteorological conditions in the Meadowlands, and there is a strong relationship between hospital admission and personal exposure to NO\textsubscript{x}. There is no direct relationship between O\textsubscript{3} and hospital admission (r=0.092), whereas hospital admission and NO\textsubscript{x} correlate (r=0.317) but more strongly with NO\textsubscript{2} (r=0.359) at a significance level of 0.01. Hospital admission rates are indirectly affected by relative humidity (r=-0.077). The seasonal dependence of pollutants is caused mainly by low wind speed and differences in chemical processing, making them interdependent. Seasonal variations of NO\textsubscript{x} were less distinct with strong diurnal patterns of traffic-related peaks during the early morning rush hour. There was a strong association between NO\textsubscript{x} and respiratory hospital admissions in the fall, winter and spring seasons. The variability of NO\textsubscript{x} and O\textsubscript{3} was altered by distinct atmospheric conditions and chemical inter-conversions of the pollutants. There was an inverse relationship between concentrations of NO\textsubscript{x} and O\textsubscript{3}; the latter was dominant in summer and specific time of the day (early afternoon). For O\textsubscript{3}, association with hospital admissions was strongest at 2 lag days. Both climate-induced and pollution-induced health effects of NO\textsubscript{x} and O\textsubscript{3} suggest that current national standards may not adequately provide a safe threshold for air pollutants from a public health perspective.

Uranium isotopes as a novel tracer of paleo-hydrology?

LAURA F ROBINSON \textsuperscript{1} JOHN M SWARTZ \textsuperscript{2} AND WILLIAM G THOMPSON \textsuperscript{3}

\textsuperscript{1}University of Bristol, BS8 1RJ, Bristol UK (laura.robinson@bristol.ac.uk)
\textsuperscript{2}Institute for Geophysics | J.J. Pickle Research Campus, Austin, TX (jmswartz@gmail.com)
\textsuperscript{3}Woods Hole Oceanographic Institution, Woods Hole, MA 02543 USA (wthompson@whoi.edu)

Uranium series isotopes provide unique insights into the rates and amplitude of geologic processes through their range of chemical behaviours in different environments, and their radioactive decay. In this case we use \textsuperscript{234}U and \textsuperscript{238}U isotopes to examine and quantify the controls of uranium input to rivers with an emphasis on watershed precipitation and discharge. First we show data from contrasting hydrological zones in two dynamic regions: New Zealand and Chile. After controlling for lithology and physical weathering caused by uplift we show that the strength of the hydrologic cycle plays a distinct role in controlling the \textsuperscript{234}U/\textsuperscript{238}U ratio in river waters as they move through a water shed. Hydrothermal systems, subsurface processes and lakes may also act to affect the final ratio as rivers discharge into the ocean. The hydrologic cycle is thought to have changed markedly over millennial and glacial interglacial timescales leading to the possibility of a shift in the \textsuperscript{234}U/\textsuperscript{238}U ratio of rivers, groundwater and seawater. Terrestrial speleothem \textsuperscript{234}U/\textsuperscript{238}U records appear to provide supporting evidence for a lower regional hydrologic cycles during the last glacial period. By contrast, a compilation of seawater \textsuperscript{234}U/\textsuperscript{238}U recorded in corals point to a shift in the opposite direction.
Structure and Radiation Damage in Y\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} and Y\textsubscript{2}TiO\textsubscript{5}

M. ROBINSON\textsuperscript{1,}, N.A. MARKS\textsuperscript{1,}\textsuperscript{a}, D.J. CARTER\textsuperscript{1,}, M.J. QIN\textsuperscript{2,}, S.C. MIDDLEBURGH\textsuperscript{2,}, G.J. THOROGOOD\textsuperscript{2,}, E.Y. KUO\textsuperscript{2,}, R.O. AUGHERSON\textsuperscript{3} and G.R. LUMPKIN\textsuperscript{2}

\textsuperscript{1}Nanochemistry Research Institute, Curtin University, Australia (*correspondence: N.Marks@curtin.edu.au)
\textsuperscript{2}Australian Nuclear Science & Technology Organisation, Locked Bag 2001, Kirrawee DC, 2232, NSW, Australia

Yttrium titanate is a rich solid-state system with important applications in a nuclear context. When it takes the stoichiometry Y\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}, yttrium titanate adopts the pyrochlore form, a crystal structure which has been extensively studied as an immobilization matrix for nuclear waste. Y-Ti-O nanoparticles are also key ingredients in high-performance oxide-dispersion-strengthened (ODS) steels needed for next-generation fission and fusion reactors. The structure of these nanoparticles is complex and not fully clear, spanning a range of possibilities including enriched clusters, defective rocksalt-type TiO phases as well as stoichiometric Y\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} and Y\textsubscript{2}TiO\textsubscript{5}.

Here we develop a new interatomic potential for yttrium titanate and apply it to both the determination of structure and irradiation response. The potential employs partial charges and is fitted to lattice parameters, internal coordinates and elastic constants obtained from density-functional-theory. For both Y\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} and orthorhombic Y\textsubscript{2}TiO\textsubscript{5}, the potential provides a substantial improvement over existing literature models.

Recent experiments [3] have shown that cubic Y\textsubscript{2}TiO\textsubscript{5} exhibits a pyrochlore-derived superstructure involving a tripling of the unit cell along 111 directions. To determine its structure, Monte Carlo simulations were performed to order the cations and anions within a large \(3 \times 3 \times 3\) tiling of the 88-atom unit cell. Experimental diffraction reflections were used to arrange the cations by calculating the structure factor, while the potential was used to order vacancies on the oxygen sublattice. The potential was also employed in Molecular Dynamics calculations of threshold displacement energies, thermal spikes and radiation damage cascades in Y\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} and Y\textsubscript{2}TiO\textsubscript{5}. Using these simulations we interpret experimental studies of amorphization and quantify the role of anti-sites and structure in radiation response.


A new model for the formation of podiform chromitites in ophiolites

PAUL T. ROBINSON\textsuperscript{1,}, JINGSUI YANG\textsuperscript{1,}, MEI-FU ZHOU\textsuperscript{2} and FAHUI XIONG\textsuperscript{1}

1Chinese Academy of Geological Sciences, Beijing, China
(*correspondence: paulrobinson94@hotmail.com)
2Department of Earth Sciences, Univ.of Hong Kong, Hong Kong, SAR, China (mfzhou@hku.hk)

Podiform chromitites occur in the upper mantle sections of ophiolites where they are typically surrounded by dunite envelopes formed by melt-rock reaction. Both high-Cr and high-Al varieties are common, but rarely in the same ophiolite. In contrast, residual chromite grains in the host peridotites and dunites show a wide range of composition. The podiform chromitites are generally thought to be magmatic precipitates from suprasubduction (SSZ) melts migrating through the mantle wedge. However, the recent confirmation of diamonds in both podiform chromitites and peridotoids of several ophiolites, and evidence suggesting depths of formation \(>300\) km for some of the chromites, challenges this model. All UHP minerals would be destroyed if they were exposed to SSZ melts at shallow mantle levels. We suggest that residual chromites first crystallize as discrete grains in mantle peridotoids beneath mid-ocean spreading centers near the top of the transition zone, where they encapsulate diamonds and highly reduced phases carried by fluids from greater depths. These would be high-Al chromites, indicating relatively low degrees of partial melting of the host peridotites. Some of these chromite-bearing mantle sections in which diamonds occur are eventually trapped in suprasubduction zones where they are infiltrated by hydrous SSZ melts, either arc tholeiitic or boninitic in composition. As these melts migrate through the mantle wedge they react with the host peridotites, dissolving pyroxene, precipitating olivine in dunite 'channels', and becoming progressively enriched in Cr. These melts react with and locally remobilize the 'residual' chromite grains, increasing their Cr\#.

The residual chromite grains are not melted but become more Cr rich by diffusion. The remobilized chromite grains are carried to shallow levels by the rising melts where they are deposited, along with newly precipitated grains, as podiform chromitites. The UHP minerals within the chromite grains are not destroyed because they are protected from the melts. This model accounts for the fact that podiform chromitites are found only in ophiolites and for the preservation of UHP minerals in both podiform chromitites and residual chromitites within the host peridotites.

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The age of the Moon from U-Th-Pb systematics on terrestrial and lunar primitive mantles

KACEM ROCHD
Chouaib Doukkali University, El Jadida, Morocco
rochdkacem@yahoo.com

U-Th-Pb systematics of the primitive mantles reflect early mantle differentiation and core formation processes and may provide key constrain on the genetic relationship between the different planets. Here, we show that the Pb data for the terrestrial and lunar primitive mantles define a system of isochrons centred on unequilibrated primitive meteorites (e.g.; Mezo Madaras meteorite), which suggests that the Earth and Moon were formed at different times by direct accretion from the solar nebula. Following this result, we determine the age of the Moon to be exactly 5.13 Gyr. In principle, this new method of portraying a solar system by secondary isochrons centred on unequilibrated primitive meteorites can be used for precise dating all other objects in the solar system provided they are formed by direct accretion from the collapse of solar nebula and have experienced core-mantle segregation early in their planetary evolution. An other example is Mars whose Pb data for its primitive mantle might be available in the near future.

Figure 1: $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ plot for 4.55 Gyr geochron, including data point of terrestrial mantle calculated with $\mu = 8.05$ (Rochd, 2009), and 5.13 Gyr lunar isochron, including data points of plagioclase ($p < 2.89$) from Apollo 17 anorthositic gabbro 78155 (Nunes, 1975).


Carbonation of cement within a repository for radioactive wastes: Impact of CO$_2$ on cement mineralogy and permeability

C.A. ROCHELLE*1, G. PURSER1 AND A.E. MILODOWSKI1
1British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK
(*correspondence: caro@bgs.ac.uk)

Large quantities of cementitious materials will be used for radioactive waste repository construction and buffer/backfill. Degradation of organic material within the waste will produce CO$_2$, leading to cement carbonation. This will reduce its capacity to maintain highly alkaline conditions, thus possibly aiding radionuclide migration. Conversely, some carbonation reactions might improve material properties, e.g. by reducing cement permeability. Currently, it is unclear whether the overall changes due to carbonation will be beneficial or deleterious to long-term radionuclide immobilisation.

As part of the pan-European FORGE project we have undertaken a laboratory study to examine the impact of carbonation on ‘Nirex reference vault backfill’ (NRVB) cement. Aims for the work were to quantify changes in cement mineralogy, structure, porosity/permeability, and the composition of coexisting aqueous fluids. Lab investigations exposed samples of cement to free phase and dissolved CO$_2$ under a range of potential in-situ conditions; 20°C or 40°C, 4 MPa or 8 MPa, ‘young’ (Na/K/Ca-rich) or ‘evolved’ (Ca-rich) cement porewaters. The experiments involved static and flowing experiments lasting 10-365 days.

Reaction was rapid in all experiments, with samples increasing in weight by up to 9% with no change in overall size. Key reactions were breakdown of portlandite and calcium silicate hydrates and formation of carbonates and silica. Reaction fronts moved through the cement over time, demarking regions of low, partial and full carbonation. The fully carbonated zone showed evidence for higher-density carbonate-filled fractures and concentric ‘relic’ reaction fronts, which separated areas having lower-density and high porosity. Appreciable amounts of a Cl-rich phase formed in the partially carbonated zone.

Controlled flow-rate experiments revealed decreases in overall sample permeability for gaseous, supercritical and dissolved CO$_2$. Carbonation was fastest with supercritical CO$_2$, but the greatest permeability reduction occurred with dissolved CO$_2$. Permeability decreases reflect porosity reduction due to conversion of portlandite and CSH to secondary carbonate minerals. The greatest reductions in porosity and permeability occurred in a very narrow zone at the leading edge of the visible alteration front.
Design Overview of the Potsdam 1280-HR SIMS Instrument

A. ROCHOLL1 AND M. WIEDENBECK1

1Helmholtz-Centre Potsdam, GFZ, German Research Centre of Geosciences, Telegrafenberg, 14473 Potsdam, Germany (*correspondence: Alexander.Rocholl@gfz-potsdam.de)

The Helmholtz Zentrum Potsdam is currently installing a Cameca 1280-HR SIMS, which will begin producing user data in the autumn of 2013. This state-of-the-art, ultra-high sensitivity and large geometry ion microprobe will function as an open user facility, in accordance with the Helmholtz Society’s support of the global scientific community through providing access to top-end infrastructure. The new 1280-HR instrument will be integrated into the Helmholtz SIMS network, whereby the activities in the Potsdam laboratory will be closely coordinated with new SIMS infrastructure currently being installed in both Dresden (accelerator SIMS) and Leipzig (NanoSIMS 50L). While the 1280-HR is intended mainly for geoscience studies, the facility will also support a limited number of well defined material science investigations as well as serving as a platform for instrumentation development work. This abstract provides a brief overview of the new facility’s design and operational goals.

The instrument currently being installed consists of the basic 1280-HR design, including the five trolley multi-collection system along with a Resistive Anode Encoder, thus making the system optimized for both low uncertainty isotope ratio determinations (e.g., δ13C, δ18O and δ34S) as well as quantification and distribution mapping of low concentration elements in minerals, glasses or biological materials. The possibility of very high mass resolution of M/ΔM ≥ 25,000 allows the separation of isobaric masses, such as 40Ca and 40K. The sample loading system consists of the standard 2-position carousel; a high capacity 500 l/s turbo pump with vibration damping provides improved vacuum in the sample source chamber. The most significant design modification unique to the Potsdam instrument is the addition of 5 flanges in the coupling and projection sections of the machine, including one intended for the integration of a total ion current measuring capability. Factory testing has shown a repeatability for δ18O determination (n= 10) of ± 0.25 ‰ (1σd) on a quartz disk, with further improvements in analytical uncertainty expected once the instrument enters routine service. Envisioned key analytical topics include H, B, C, O, S and Pb isotopic studies, geochronological applications and the quantification of volatile elements in geological materials.

Trace-elements distribution in tourmaline, micas and K-feldspar from the Berry-Havey pegmatite (Maine, USA): implications for the pegmatitic evolution

E. RODA-ROBLES1, W. SIMMONS2, A. PESQUERA1, P. P. GIL-CRESPO1, J. NIZAMOFF2 AND J. TORRES-RUIZ3

1Dpto. Mineralogía y Petrología, UPV/EHU, Bilbao, Spain, encar.roda@ehu.es
2Earth and Environmental Sciences, University of New Orleans, USA. wsimmons@uno.edu
3Dpto. Mineralogía y Petrología, Universidad de Granada, Spain. jotorres@ugr.es

The Berry-Havey pegmatite (Oxford pegmatite field, Androscoggin County, Maine, USA), is a highly evolved pegmatite enriched in Li, F, B, Be and P. The pegmatite has a complex internal structure, with four texturally and compositionally different zones, which show an increasing degree of evolution inwards: wall zone, intermediate zone, core margin and core zone, where gemmy tourmaline-bearing pockets are common. The main minerals are quartz, feldspars, Al-micas (muscovite-lepidolite series), tourmaline (schorl-elbaite-rossmanite), and minor Fe-micas (biotite and zinnwaldite). Garnet, beryl, amblygonite-montebrazite, and apatite are common accessory minerals.

Most trace elements do not show a clear preference for any of the main minerals. However, Li, Cs, Mn, Ba, Nb, and Ta mainly partition into the Fe-mica, whereas Be, Sn, W and Zr partition preferentially into the Al-mica. P and Sr partition into the K-feldspar. Tourmaline is the poorest of the four phases in trace elements. Li content increases from the wall zone to the core in all the phases. Rb, Cs and Ba show a similar trend for micas and K-feldspar, with Rb and Cs increasing gradually from the wall zone to the core zone, simultaneously to the decrease of Ba. In tourmaline Li, Be, Mn, Sn, Nb and Ta contents increase from the wall zone to the core zone, and finally decrease in the gemmy tourmaline from the pockets. Overall, REE contents are very low. The origin of these differences relates to the concentration of the elements in the melt and the variations in the compatibility of these elements between the minerals and melt during fractional crystallization, which in turn depends on the behavior of major elements. Micas, K-feldspar and tourmaline are good geochemical monitors using trace elements such as Li, Rb, Be, Sr and Ba, to understand the petrogenesis of pegmatites.
Chromium isotope record of the Otavi Group, Namibia

A RODLER1,2,4, R FREI2,4, C GAUCHER3,4, AR VOEGELIN2,4, CV ULLMANN2,4 AND C KORTE2,4

1Natural History Museum of Denmark (alexandra.rodler@reflex.at)
2University of Copenhagen (robertf@geo.ku.dk, andrea.voegelin@geo.ku.dk, cu@geo.ku.dk, korte@geo.ku.dk)
3Universidad de la República, Uruguay (gaucher@chasque.net)
4Nordic Center for Earth Evolution (NordCEE)

Due to its redox-sensitivity, the chromium isotope system is an interesting paleoclimatic tracer particularly powerful in recording fluctuations of atmospheric oxygenation and continental weathering [1]. Here we seek to investigate detailed $\delta^{53}$Cr records associated with intense climatic changes during Neoproterozoic glaciations.

We present a $\delta^{53}$Cr record of late Neoproterozoic marine carbonates stretching from the Chuos (746±2 Ma [2]) to the Ghaub Fm (635.6±0.5 Ma [3]), exposed in northern Namibia, covering shallow water sedimentation during the Cryogenian glaciations. The $\delta^{53}$Cr stratigraphy was complemented with $\delta^{13}$C$_{\text{carb}}$ as well as major and trace element concentrations. The Chuos $\delta^{53}$Cr signal is close to mantle inventory [4], but recovers rapidly to positive values after the glacial sequence, indicating a sufficiently oxygenated atmosphere. Prior to the Ghaub glaciation, $\delta^{53}$Cr values are positively fractionated (+0.12±0.02‰) and correlate to $\delta^{13}$C$_{\text{carb}}$, while in post-Ghaub carbonates $\delta^{53}$Cr values decrease to ~-0.08‰, similar to drops observed in post-Chuos sediments, and accompanied by increased Cr, Sc, and Ti concentrations. These $\delta^{53}$Cr results suggest increased continental-derived detrital input as a consequence of enhanced weathering processes related to rapid climate change, elevated post-glacial $p$CO$_2$ [5], proximity to the continent and/or increased hydrothermally-derived Cr input.

The observed $\delta^{53}$Cr fluctuations indicate sufficiently high atmospheric oxygen levels to oxidize and mobilize Cr during weathering processes on land prior and after the major Neoproterozoic glaciations. Increased weathering due to rapid post-glacial rise of $p$CO$_2$ render the $\delta^{53}$Cr signal unfractonated, also potentially indicating the predominance of accumulated hydrothermally-derived Cr in the shallow seawater pool during the Ghaub aftermath.


A new experimental approach to silicic magma differentiation

CARMEN RODRIGUEZ1,*, ANTONIO CASTRO2 AND ANTONIO SÁNCHEZ-NAVAS3

1University of Huelva Campus El Carmen, 21071 Huelva, Spain (*correspondence: carmen.rodriguez@dgeo.uhu.es)
2Unidad Asociada de Petrología Experimental, CSIC-University of Huelva, Campus El Carmen, 21071 Huelva, Spain (dorado@uhu.es)
3University of Granada Campus Fuentenueva 18071

The separation of fluid and crystals from melt at diverse stages in the evolution of magmatic systems is inferred on the basis of thermomechanical modelling [1], geochemical relations of zoned silicic plutonic bodies [2] and phase equilibrium studies [3]. However, experimental tests dealing with magmatic differentiation of natural magmas at real pressures and temperatures are very scarce [4, 5].

In our laboratory experiments, gravity effects are separated from those imposed by thermal gradients, which simulate natural conditions of crystallization in a cooling magma chamber. Major and trace element distribution profiles result from the thermal gradient for water-bearing magma systems. The observed profiles are exclusively explained by diffusion in the liquid and boiling-assisted crystal-liquid separation, without invoking gravity crystal settling. These experiments confirm the key role of fluids in silicic magma differentiation and their implications on explosive volcanism and ore deposit generation.

**Origin of Grande Ronde Basalts, Columbia River Basalt Group**

**SEDELIA RODRIGUEZ**\(^1\) AND GAUTAM SEN\(^2\)

\(^1\)Florida International University, Miami, FL, USA
\(^2\)American University of Sharjah, Sharjah, UAE, gsen@aus.edu

The Grande Ronde Basalt lavas contain 0-5% phenocrysts of plagioclase, augite, pigeonite, and olivine. Plagioclase hysteresis shows that the erupted lavas contained less than 0.3% dissolved H\(_2\)O. The presence of rare An\(_{96}\) plagioclase megacrysts suggests ~4.5wt% dissolved H\(_2\)O in some parent magmas. All magmas degassed during ascent and eruption. Size of plagioclase phenocrysts suggests an average phenocryst residence time in magma of 160 years. Ignoring hiatuses between eruptions, we estimate that the 110 flows of the GRB erupted over a cumulative time of 17,600 years, with an average eruption rate of about 8.6 km\(^3\)/year. The average interval between eruptions is estimated to be 3658 years. Model simulations and petrological reasoning indicate that the primary melts were generated from spinel peridotite at 1.5 GPa, perhaps under hydrous conditions. Extensive melting of lfrac{\text{fithospheric eclogite may have played a role as well; however, this is not constrained by our simulations. Magmas underwent contamination, mixing, and partial crystallization during and prior to their short residence within shallow (6 km) intrusives. Our petrologic conclusions lead us to present a petrotectonic model that supports the hypothesis that the CRBG magma generation was greatly aided by a thinned lithosphere and H\(_2\)O that may have come off the mantle wedge.**

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**The role and effect of Mg on the formation of carbonates**

**JUAN DIEGO RODRIGUEZ-BLANCO**\(^1,2,\ast\), **SAMUEL SHAW**\(^1,3\), **PIETER BOTS**\(^1,3\), AND **LIANE G. BENNING**\(^1\)

\(^1\)School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK. (\ast\) presenting author
\(^2\)Nano-Science Center, Department of Chemistry, University of Copenhagen, Denmark.
\(^3\)School of Earth, Atmospheric and Environmental Sciences, The University of Manchester.

Mg is the most abundant divalent cation in seawater. It plays an important role in the crystallization of CaCO\(_3\)-based biominerals that control the marine global carbon cycle. However, the mechanisms of CaCO\(_3\) crystallization from solution in the presence of Mg are still poorly understood. Here we show that a spherulitic growth mechanism often controls the nucleation, growth and crystallization of Ca-Mg carbonate polymorphs produced with variable Mg contents (0-50%) and at different temperatures (7.5-220°C). Combining in situ and realtime synchrotron-based diffraction and scattering with time-resolved UV-Vis spectrophotometry and high-resolution imaging we quantitatively evaluated the kinetics and mechanisms of the formation and crystallization reactions in the Ca-Mg-CO\(_3\) system.

Under all conditions an initial, variable Mg containing, poorly-ordered, nanoparticulate precursor (amorphous calcium carbonate, ACC) forms from solution and transforms to various nanocrystalline intermediates via a spherulitic growth mechanism. In turn these intermediates crystallize via a dissolution and reprecipitation mechanisms to end products. The composition, kinetics of formation, local structure and stability of the ACC are dependent on the initial Mg/Ca/CO\(_3\) ratio, the temperature, supersaturation and pH of the reactions. At 0% Mg, pure ACC rapidly (\(<2\) min at 21°C) crystallizes to vaterite via spherulitic growth (image a, bottom) and later transforms slower (hours) into calcite through dissolution-reprecipitation [1,2]. With 10% Mg, ACC is ~1 order of magnitude more stable than pure ACC, and transforms to Mg-calcite with no vaterite intermediate [3] (b). Higher Mg contents further stabilize the ACC for hours to days. These high Mg-ACC phases crystallize spherulitically either to monohydrocalcite (c; \(\text{Mg/Ca} > 0.25; \text{T<60°C;} \text{[4]}\)), dolomite (d; at Mg/Ca \(< 1; \text{T>60°C;} \text{[5]}\)) or various Mg-rich carbonates (e.g., at Mg/Ca\(\geq 1 \) hydromagnesite).

Modeling of enhanced \textit{in situ} biodenitrification in fractured aquifer: Biogeochemical interactions and isotope fractionation

P. RODRÍGUEZ-ESCALES\textsuperscript{1,2,\,*}, B.M. VAN BREUKELEN\textsuperscript{3}, G. VIDAL-GAVILAN\textsuperscript{1,2}, A. SOLER\textsuperscript{2} AND A. FOLCH\textsuperscript{4}

\textsuperscript{1}Dept. Geologia. UAB. 08193, Bellaterra, Spain. 
\textsuperscript{2}Correspondence: prescales@gmail.com.
\textsuperscript{3}D'ENGINY biorem S.L., C. Madrazo 68, 08006 Barcelona, Spain.
\textsuperscript{4}Dept. Cristal·lografia, Mineralogia i Dipòstits Mineals, UB, Martí Franquès s/n, 08028, Barcelona, Spain.
\textsuperscript{5}Dept. of Earth Sciences, VU University Amsterdam, De Boelelaan 1085, NL-1081 HV Amsterdam, The Netherlands.
\textsuperscript{6}GHS, Dept. of Geotechnical Engineering and Geo-Sciences.UPC. Jordi Girona 1-3, Mòdul D-2. 08034, Barcelona, Spain.

Enhanced \textit{in situ} biodenitrification (EIB) is a feasible technology to clean up nitrate-polluted groundwater and achieve drinking water standards. We developed a reactive transport model that considers biogeochemical processes as well as isotope fractionation to enable better monitoring and management of this technology. In this work, we applied this model to interpret data from batch experiments on EIB. Furthermore, 2-D simulations at field scale are in progress to model an EIB pilot conducted in a fractured aquifer system. The used codes were PHREEQC for batch scale and PHAST for field scale. The fractured media were modeled as equivalent continuum media with two hydraulic conductivity zones. The flow model was validated with experimental data from a tracer test with bromide. The reactive transport model at batch and field scale was validated with experimental values of Vidal-Gavilan \textit{et al.} (2013) \cite{1}. The preliminary results show that parameters determined in batch experiments can be used as first estimates to reproduce field observations provided groundwater flow is well known. Moreover, the inclusion of isotope fractionation processes allowed to determine the real scope and exact degree of EIB at field scale.


Uptake of Pb\textsuperscript{2+}\textsubscript{(aq)} by baryte-celestine solid-solution crystals

R. M. RODRÍGUEZ-GALÁN, J. CARNEIRO AND M. PRIETO
Department of Geology, University of Oviedo, Spain

The interaction of dissolved toxic metals with minerals frequently leads to dissolution-coprecipitation processes in which the metal ion incorporates into the solid phase substituting for the major ion in lattice positions. The fact that the solubility of a minor constituent in a solid solution is smaller than the solubility of its equivalent pure solid explains the environmental relevance of these coprecipitation reactions. Interaction studies are typically carried out by using stoichiometric minerals as host phases. However, in most cases the effectiveness of this removal mechanism could be significantly increased using suitable solid-solutions instead of pure minerals. In this work we study the interaction of Pb-bearing aqueous solutions with baryte (BaSO\textsubscript{4}) and intermediate (5-15 \% molar Sr) members of the (Sr,Ba)SO\textsubscript{4} solid solution.

Compositionally homogeneous crystals of the solid solution were obtained by precipitation & aging in a closed reactor at 90ºC. The obtained precipitates were checked for compositional homogeneity by considering the full width at half maximum intensity values (FWHM) of some selected reflections of the XRD patterns. The precipitate compositions were determined by analyzing the remaining solutions by ICP-AES. Moreover, samples of each precipitate were analyzed by SEM-EDS.

The interaction experiments were carried out in closed reactors at 25ºC. The aqueous composition was analyzed repeated times during the experiments, which lasted one month. In the case of the interaction with strontian baryte, lead incorporates into the solid phase while some barium and a large proportion of strontium incorporate to the aqueous solution. As result the aqueous solution becomes depleted in lead at a significantly greater extent than during the interaction with pure baryte.

Future work will deal with the implementation of an equilibrium model for the (Pb,Sr,Ba)SO\textsubscript{4}-H\textsubscript{2}O system. An added implication is related to the effectiveness of Sr-bearing baryte as a sequestering phase for radium. The interaction with baryte leads to a significant removal of dissolved Ra\textsuperscript{2+}, but the depletion could be considerably greater using strontian baryte.

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Biominalization of Mg-rich Calcite (Mg_xCa_{1-x}CO_3) by Proteus mirabilis

YUL ROH^1* and SERKU KANG^2

^1Chonnam National University, Gwangju, Korea,
^2Chonnam National University, Gwangju, Korea,
(*correspondence: rohy@jnu.ac.kr)

Recently biologically induced carbonate precipitation has been proposed as an environmentally friendly method to apply CO_2 sequestration and fixation [1]. The objectives of this study were to investigate biominalization of the carbonate minerals using microorganisms enriched from rhodoliths and to identify environmental factors that control the formation of calcite by the microorganisms.

Carbonate forming microorganism (CFM) was enriched from rhodoliths using D-1 medium for microbial activity and aerobically cultured at 25°C using D-1 medium with containing 30:30 mM Ca::Mg-acetate concentrations to confirm formation of carbonate minerals. Enriched microorganisms were analyzed by 16S rRNA gene DGGE analysis to confirm microbial diversity. Various ratios of Ca and Mg-acetate concentrations (60:0, 60:20, 20:60, 0:60 mM) were added to D-1 medium to examine how different Ca and Mg ratios affect the biominalization of carbonate minerals. Mineralogical characteristics of bio-precipitates were determined by XRD and SEM-EDS analyses.

A 16S rRNA sequence analysis showed the enriched microorganisms contained CFM such as Proteus mirabilis [2]. XRD analyses showed that the precipitates were calcite with Ca::Mg-acetate (60:0, 60:20 mM), Mg-rich calcite with Ca::Mg-acetate (30:30, 20:60 mM) and hunte and Ca::Mg-acetate (0:60 mM) were formed, whereas any carbonate minerals were not formed without the microorganisms in D-1 medium. Also, through various ratios of Ca/Mg concentrations, we observed that the formation of Mg-rich calcite and huntite occurred when the level of Mg ion was much higher than that of Ca ion in D-1 medium. SEM-EDS analyses showed that the carbonate minerals formed by the microorganisms were a rhombohedron shape consisted of Ca, Mg, C. and O and irregular shaped extracellular polymeric substance (EPS) with Ca, Si, and Mg component.

These results indicate that the microorganisms induce precipitation of carbonate minerals on the cell walls and EPS via the accumulation of Ca and/or Mg ions on the cells. Therefore, microbial precipitation of carbonate minerals may play one of important roles in metal and carbon biogeochemistry as well as carbon sequestration in natural environments.


Redox processes in the Earth’s mantle

ARNO ROHRBACH^1

^1Institut für Mineralogie, Westfälische Wilhelms-Universität Münster, Germany, arno.rohrbach@uni-muenster.de

Redox reactions are crucial for many geological processes, but especially how Earth’s surface and atmosphere became oxidized enough to form a habitable planet is a key question. To understand redox controls in Earth’s mantle is of prime importance, because oxygen fugacity (fO_2) regulates the biogeochemical cycles of volatiles such as C-O-H or S and their respective fO_2-dependent species. These volatiles also link deep mantle reservoirs and Earth’s surface because they promote mantle convection and initiate volcanism through solidus depression in various tectonic settings.

The redox state of the mantle may be reconstructed, for instance, by investigating mantle melts. Subduction related basalts (LAB) have higher Fe^{3+}-ΣFe ratios than mid-ocean ridge basalts (MORB) or ocean island basalts (OIB) [1]. A matter of debate is, whether these higher redox states are a source signal from the mantle wedge with higher Fe^{3+}-ΣFe compared to the MORB source [2], or, if IAB melts are affected by post genetic oxidation at some stage between early crystallization and solidification. Fe^{3+}-ΣFe ratios in basalt glasses correlate with H_2O content [1] but differ from results based on other redox proxies such as V/Sc [3,4], Zn/Fe [5], or Fe isotopes [6]. Key problems, e.g., if and how subduction related fluids oxidize the mantle, if subduction causes a secular variation in mantle fO_2, or if the mantle is buffered with respect to fO_2 remain highly controversial.

Oceanic crust, lithosphere and overlying sediments are generally more oxidized than the ambient mantle if subducted to depths >100 km, because cratonic lithosphere and potentially also the asthenosphere become increasingly reduced with increasing depth [7,8]. The redox contrast between delaminated oxidized blocks from the slab and reduced ambient mantle sets the frame for hydrous and carbonatitic redox melting processes in the deeper mantle [9,10].

Lipid biomarker records of microbial community structure during the Late Ordovician through Early Silurian (~449-439 Ma) indicate substantial differences in the balance of bacterial versus algal primary production through the Late Ordovician, largely in response to climatic change associated with the Hirnantian glaciation ([1]). Our biomarker records suggest that these warm Palaeozoic intervals were associated not only with elevated atmospheric $p$CO$_2$ (~4-16x preindustrial atmospheric levels, PAL), but also with a higher average flux of oceanic methane, exerting a potential positive feedback on hothouse climates in the Palaeozoic. To refine the assessment of a methane, exerting a potential positive feedback on hothouse climates in the Palaeozoic, we have conducted compound-specific carbon isotope analyses on hydrocarbon extracts from Anticosti Island (Canada) the Vinini Formation (USA), the Maquoketa Formation (USA), and OM9 drill core (Estonia).

Recent models have demonstrated that a relatively modest increase of 4-5x preindustrial $p$CH$_4$ can generate 2-3°C of warming [2]. Methane cycling feedbacks on climate must have been of similar or greater impact in the Palaeozoic, a period of warm intervals and reduced oxidant availability [3] which may have driven a larger proportion of remineralized organic matter through microbial methanogenesis and attenuated the efficacy of combined anaerobic methane oxidation processes as a throttle for methane fluxes to the atmosphere. Because the loss rate of atmospheric methane scales inversely with the atmospheric methane abundance [4], increased fluxes to the atmosphere will often translate into higher steady-state concentrations. We explore the possible effects of this for Palaeozoic times with a series of simple mass balance calculations given a range of carbon flux and anaerobic remineralization scenarios.

Importance of reference materials and of the determination of matrix effects for precise and accurate measurements by SIMS

C. ROLLION-BARD1 AND NANCY ION MICROPROBE TEAM1

1Centre de Recherches Pétrographiques et Géo chimiques, Univ. de Lorraine, UMR 7358, 15 rue Notre Dame des Pauvres, F-54500 Vandoeuvre-lès-Nancy, France, rollion@crpg.cnrs-nancy.fr

SIMS technique (Secondary Ion Mass Spectrometer) has been used for several decades to examine element and isotope compositions at micrometer scale in various geological samples [1]. But SIMS measurements are subject to matrix effect at the time of sputtering process. To overcome these matrix effects in order to achieve precision and accuracy of the analyses, reference materials are needed. These reference materials must have the same chemical composition and mineralogy of the sample, or at best, must be the closest possible.

We will show different examples of determination of matrix effect for oxygen isotopes: in CaCO3 polymorphs, in different carbonates (magnesite, dolomite, siderite, rhodochrosite and ankerite, [2]), and in a solid-solution, i.e. Fe-Ca-Mg garnets [3,4]. We will highlight the importance of the choice of the reference materials and the determination of possible matrix effect. When all the precautions regarding these effects are taken, a precision better than 0.5 ‰ can be achieved, the more complex the correction, the worse precision is reached.


Differentiating magma sources from conglomerate and breccia clasts, IODP Site U1349, Ori Massif, Shatsky Rise Oceanic Plateau

I.V. ROMANOVA* AND D.T. MURPHY

School of Earth, Environmental and Biological Sciences, Queensland University of Technology, 4001, Brisbane, Australia (*correspondence: i.romanova@qut.edu.au)

Shatsky Rise in the northwestern Pacific is one of the largest (~500,000 km2) and oldest (145-135 Ma) Large Igneous Province on the oceanic floor. Studies of magnetic lineations and bathymetry showed that Shatsky has an elongated structure with three edifices (Tamu, Ori, Shirshov) progressively decreasing in age and in volume [1]. Integrated major and trace elements and Sr-Nd-Pb-Hf isotopes for the Shatsky Rise basalts show 4 distinct magma types and MORB-like compositions with trends towards the enriched plume(?)-source for Ori and Shirshov Massifs [2-4]. Deciphering deep plume vs. shallow mantle contributions to the Shatsky magmatism remains a fundamental problem.

During the IODP Expedition 324, site U1349A penetrated Ori massif near its summit [5] and recovered volcaniclastic sandstones, volcanic breccia, a clay-rich layer and polymictic volcaniclastic conglomerate (Unit III, ~20 m) between sedimentary layers and igneous basement. The breccia clasts range in size from 2-20 mm and the conglomerate clasts from 2-80 mm. These fragments represent eroded volcanic material originating from locally sourced portions of the Ori Massif.

All clasts are heavily altered picritic and tholeiitic basalts with little or no primary magmatic minerals preserved and significant enrichments in fluid mobile elements (Ca, Na and K). For the fluid immobile element Ti the concentration of TiO2 ranges from 1.8-4 wt. %, whereas the Shatsky Rise basement lavas have no TiO2 contents higher than 2.7 wt. %. This implies that the clasts are derived from different lavas with distinct petrogenesis and geochemistry relative to the rest of the basement lavas sampled to date. Thus, at least 5 magma types compose Ori Massif. Trace element and Nd-Hf isotope data on the new High-Ti magma type will allow further investigations into source heterogeneities.

A 2000-year rainfall record from the Eastern Tropical Pacific and ENSO variability during the Common Era

LIDIA ROMERO VIANA1,2, ULRIKE KIENEL2 AND DIRK SACHSE1

1University of Potsdam, Institute of Earth and Environmental Science, Karl-Liebknecht-Str. 24-25, 14476 Potsdam-Golm, Germany
2GFZ German Research Centre for Geosciences, Telegrafenberg, 14473 Potsdam, Germany

The ENSO is the dominant mode of interannual tropical climate variability with widespread global teleconnections. Understanding its natural variability is a key factor to evaluate its effect on the internal variability in the global climate system. We present a 2000-year rainfall reconstruction from the Eastern Tropical Pacific based on a calibrated lipid biomarker ratio, the DiTe index [1], using the annually laminated sedimentary sequence of a crater-lake located in Isabel Island (Mexico). In the region, the highly seasonal rainfall pattern is dominated by ENSO dynamics, resulting in drier/wetter conditions during positive (El Niño)/negative (La Niña) anomalies. Our inferred past rainfall variability shows negative anomalies at millennial and centennial scale coinciding with periods of high frequent and strong El Niño events being coherent with other hydroclimatic records, based on independent proxies within the target region. Our record of subdecadal resolution allows for detailed evaluation of regional rainfall variability during key periods, such as, the Medieval Climate Anomaly and Solar minima and therefore, contributes to the understanding of climatic variability in the Tropical Pacific. [1] Romero-Viana, Kienel & Sachse (2012), Palaeogeogr. Palaeoclimatol. Palaeoecol. 350, 49-61.

Are the anhydrite and gypsum carbonation pathways the same?

T. RONCAL-HERRERO1, P. BOTS1,2, J.D. RODRIGUEZ-BLANCO1,3, J.M. ASTILLEROS4,5*, M. PRIETO6, L.G. BENNING1 AND L. FERNÁNDEZ-DÍAZ1,2

1School of Earth & Environment, University of Leeds, LS2 9JT, United Kingdom
2School of Earth Atmospheric and Environmental Sciences, University of Manchester, M13 9PL, United Kingdom
3Nano-Science Center, Department of Chemistry, University of Copenhagen, Denmark
4Department of Crystallography and Mineralogy, Complutense University of Madrid, Spain. (*correspondence: jmastill@ucm.es)
5Institute of Geoscience (CSIC, UCM), Madrid, Spain.
6Department of Geology, University of Oviedo, Spain.

Coupled dissolution-recrystallization reactions during interactions between carbonate-bearing fluids and calcium sulphate minerals lead to de novo formation of CaCO3 polymorphs. The carbonation of anhydrite (ANH, CaSO4) and gypsum (GYP, CaSO4.2H2O) produces dramatic changes in both textural and chemical properties of the starting calcium sulphate phase (e.g., porosity, composition etc.). However, our understanding of such processes is still fragmented. Here we present an experimental study comparing the carbonation of ANH and GYP at 25 ºC. In both cases, the formation of various CaCO3 polymorphs occurred immediately upon contact between the solid phase and a Na2CO3 solution. However, differences in textural features and reaction pathways were observed between both systems. GYP carbonation produces a large volume of porosity with a prominent gap between parent and product phases. Conversely during ANH carbonation such a gap does not form and porosity generation is minimal. Furthermore, the produced CaCO3 polymorphs are spatially differently distributed on ANH vs. GYP surfaces and within the replaced layer indicating that the nature and reactivity of the parent phases control the CaCO3 polymorph and the evolution of textural features during carbonation. These results have implications for biomineralization, CO2 sequestration and industrial applications.

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Opal-CT precipitation in a clayey soil explained by geochemical transport model of dissolved Si (Blégny, Belgium)

B. RONCHI1*, A.L. BARAO2, F. VANDEVENNE2, N. VAN GAELEN1, D. VERHEYEN1, R. ADRIAENS1, O. BATELAAN1, A. DASSARGUES1, E. STRUYF2, J. DIELS1 AND G. GOVERS1

1KULeuven, Celestijnenlaan 200E, 3001 Heverlee, Belgium
(*correspondence: benedicta.ronchi@ees.kuleuven.be)
2UA, Campus Drie Eiken, D.C.116, Universiteitsplein 1, 2610 Wilrijk, Belgium

Dissolved Si (DSi) exported by rivers are controlled by geological, hydrological and biological cycle processes [1]. The DSi concentrations measured in a river of an upstream catchment in eastern Belgium (Blégny, Land of Herve) don’t vary seasonally (6.91±0.94mgL⁻¹; n=363). Si concentrations in pore water are often higher and vary more (8.65±3.65mgL⁻¹; n=128). The decrease of DSi along the flowpath of water is due to sink processes, i.e. precipitation, adsorption or uptake by vegetation. As the DSi in the river does not show any seasonal variation, uptake by vegetation can be ruled out [1] whereas precipitation or adsorption can control the DSi drained by the stream water. This hypothesis is confirmed by XRD and DeMaster analysis. At 0.1m depth the soil is constituted of 62% quartz, 7% K-feldspar, 6% plagioclase, 3.2% carbonates, 18.9% Al-clay, 1.47% Kaolinite, 0.63% Chlorite and 0.2% amorphous Si, probably of biogenic origin. At 1.5m depth, the amounts of several minerals (35.8% quartz, 0.6% K-feldspars, 0.9% plagioclase, Al-clay 14.7%) drop drastically. Carbonates, chlorite and kaolinite are absent whereas 40.4% opal-CT appears. The precipitation of opal-CT controls the DSi export of this catchment.

To describe DSi export from a catchment a geochemical transport model is developed in HP1 which couples the water flux model Hydrus with the geochemical model PHREEQC [2]. Our model is based on the conceptual model developed in [3]. First results show different DSi export dynamics in the unsaturated zone than in the aquifer due to different pCO₂ values and varying soil moisture conditions. Further development of the model will help to find out the reason of opal-CT precipitation in this setting.


Constraining the origin of sulfur isotopic variability through the end-Ordovician Hirnantian glaciation and mass extinction

CATHERINE V. ROSE1* AND DAVID A. FIKE1

1Department of Earth & Planetary Sciences, Washington University, St. Louis, MO 63130, USA
(*)rose@eps.wustl.edu

Geochemical records of the end-Ordovician Hirnantian Stage show parallel positive excursions in the stable isotope compositions of sedimentary pyrite sulfur (δ³⁴S_pyr), organic carbon, and carbonate carbon; these isotope excursions coincide with the end-Ordovician glaciation and mass extinction. An increase in pyrite burial attributed to marine anoxia has been proposed to explain the sulfur isotope excursion and link oceanic redox conditions to the extinction of marine fauna. Such an increase in pyrite burial would generate a parallel excursion of equal magnitude in the isotopic composition of coeval marine sulfate. However, paired sulfur isotope data from the Hirnantian Stage of Anticosti Island, Quebec, do not covary, which suggests enhanced pyrite burial is not the cause of the Hirnantian δ³⁴S_pyr excursion and questions the role of anoxia in the mass extinction. We present new high-resolution paired sulfur isotope data from carbonate-associated sulfate (CAS) and pyrite during the Hirnantian Stage from the Girardeau Formation, Missouri, USA, to test these hypotheses. The results show a 28% enrichment in δ³⁴S_pyr but no parallel excursion in δ³⁴S_CAS, indicating that enhanced pyrite burial did not generate the Hirnantian δ³⁴S_pyr excursion. These observations may best be explained by a transient reduction in the expressed isotopic fractionation during microbial sulfate reduction associated with Hirnantian sulfur cycling possibly caused by: a change in actual biological fractionation; a shift in the chemocline leading to restricted exchange of porewater sulfate; or glacio-eustatic sea-level drawdown corresponding to syndepositional sediment reworking and increased oxidation.

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Fe Isotope Fractionation During Reduction of Fe(III) to Fe(II)

A.D. ROSENBERG*, C.E. HODIERNE AND S.G. JOHN
Dept. of Earth and Ocean Sciences, University of South Carolina, USA (*correspondence: arosenberg@geol.sc.edu)

Phytoplankton growth, and thereby primary productivity, is limited in many regions of the ocean by insufficient iron (Fe) availability. In seawater iron exists in two different oxidation states – Fe(III) and Fe(II). While Fe(III) is thermodynamically stable in oxic environments, it can be reduced to Fe(II) by photochemical or biological reduction. In the ocean release of Fe(III) from ligands by reduction to Fe(II) is often necessary for Fe to become bioavailable to phytoplankton. Recently, techniques have been developed to measure dissolved Fe stable isotope ratios (δ56Fe) in seawater and marine plankton, opening the door to using δ56Fe as a tracer for biologically important Fe redox cycling in the oceans.

In order to clarify the impact that various reduction pathways have on Fe isotopic fractionation, the natural reduction of Fe(III)-L to Fe(II) was simulated in the lab by the reduction of Fe(III)-EDTA to Fe(II) in three ways: photochemically, chemically, and electrochemically. During photochemical reduction, Fe(III)-EDTA was reduced upon exposure to direct sunlight which promotes ligand-to-metal charge transfer. Chemical reduction was achieved by the addition of a reducing agent such as hydroxylamine hydrochloride. Electrochemical reductions were carried out using a rotating-disc electrode at a variety of overpotentials.

The reduction pathway has a large impact on the observed isotope effect. Photochemical reduction produces positive δ56Fe values (+0.95 to +1.03 ‰) while chemical reduction produces negative δ56Fe values (-1.73 to -2.20 ‰) with electrochemical reduction iron isotope ratios (δ56Fe) falling in between the two. Further investigation into isotopic fractionation during reduction of Fe(III) to Fe(II) may provide insight into the pathways by which Fe(III) is reduced and made bioavailable to phytoplankton in the oceans, leading to an overall greater understanding of marine iron cycling.

Linking nutrient and contaminant dynamics in rhizospheres of hyperaccumulators

C.E. ROSENFELD1*, R.L. CHANEY2, A. LANZIROTTI3 AND C.E. MARTÍNEZ1
1Pennsylvania State University, Department Ecosystem Science and Management, University Park, PA, USA, cer196@psu.edu (*corresponding author), cem17@psu.edu
2USDA ARS Environmental Chemistry Laboratory, Beltsville, MD, USA Rufus.Chaney@ars.usda.gov
3Consortium for Advanced Radiation Sources, University of Chicago, Chicago, IL, USA lanzirotti@uchicago.edu

Trace metal contamination in soils is a global problem, causing plant and microbial toxicity, diminished crop production or decreased land cover. Some plants can grow, and even thrive, in heavily polluted soils though it is generally unclear how. Our goal was to elucidate linkages between contaminant and nutrient uptake in plants grown in metal contaminated soil.

We examined two ecotypes (Ganges and Prayon) of the metal hyperaccumulator, N. caerulescens (formerly Thlaspi caerulescens) grown on field-contaminated soil. Both ecotypes are known zinc (Zn) hyperaccumulators, while only the Ganges ecotype hyperaccumulates cadmium (Cd). At harvest, rhizosphere and plant thin sections were obtained for synchrotron-based μ-X-ray fluorescence (μ-XRF) and Zn-μ-X-ray Absorption Near Edge Structure (Zn-μ-XANES) spectroscopy.

Substantial Zn was accumulated by the plants (1390 mg Zn/kg), though there was no significant difference between ecotypes. Cadmium uptake, was significantly greater in the Ganges ecotype (750 mg Cd/kg) than the Prayon ecotype (90 mg Cd/kg). There was also greater Cd root-to-shoot translocation (root:shoot ratio = 0.13) than Zn (root:shoot ratio = 0.81). The Ganges ecotype took up significantly less Ca, which was also evident by the reduced rhizosphere Ca/Zn correlation in that ecotype. All rhizosphere soil regions investigated contained spectral features consistent with a combination of ZnS and ZnO, while bulk soil regions only occasionally contained such features. Inside the Ganges root, Zn speciation was most consistent with complexation by soft ligands (e.g. cysteine or histidine) while the Prayon roots contained Zn in a combination of mineral ZnO/Zn(OH)2-like forms and hard-ligand (e.g. organic acids) complexes.

Nutrient biogeochemical cycles are often linked to differential metal accumulation in plants, as nutrient acquisition may be enhanced or inhibited because of contaminant uptake. In our plants, increased Cd uptake was correlated with decreased Ca uptake, decreased Zn-Ca co-location, and altered Zn speciation. On a larger scale, shifting Zn complexation in roots and the rhizosphere may impact Zn bioavailability to other organisms and mobility within contaminated ecosystems.

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Particulate Organic Carbon Age Spectra: Evaluating Different Spectra from Different Basin Types

BRAD E. ROSENHEIM¹; VALIER GALY²; ELIZABETH K. WILLIAMS³; BRIAN J. ROBERTS⁴; MEAD A. ALLISON⁵; KATHRYN SCHREINER⁶ AND THOMAS S. BIANCHI⁷

¹Tulane University, brosenhe@tulane.edu
²Woods Hole Oceanographic Institution, vgaly@whoi.edu
³Tulane University, ewillia6@tulane.edu
⁴Louisiana Universities Marine Consortium, broberts@lumcon.edu
⁵The Water Institute and Tulane University, mallison@thewaterinstitute.org
⁶Northwestern University, kathryn.schreiner@northwestern.edu
⁷University of Florida, tbianchi@ufl.edu

We compare age spectra from a multi-year sampling effort on the Mississippi-Atchafalaya River System (MARS), in which several different discharge regimes were sampled, the Narayani River in Nepal, and the Colville River Delta, for application of ramped pyrolysis ¹⁴C analysis to samples from different basin types. The emerging picture from the MARS is one of consistency, with some variability related to flood provenance and discharge. Large river systems such as the MARS are integrative of a range of different lithologies and carbon sources. In contrast, the Narayani River, where high incision rates erode old carbonaceous rocks more efficiently during high discharge events, shows more variability and wider overall age spectra. Limited sedimentary storage of watershed primary productivity in the Narayani River watershed results in substantially wider age spectra than from the MARS system. It is likely that the Narayani River is less consistent in time than the MARS as contributions of old carbonaceous material are likely driven by discharge regime. We add to this comparison density-separated fractions from POC samples of the Arctic Colville River to further test a recent conceptual model of basin-control on POC age structure (Blair and Aller, 2012).

The fate and behaviour of volatiles during subduction of oceanic crustal material towards the deep mantle

A. ROSENTHAL¹* AND D.J. FROST¹

¹Bayerisches Geoinstitut, University of Bayreuth, 95440 Bayreuth, Germany (*correspondence: Anja.Rosenthal@Uni-Bayreuth.de)

Knowledge of the abundance and distribution of H₂O in the Earth’s deep interior (i.e. mantle and core) remains highly controversial.

The chief means of replenishment of the Earth’s interior with volatiles over much of geological time is subduction (i.e. the transport of crustal material into the deep Earth by large-scale tectonic processes) but constraints are very poor as natural samples from the deep Earth’s interior subduction zones are inaccessible. High pressure experimental investigations however can overcome that problem by simulating deep mantle conditions and processes.

The aim of this study is to experimentally determine the maximum storage capacity, solubility and behaviour of H₂O in hydrous and nominally anhydrous minerals (NAMs) during subduction of hydrated oceanic crustal material into the deep upper mantle. We apply a novel experimental approach, which will for the first time enable determination of maximum H₂O contents of NAMs (and hydrous phases) in equilibrium with the full phase assemblage in subducted oceanic crust. This was not achieved in numerous previous studies which concentrated on simple, monomineralic systems.

Here, we present first results of experimentally determined melting and phase relations of an altered oceanic basalt composition GA1 [1] containing varying amounts of water (<1 wt%) at varying temperatures (sub-solidus to near solidus) and pressures (6-9 GPa; i.e. ~200 to ~300 km depth) using multi anvil apparatuses at University of Bayreuth, Germany.

Outcomes will allow constraints to be placed on the fluxes of H₂O recycled into the mantle at subduction zones, a critical step in the Earth’s overall volatile budget.

Redox and pressure controls on iron isotope variations in MORBS determined by NRIXS spectroscopy


1*Unité Matériaux et Transformations, Université de Lille, mathieu.roskosz@univ-lille1.fr
2Origins Laboratory, The University of Chicago,
3Advanced Photon Source, Argonne National Laboratory
4Institut de Physique du Globe de Paris
5Centre de Recherches Pétrographiques et Géochimiques, Nancy
6Laboratoire Magmas et Volcans, Clermont Université.

Iron isotopic variations are commonly reported in materials produced in high temperature environments such as planetary mantles. However, a reliable database of equilibrium fractionation factors between melts and igneous minerals is still lacking to interpret the rock record. In the case of iron, these factors can be directly derived from Nuclear Resonant Inelastic X-ray Scattering (NRIXS) experiments at a synchrotron facility [1, 2] through the determination of mean force constants. This method is insensitive to kinetic effects during mineral and glass synthesis, contrasting with conventional experimental approaches [3].

Because iron is a multivalent element, its isotopes could be good tracers of redox conditions during melting [4, 5]. To establish Fe isotope systematics as a redox proxy, we used NRIXS to measure mean force constants of synthetic 57Fe-labelled olivine and silicate glasses synthesized at different pressures with and without dissolved oxygen fugacities in a gas mixing furnace and in piston cylinders at different pressures with and without dissolved water.

At a given Fe3+/Fe2+ ratio, the force constants of tholeitic to andesitic glasses are almost identical. For all samples, the force constant increases linearly with Fe3+/Fetot. The effect of pressure and water content is moderate. Thus, for mafic melts, there is little structural control; redox effects seem to be good tracers of redox conditions during melting [4, 5]. To establish Fe isotope systematics as a redox proxy, we used NRIXS to measure mean force constants of synthetic 57Fe-labelled olivine and silicate glasses synthesized at different pressures with and without dissolved water.

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Approaching real uncertainty estimates for δ11B data

MARTIN ROSNER1 AND JOCHEN VOGL 2
1IsoAnalysis UG, martin.rosner@isoanalysis.de
2BAM Ferderal Institute of Materials and Testing, jochen.vogl@bam.de

The measurement uncertainty is an indispensable quality criterion of isotope ratio data and sets important limits for the general use and geochemical interpretation of such data. Despite traceability to the International System of Units (SI) or an accepted standard an uncertainty statement allows the direct comparison of isotope data which have been obtained in different laboratories and/or using different procedures. To realise traceability and comparability of isotope data a realistic uncertainty statements should include uncertainty contributions from all influence quantities. In isotope geochemistry, however, often the term uncertainty is used for terms describing the statistical dispersion of measurement results such as precision, repeatability or reproducibility. Because an measurement uncertainty must include all influence quantities even the so-called external precision or reproducibility will underestimate the overall uncertainty.

Without uncertainty statement traceability and comparability of measurement results cannot be established. In cases where no uncertainty for isotope ratio data is presented it is highly recommended that at least the measurement results of a quality control sample with known isotope composition are presented which can be used to evaluate the accuracy and roughly estimate uncertainty.

Here we present an approach to calculate uncertainty budgets for δ11B data which can easily be used for other δ-values. Our approach considers uncertainty components from the mass spectrometric isotope ratio determination (repeatability and reproducibility), the chemical preparation (contamination, isotope fractionation) and the isotope reference material (or δ-zero material). Having quantified the single uncertainty components the identification of the most important contributors to the overall uncertainty is possible and strategies to improve the measurement uncertainty can be investigated. The here presented expanded uncertainties for δ11B values between 1.2 and 0.4 ‰ of matrix standards (IAEA B1-3) and processed isotope reference materials (NIIST SRM 951, ERM-AE101) show that typically intense sample preparation is the biggest uncertainty contributor. Uncertainties derived from unprocessed reference materials or standards will therefore significantly underestimate the uncertainty of real samples.
Effect of Fluid Salinity on Subcritical Crack Propagation in Calcite

ROSTOM F, ROYNE A, DYSTHE D AND RENARD F
fatma.rostom@ens-lyon.fr

The slow propagation of cracks, also called subcritical crack growth, is a mechanism of fracturing responsible for a ductile deformation of rocks under crustal conditions. In the present study, the double-torsion technique was used to measure the effect of fluid chemistry on the slow propagation of cracks in calcite single crystals at room temperature. Time-lapse images and measurements of force and load-point displacement allowed accurate characterization of crack velocities in a range of $10^{-8}$ to $10^{-4}$ m/s. Velocity curves as a function of energy-release rates were obtained for different fluid compositions, varying NH$_4$Cl and NaCl concentrations. Our results show the presence of a threshold in fluid composition, separating two regimes: weakening conditions where the crack propagation is favored, and strengthening conditions where crack propagation slows down. We suggest that electrostatic surface forces that modify the repulsion forces between the two surfaces of the crack may be responsible for this behavior.

Halogens in the early Solar System inferred from meteoritic phosphates

J. ROSZJAR1*, T. JOHN2, M. J. WHITEHOUSE3, A. BISCHOFF4 and G. D. LAYNE5

1Institut für Geowissenschaften, FSU Jena, Germany
*(correspondence: julia.walter-roszjar@uni-jena.de)
2Insitut für Mineralogie, WWU Münster, Germany
3Swedish Museum of Natural History, Stockholm, Sweden
4Institut für Planetologie, WWU Münster, Germany
5Department of Earth Sciences, Memorial University, St. John’s, NL Canada

Although F, Cl, Br, and I are relatively abundant elements in the Solar System, their distribution, abundances and the related fractionation processes in early formed meteoritic material is poorly constrained. Owing to different condensation temperatures, the halogens each have different volatility, which makes them suitable for constraining early Solar System processes such as degassing and fluid-rock interactions. The halogen budget of individual meteorite samples appears dominantly controlled by apatite, which preferentially incorporates halogens. However, merrillite, if present, also contributes to the bulk halogen budget. Although these phases are accessory rock components, they are widely distributed among meteorite classes. Fluorine, Cl, Br, and I concentrations together with the stable Cl isotope composition of individual apatite and merrillite grains were determined in ordinary (OC) and Rumuruti chondrites (RC), primitive acondhrites (PA), eucrites (EUC), and silicate-bearing IAB iron meteorites. Petrography and chemistry of phosphate grains were determined using SEM and EPMA. Halogen concentrations and stable $^37$Cl values were determined using a Cameca IMS 1280. $^37$Cl values of most meteorite groups are in the range of $-0.05\pm1.20$ ‰ ($2\sigma$), consistent with results from [1], but with an evolutionary trend from chondritic to more evolved differentiated rocks. The EUC apatite is in the range of $-4.49\pm0.33$ ‰ to $+11.93\pm0.33$ ‰, similar only to the Moon. For the latter dry fractionation processes were discussed [2]. Thus, the EUC parent body was either as dry as the Moon, or other mechanisms such as metasomatism [3] may fractionate the Cl isotopes. The same evolutionary trend is seen for halogen concentrations, which are dominated by Cl- and Br-rich apatite in OC, and IAB irons, and F- and I-enriched EUC apatite, with PA being intermediate. Compared to apatite, merrillite halogen concentrations are an order of magnitude lower, with limited Cl variation, except for EUC, consistent with a parent body halogen fractionation process.

Evidence for volatiles on Mercury

D. A. ROTHERY1*, R. J. THOMAS1 AND L. KERBER2

1Dept of Physical Sciences, The Open University, Milton Keynes, MK7 6AA, UK
(*correspondence: d.a.rothery@open.ac.uk)
2Laboratoire de Météorologie Dynamique du CNRS, Université Paris 6, Paris, France

Several independent lines of evidence provided by MESSENGER suggest that Mercury is surprisingly rich in volatiles: (i) Gamma-ray spectroscopy reveals a high K/Th ratio in its surface regolith similar to Mars, and very much higher than the Moon [1]. (ii) Xray spectroscopy reveals 2-5% S in its surface regolith [2]. (iii) It has recognisable pyroclastic deposits around vents, requiring explosive exsolution of an unknown magmatic volatile phase in the range 3600-13,000 ppm [3]. (iv) It exhibits patches of steep-sided, flat-bottomed ‘hollows’ (10s of m deep and 100s of m to km wide) associated with a spectrally distinct (blue, high albedo) unit that appear to form by sublimation, or some similar process capable of dispersing material to space [4]. (v) Neutron spectrometer measurements [5] show a hydrogen-rich phase, interpreted as water-ice, within permanently-shadowed polar craters [6].

Polar-ice (v) is probably cold-trapped from on-going cometary impacts, but (i)-(iv) are likely to reflect volatiles intrinsic to Mercury. It has been argued [7] that (i) and (ii) could result from low oxygen fugacity affecting geochemical affinities rather than demonstrating volatile-richness on a volumetric planetary scale. Nevertheless it is clear from study of volcanic vent architecture, pyroclastic deposits and hollows that migration of volatile phases from the interior to and through the surface plays a major role in sculpting Mercury’s surface. We look forward to enhanced insights when Bepi Colombo achieves orbit.


Heavy noble gases in type 3 enstatite chondrites. Implications for the Earth primordial signature and its evolution.

C. ROUBINET* AND M. MOREIRA1

1IPGP 1, rue Jussieu 75005 Paris (*correspondence : roubinet@ipgp.fr) (moreira@ipgp.fr)

Enstatite chondrites have often been proposed as possible building rocks of telluric planets and in particular of the Earth [1]. This hypothesis is based firstly on the coincidence of their respective formation zone (inner part of solar system [2]) and also on the similarity of their isotopic composition (O, N, Ni, Mo, Ru, Os, 53-54Cr…) [1]. Moreover, enstatite chondrites of type 3 in particular are the only chondrites to display close 142Nd/144Nd ratio to Earth [3]. Thus their study may bring information about primordial composition of the Earth concerning noble gases.

Analysis of E3s by mass spectrometry coupled to stepwise heating allows us to highlight that their primordial composition for Xe and Kr is related to phase Q. So, regarding the ubiquity of this phase, its resistance to high temperatures and also its high noble gases content, it seems appropriate to consider it is the most likely primordial signature of the Earth.

We will discuss the possibility of a terrestrial evolution starting with a phase Q composition, as nowadays, Earth’s mantle and atmosphere don’t display the same isotopic signature. This discrepancy can be due first to fractionation during accretion process as it has been suggested for Nd [4]) or to post-accretionnal processes like partial loss of primary atmosphere [5] and also noble gases subduction which can have modified in the long run mantle’s signature [6].

Decoupling of the sub-basinal CO₂ and He mantle fluxes as evidenced by intense CO₂/³He fractionation of natural gases from Brazilian south Atlantic margin basins

VIRGILE ROUCHON¹, EUGENIO VAZ DOS SANTOS NETO², AND ERICA TAVARES DE MORAIS²

¹IFP Energies Nouvelles, Rueil-Malmaison, France. virgile.rouchon@ifpen.fr
²PETROBRAS R&D Center, Rio de Janeiro, Brazil

Fluxes of mantle CO₂ in sedimentary basins are of present concern regarding deep basin oil and gas exploration. Such degassing of the mantle, although of lower amplitude than that of MOR and convergent margin magmatism, has some influence on the global carbon cycling and on the carbon mass balance of sedimentary basins.

Nearly 150 samples of various basins of the Brazilian Atlantic margin have been analyzed for their molecular composition, stable isotopic ratios of carbon, hydrogen and of the nobles gases (³He/⁴He, ⁴⁰Ar/³⁶Ar). The gases analyzed show a full compositional range corresponding to the mixing of thermogenic gas (average ¹³CCH₄-PDB = -39‰) with inorganic CO₂ (average ¹³CCO₂-PDB = -5.5‰), with CO₂ contents from 0.1 up to 78%. The ³He/⁴He ratio shows a consistent increase with the CO₂ concentration from 3.4e⁻⁷ up to 8.9e⁻⁶. The CO₂/³He ratio of the richest CO₂ samples is reaching that of MORB between 1.2-1.6e⁹. A decreasing trend in the CO₂/³He ratio defined by the whole sample set correlates with decreasing ³He/⁴He ratio and CO₂ abundance. The data support a large scale loss of CO₂ (of up to 99%) from an initial mantle fluid during its ascent towards the surface, in addition to mixing of this fractionated fluid with thermogenic gases from within the basins.

The potential loci and processes of this fractionation are discussed along with their consequence for the relative fluxes of mantle C and He to sedimentary basins.

Interactions of Arsenic and Chromium with Struvite During Mineralization

ASHAKI A. ROUFF* AND NING MA

School of Earth and Environmental Sciences, Queens College, CUNY, Queens NY 11367, USA
The Graduate Center, CUNY, 365 Fifth Ave., New York, NY 10016, USA
(*correspondence:Ashaki.Rouff@qc.cuny.edu)

Struvite (MgNH₄PO₄·6H₂O, MAP) recovered from wastes may be a viable alternative to phosphate fertilizers [1]. However, the potential for sorption of trace elements in wastes with struvite has not been fully addressed. This study evaluates the sorption of arsenic (As) and chromium (Cr) with struvite as impacted by oxidation state, pH and initial solution concentration [2, 3]. The As content of struvite precipitated in the presence of As(V) as AsO₄³⁻ and As(III) as AsO₃³⁻ increased with pH from 8-11. Struvite recovered from As(V) solutions had As concentrations greater than fertilizer limits over the entire pH range. X-ray absorption fine structure (XAFS) analysis revealed that As(V) was coprecipitated into the struvite structure, and that As(III) was adsorbed to the mineral surface. Oxidation state also dictated Cr sorption with struvite precipitated in the presence of Cr(III) as Cr³⁺ and Cr(VI) as CrO₄²⁻ at concentrations of 1-100 µM. Less Cr was associated with struvite recovered from Cr(VI) solutions compared to Cr(III) solutions over the range of concentrations. For struvite formed in the presence of Cr(III), XAFS confirmed the formation of adsorbates at low initial Cr concentrations, with surface precipitates dominating at higher solution concentrations. Where surface precipitates were detected, the Cr content of struvite exceeded the limit for fertilizers. Fourier transform infrared analysis (FT-IR) suggested that Cr(Ⅵ) may be adsorbed and/or coprecipitated with struvite. The extent and mechanisms of sorption for As and Cr have implications for the use of struvite as a fertilizer. Coprecipitated As(V) and precipitated Cr(Ⅲ) are likely to be delivered to agricultural soils along with struvite, introducing contamination to soils and plants. Conversely, low concentrations of As(Ⅲ) and Cr(Ⅵ) pose less of a risk, and adsorbates may be removed from the struvite surface prior to application.

A 30ka Sponge-Diatom Silicon Isotope Record of Dissolved Silicon Concentration in Subantarctic Mode Water

J. ROYSEAU1*, M.J. ELLWOOD1, H. BOSTOCK2, H. NEIL2, AND S. FALLON1

1Research School of Earth Sciences, Australian National University, Canberra, Australia (*correspondence: u4406548@anu.edu.au)
2National Institute of Water and Atmospheric Research, Wellington, New Zealand

Here we present silicon isotope records for biogenic sponge (δ30Si_sponge) and diatom (δ30Si_diatom) silica from Southern Ocean sediments. For two cores located in Subantarctic Mode Waters (SAMW) on the Campbell Plateau, NZ, we observe a decrease in δ30Si_sponge values from the late Holocene through to the mid-deglacial period. From the mid-deglacial δ30Si_sponge values increase through to the LGM. δ30Si_sponge results for a core located within Antarctic Intermediate Waters (AAIW) generally follow the same trend during the Holocene, but are consistently and expectedly more negative than the shallower SAMW values. During the deglacial period the difference between Intermediate Water and Mode Water depth δ30Si_sponge is variable within the Subantarctic Zone during this time. A diatom silicon isotope record (δ30Si_diatom) from the Macquarie Ridge, located further south and upstream of the sponge records, suggests a similar degree of silicon utilisation between the Holocene and the LGM and higher utilisation for a short period during the deglacial.

Modelling dissolved Silicon concentration ([DSi]) in SAMW from a comparison of the Macquarie Ridge δ30Si_diatom and Campbell Plateau δ30Si_sponge records we find that [DSi] in SAMW may have been 100-150% higher in the LGM compared to the Holocene, which is consistent with the Silicic Acid Leakage Hypothesis. This prediction however is not corroborated by a model using a more distal Indian Ocean δ30Si_diatom record for the comparison, pointing towards significant regional differences in SO Silicon dynamics over this period.

Dynamics of chemical characteristics of solubilized organic matter in wetland soils under aerobic or anaerobic conditions.

ASMAA ROUWANE, ISABELLE BOUVEN, MARION RABIET, GILLES GUIBAUD AND MALGORZATA GRYBOS
Groupe de Recherche Eau-Sol-Environnement, Université de Limoges, 123 av. A. Thomas, Limoges, 87060, France.

Soil organic matter plays an important role in the release and potential transport of metal(loid)s. Wetlands are a large terrestrial carbon pool, thus understanding the chemical quality of dissolved organic matter (DOM) in wetland soils is crucial.

Controlled incubations of a wetland soil (Roselle catchment, France) were carried out under aerobic and anaerobic conditions (simulating temporarily and permanently flooded soil). Solubilized organic matter was quantified and characterized. Anaerobic incubation involved strong releases of dissolved organic carbon (DOC) to the soil solution (2 mg of C per g of soil), which was correlated with an increase of solution pH (from 6.0 to 7.3) and Fe reduction. In contrast, aerobic incubation (preventing soil reduction) at pH 6.0 induced a smaller DOM release (0.8 mg of C per g of soil). Released DOM under both experimental conditions had an increasing trend in aromaticity with incubation time. Indeed after 500 h of anaerobic incubation, DOM exhibited aromaticity of 60% whereas the aromaticity of DOM released in aerobic experiment was 40%. Using size exclusion chromatography coupled to UV and fluorescence detection, three main size fractions (labeled i, ii, iii) of released DOM were identified. The first fraction (i) with an apparent molecular weight (aMW) >10kDa was constituted of protein-like compounds and had a disappearance trend with incubation time. The second fraction (ii) with an aMW from 1kDa up to 10kDa, exhibited aromatic characters and was composed of a mixture of protein-like and humic substances-like compounds. The fraction (ii) had an increasing trend with incubation time whatever experimental conditions.

In conclusion, evolution of DOM solubilization in reduced wetland soils comparing to DOM released under aerobic conditions is different in terms of chemical characteristics and of MW distribution.

1Frimmel and Huber, 1996; 2Grybos et al., 2009; *calculated according to Weishaar et al., 2003
Non-traditional Stable Isotope Systematics of Seafloor Hydrothermal Systems

OLIVIER ROUXEL¹

¹IFREMER, Centre de Brest, 29280 Plouzané, France

Seafloor hydrothermal activity at mid-ocean ridges is one of the fundamental processes controlling the chemistry of the oceans and the altered oceanic crust. Past studies have demonstrated the complexity and diversity of seafloor hydrothermal systems and have highlighted the importance of water-rock reactions and subsurface environments in controlling the composition of hydrothermal fluids and mineralization types. In addition, the far-field consequences of hydrothermal venting on deep oceanic metal reservoirs, in comparison to other marine sources, is just starting to be recognized.

Isotope ratios of various metals and metalloids, such as Fe, Cu, Zn, Ge, Se, Cd and Sb have recently provided new approaches for the study of seafloor hydrothermal systems. Here, I will present new results of non-traditional isotope systematics of seafloor hydrothermal systems, in particular:

1. The mechanisms of metal isotope fractionation in hydrothermal chimney environments through paired isotopic analysis of mono-mineralic sulfides in contact with hydrothermal fluid;
2. The controlling parameters of metal isotope signatures of hydrothermal vent fluids through the study of mid-oceanic and back-arc hydrothermal vent fields, spanning wide ranges of pH, temperature, metal concentrations and contributions of magmatic fluids enriched in SO2;
3. The potential role of high-temperature seafloor venting in affecting deep sea metal isotope composition through the investigation of metal isotope systematics in hydrothermal plume.

Ultimately, the use of complementary stable isotope systems should help identify the complex interactions between fluids, minerals, and potentially organisms in seafloor hydrothermal systems and constrain metal sources in marine environments.

Mineral and Melt Inclusion Geochemistry of the Nea Kameni Dacites, Santorini, Greece

ROWE, M.C.¹, ELLIS, B.S.² AND KYRIAKOPOULOS, K.³

¹University of Auckland, School of Environment, Auckland, New Zealand. Michael.rowe@auckland.ac.nz
²ETH Zurich, Institute for Petrology and Geochemistry, Zurich, Switzerland. Ben.ellis@erdw.ethz.ch
³Department of Geology and Geoenvironment, National and Kapodistrian University of Athens, Athens, Greece. ckiriako@geol.uoa.gr

Since the voluminous 3.6 ka Minoan eruption, the Santorini volcano has been periodically erupting small volumes of dacitic magma forming the Kameni islands. This study focuses on variations in mineral geochemistry of lavas spanning from 46-47AD to 1950 to better understand the temporal evolution of silicic magmatism at the Santorini volcano. In addition to feldspar geochemistry, this study utilizes silicate melt inclusion analyses to document melt compositions associated with different feldspar populations. On a bulk level, the dacites of Nea Kameni have remained compositionally homogeneous while containing a mixture of mafic grains and crystal clots. The Kameni dacites contain two populations of feldspar, one An38-65 interpreted as crystallising from the dacitic liquid and a second An86-94 derived from a mafic magma. The two feldspar populations are distinct in terms of 87Sr/86Sr as determined via LA-ICPMS with the higher anorthite plagioclase having higher 87Sr/86Sr. The same two isotopic populations appear to be contributing to the Kameni magmatic system for the past 1900 years.

Analysis of glassy melt inclusions from the 1940 eruption preserve a similar bimodal distribution of glass compositions consistent with host compositions. Interestingly, despite their assumed cumulate nature, high-An feldspars retain euhedral, undegassed glassy melt inclusions. High-An plagioclase contain mafic melt inclusions whereas the lower An plagioclase contains melt inclusions more similar to the groundmass glass. Pre-eruptive volatiles (S, Cl, H2O) are maintained in both populations of melt inclusions.

The 87Sr/86Sr data indicate that the dacitic magmas cannot represent fractionated equivalents of the mafic input to the Kameni system (similar to the Minoan eruption). The presence of abundant glassy clasts of dacite as lithics within the Minoan deposits suggests that prior to the last catastrophic eruption a similar period of relative quiescence may have occurred. Kameni-style volcanism may be a common occurrence at Santorini, just with low preservation potential.
**Distribution of $^{230}$Th and $^{232}$Th along the Bonus GoodHope section in the SouthEast Atlantic Ocean**

M. ROY-BARMAN1, S. MARCHANDISE1, F. THIL1, LOUISE BORDIER1, SOPHIE AYRAULT1, E. GARCIA-SOLSANA2 AND C. JEANDEL2

1Laboratoire des Sciences du Climat et de l’Environnement, France. (*correspondence: Matthieu.Roy Barman@lsce.ipsl.fr)
2Laboratoire d’Etudes en Géophysique et Oceanographie Spatiale, France.

Dissolved concentrations of $^{230}$Th and $^{232}$Th have been measured in seawater on 5 profiles along the Bonus GoodHope (GEOTRACES/IPY) section in the SouthEast Atlantic Ocean.

Most dissolved $^{232}$Th concentrations range from 5 to 98 pg•kg$^{-1}$. There is a general increase of the $^{232}$Th concentration from the surface to the deep waters. A strong $^{232}$Th gradient exists between the stations located off the African continents (where strong $^{232}$Th inputs occur) and the stations located in the middle of the section. A distinctly high $^{232}$Th concentration of 283 pg•kg$^{-1}$ is found at the bottom of the station closest to the African coast, likely linked to an input from the sediment.

Dissolved $^{230}$Th concentrations range from 0.7 to 36.4 fg•kg$^{-1}$. The $^{230}$Th data of the Bonus GoodHope section compare well with the $^{230}$Th data of ANT III section obtained near the Polar Front [1]. There is a general increase of the $^{230}$Th concentration with depth. In the Cape basin, concentrations increase linearly, with a lower scavenging rate north of the subtropical front than south of it. At the Polar front level, a distinctly low $^{230}$Th concentration is found in the deepest sample (9 fg•kg$^{-1}$ at 4300 m against 15 fg•kg$^{-1}$ at 3048 m) suggesting occurrence of boundary scavenging. South of the Polar Front, upwelling of deep waters create non linear profiles.

Particulate samples collected with in situ pumps are under process for the determination of $^{230}$Th and $^{232}$Th.


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**Dissimilatory Sulfate Reduction in Hypersaline Environments: What is regulating sulfate uptake?**

A.N. ROYCHOUDHURY1* AND D.PORTER2

1Dept. of Earth Sciences, Stellenbosch University, Stellenbosch 7602, South Africa (*correspondence: roy@sun.ac.za)
2Department of Genetics, University of Pretoria, Pretoria, South Africa

Microbes in engineered systems such as wastewater treatment facilities and mine tailings are often subjected to extremes of salinities. Little is known; however, about the activity and survival mechanisms of sulfate reducers in such extreme environments. Hypersaline pans, a prototype for engineered systems, are used here to understand sulfate uptake and regulatory mechanisms among sulfate reducers.

Thermodynamic and kinetic parameters for dissimilatory sulfate reduction (DSR) were quantified in five hypersaline coastal salt pans located in South Africa. Compared to normal marine environments, salinity and sulfate concentration at the studied salt pans was higher by up to 10 and 20 times, respectively. Determined apparent activation energies (28 – 62 kJ/mol) and Q$_{10}$ values (2.0 – 2.3) for DSR suggest no gross physiological adaptations in bacteria, such as changes in membrane structure, to temperature.

Sulfate uptake affinity, quantified in terms of apparent half-saturation concentration ($K_s$); however, indicates adaptation with respect to high ionic status of the salt pans. The $K_s$ values (64 – 780 mM) for sulfate reduction determined for the first time from hypersaline environments are two to three orders of magnitude larger than those determined for normal marine ecosystems. This indicates that in hypersaline environments there exists a third transport mechanism, which attenuates even the low-affinity system observed among marine sulfate reducers. We propose that the observed extremely low-affinity, high accumulation system is a consequence of increased regulation of sulfate uptake and accumulation because of adaptation mechanisms employed by halophiles to survive under extremes of salinity.
Redox chemistry profiling in the Kara sea sediments (from the Ob'-river to the Saint Anna trench)

ALEXANDER ROZANOV
P.P. Shirshov Institute of Oceanology, Nakhimovsky prosp.
Moscow. 117997. e-mail: rozanov@ocean.ru

Submeridional redox profile across the bottom sediments of the Kara sea from the Ob' river (71 N) to the St. Anna trench (77 N) was studied in the course of the Russian expedition on the R/V «Akademik Mstislav Keldysh» in September 2007. Redox profile is formed under the influence of diagenetic reactions in sediments with organic matter (OM), produced into the sea and brought from the shore. The OM, which is a fundamental characteristic of sediments, is more than 1.5% (dw) in the Ol' delta (71 N), close to 1% in the estuary (72 N), 0.5-0.75% in the sediments of inner and outer shelf (72-75 N), as well as in the slope (75-76 N), 2% in the sediments of the of the St. Anna trench (77 N). OM in the deltaic part is mainly terrigenous, in the northern part of the profile the cause of increased OM content is the primary production of plankton. On the border of the estuary and the shelf there is a sharp decrease of suspended matter in the surface waters (from 7 to 1 mg/l), the Corg and many metals of the river runoff in the sediments reach maximum values (Mn 0.3%, Fe 7% dw). The growth of OM stimulates the reduction processes, as reflected in higher concentrations of the dissolved components in the pore water (Mn2+ up to 260, Fe2+ to 100 uM) and derivatives of H2S (up to 0.3 %) in the sediments. Dissolved Mn remove from the sediments to the bottom water, dissolved Fe is oxidized by oxygen of the bottom water and forms a thin oxidized layer on the surface. Recycling of Mn and Fe is accompanied by formation of ferromanganese nodules. Sedimentation in central and northern part of the profile, adjacent to the St. Anna trench are characterized by lower content of Mn due to both long distance from the river outflow and diagenetic removal of Mn from the sediments of higher Corg content. In this part of the profile derivatives of H2S are mainly represented by organic forms, which are very typical for Arctic sediments in contrast to the bottom sediments of the temperate and tropical zones, in which among H2S-forms prevails diagenetic pyrite.

Effects of lead and strontium on radium uptake by barite: Atomistic simulations and thermodynamic assessment

K. ROZOV1, V. L. VINOGRAD1,2,*, D. A. KULIK3, F. BRANDT1, B. WINKLER2 AND D. BOSBACH1

1Institute of Energy and Climate Research (IEK-6), Forschungszentrum Jülich, Germany
2Institute of Geosciences, Goethe University, Frankfurt, Germany (*correspondence: v.vinograd@fz-juelich.de)
3Nuclear Energy and Safety Research Department, Paul Scherrer Institute, Villigen, Switzerland

Experimental studies related to safety issues of the long-term disposal of spent nuclear fuel in deep geologic formations suggest that Ra released from the fuel can be efficiently immobilized as a constituent of a barite-rich solid solution (SS) [1,2]. Here the uptake of Ra by barite is investigated using the Gibbs free energy minimization method [3] at variable fractions of PbSO4 and SrSO4 in the SS. The SSs were modelled as ternary (Ba,Sr/Pb,Ra)SO4 regular mixtures. The mixing parameters (Wba= 5.4, Wpba = 1.5, Wsr= 2.5, Wsr = 8.9, Wsr = 19.6, Wsr = 0.3 kJ/mol) were computed from first principles with the aid of the single defect method [4]. The system contained 0.00214 moles of Ba1-x(Sr,Pb)xSO4, 0.1 m of NaCl, 5.0·10-6 m of RaCl2 and 1 kg of H2O. The concentration of Ra(aq) decreases with the corresponding increase in the mole fraction of RaSO4 in barite. This effect is suppressed by the decomposition of the SS in Ba- and Sr-rich phases; the concentration of Ra(aq) remains less than that in the Sr-free system up to the Sr/Ba ratio of ~10. Therefore, at certain conditions, an admixture of PbSO4 or SrSO4 in barite would lead to a more efficient immobilization of Ra. The study is funded by BMBF-IMMORAD project through the grant 02NUK019E.


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Fracture propagation driven by crystal growth and the role of interfacial fluid chemistry

A. ROYNE1*, P. MEAKIN12, A. MALTHE-SØRENSSSEN1, B. JAMTVEIT1 AND D.K. DYSTHE1

1Physics of Geological Processes (PGP), University of Oslo
(*correspondence: anja.royne@fys.uio.no)
2Carbon Resource Management Department, Idaho National Laboratory

Crystals that grow confined in pores and cracks may exert a force on their surroundings and thereby drive crack propagation in rocks and other materials. Of particular importance for engineering and cultural heritage is the degradation of building stones due to salt crystallization. The opening of fractures due to crystal growth may also open new pathways for transport of reactive fluids and therefore serve to accelerate the rate of advancement of weathering or replacement fronts.

In order for a growing crystal to actively displace the walls of the confining pore, there must be a liquid film present between the crystal face and the surface of the pore. This film acts as the transport pathway for growth units to the crystal face. The normal stress between the crystal face and the confining wall is transmitted through the disjoining pressure in the liquid film, and the maximum stress which can be exerted is determined by the fluid chemistry and surface properties. The same confined fluid is also present at the crack tip, where it plays a large role in determining the fracture threshold and velocity at low tensile stresses [1,2].

We use a theoretical model of crystal growth in an idealized crack geometry to study how the kinetics of crystal growth and crack propagation are coupled through the confined fluid and the stress in the surrounding bulk solid [3]. The rate of initial crack propagation is found to be limited by subcritical crack growth, while crystal growth becomes the rate limiting step when the crack has grown to sufficient length. The cross-over length is determined by crystal and crack tip kinetics, fluid supersaturation and elastic properties of the surrounding material.


Integration of U-Pb dating, trace elements and oxygen isotopes at the microscale

DANIELA RUBATTO1, LAURE GAUTHIEZ-PUTALLAZ1, AND KATHERINE BOSTON1

1Research School of Earth Sciences, Australian National University, 0200 Canberra, Australia.
Daniela.Rubatto@anu.edu.au

The U-Pb chronology of metamorphic events has greatly benefited from the high spatial resolution achievable with microbeam techniques that allows to date individual growth zones in accessory phases. The capability to retrieve trace elements and isotopic information at the same scale has allowed relating ages to metamorphic processes. With the newly developed capacity to analyse oxygen isotopes at the same scale as U-Pb ages, the application of this method to metamorphic fluid-rock interaction is particularly exciting.

The robustness of zircon makes it a prime candidate for retrieving the oxygen composition of pre-metamorphic history. Zircon in high pressure rocks of the Western Alps show different degrees of metamorphic recrystallization. Their age and oxygen composition constrain the timing of fluid circulation and offer insight into its origin and degree of fluid-rock interaction.

Monazite is particularly promising as monitor and timer of fluid-rock interaction as experimental and field studies have shown that monazite readily recrystallizes in the presence of fluids. Analytical protocols and standards have been developed for in-situ oxygen analysis of monazite using the SHRIMP ion microprobe. Accurate measurements require an additional correction for matrix effect due to the variable composition of monazite. This effect is found to be proportional to the Th content of monazite and produces a shift of circa in $^{18}O$ of 1‰ every 10 wt% of Th. Oxygen isotopes combined with trace element analysis to relate monazite to major mineral offer new opportunities for monazite geochronology in metamorphic rocks.

Allanite preserves multiple growth zones and retains its U-Pb age up to temperatures of at least 700°C. Geochronology of allanite requires adequate corrections for initial Pb composition, particularly for metamorphic domains formed in sub-solidus conditions. For ion microprobe data, robust results are obtained with Th-Pb isochrons. Even in allanite with high amounts of initial Pb (60-95%) isochrons return reasonably accurate and robust ages. Oxygen isotope analysis of allanite is still hampered by significant matrix effects for which a correction scheme is work in progress.
Icarus et al. [1] Raymond (2009) massive and too oxidized. the outer regions of the planetesimal disk and is thus too inner planet (“Mercury”) that accretes too much material from However, the current Grand Tack simulations result in an reduced and those forming further out are more oxidized. originate in the inner solar system (< ~1.6 AU) are highly reproduced well when the compositions of bodies that resembling those of the solar system are tested. Model Accretion simulations that produce synthetic planets closely the validity of the Grand Tack and other accretion models. Accretion occurs through impacts between growing planets and smaller bodies. Each impact delivers energy (magma ocean formation) and metal and thus an episode of core formation. The chemical evolution of the mantles and cores of growing bodies is modeled on the bulk composition of the accreting material combined with a mass balance/element partitioning approach [4]. The main constraint is the composition of Earth’s primitive mantle and the FeO contents of the mantles of Mercury and Mars (3-4 wt% and ~18 wt% respectively). Bulk composition is defined in terms of solar system (CI) relative abundances of the non-volatile elements with an oxygen content that determines the metal-silicate ratio. Accretion simulations that produce synthetic planets closely resembling those of the solar system are tested. Model parameters (metal-silicate equilibration pressure, starting compositions of embryos and planetesimals) are refined by a least squares regression in order to produce a synthetic Earth that matches Earth’s mantle chemistry.

The mantle chemistries of Earth and Mars can be reproduced well when the compositions of bodies that originate in the inner solar system (<=1.6 AU) are highly reduced and those forming further out are more oxidized. However, the current Grand Tack simulations result in an inner planet (“Mercury”) that accretes too much material from the outer regions of the planetesimal disk and is thus too massive and too oxidized.


Timescale and petrogenesis of 2009 and older W. Mata boninite magmas


1 GG Dept., Univ. of Hawaii, Honolulu, HI 96822 USA (*correspondence: krubin@hawaii.edu)
2 The Univ. of Tulsa, Tulsa, OK
3 Earth and Planetary Sciences, UCSC
4 MBARI, 7700 Sandholdt Road, Moss Landing, CA
5 LDEO and Columbia University, Palisades, NY
6 Harvard University, Cambridge, MA, USA
7 WHOI, Woods Hole, MA, USA
8 GSO, Univ. Rhode Island, Narragansett, RI
9 NMNH, Smithsonian Institution, Washington DC
10 RSES, Australian National University, Canberra
11 PMEL, NOAA-Vents, Newport, OR
12 JISAO, NOAA-Vents, Univ. Washington, Seattle, WA

The first active boninite eruption was observed by ROV in 2009 at West Mata, a small, submarine rear-arc volcano in the NE Lau Basin. Globally, boninite is a rarely erupted, arc-fluid-enriched magma. We examine rates and processes of W. Mata boninite generation, ascent, and storage, with implications for arc magma and volatile source-to-surface transport. A number of characteristics indicate magma differentiation during rapid ascent from the mantle within a poorly developed magma storage system: large, very short-lived 210Pb-226Ra disequilibria of 20-40% in glasses, Ni diffusion profiles in olivine, and a complex range of mineral textures, including rapid crystal growth and magma reactions. Geochemical and petrological studies of fresh-appearing lavas collected in 2009 and on two subsequent cruises indicate limited lithological variability throughout the volcano. W. Mata erupts a highly vesicular, crystal-rich (ca 40%) magma, having opx>>cpx>ol and a continuum of mineral compositions (e.g., opx and ol Mg# 92-82). Whole rocks (WR) are boninite sensu strictu but have more evolved coexisting glass (WR and glass have MgO=11-15 and 3-5-6.5 wt%, SiO2=54-57 and 55-58 wt%, TiO2=0.3-0.45 and 0.4-0.6 wt%). Older, non-summit lavas define distinct but similar major element trends, with variable radiogenic isotope and trace element ratios. Slab influence is indicated by glasses with extreme 238U/235Th disequilibria (40% excess U), high Fe oxidation (Fe3+/Fe2+<0.2-0.25), strong fluid-mobile element enrichments (Ba and U to 160 ppm and 0.4 ppm), high CI/K, plus up to 3 wt% H2O in melt inclusions.

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Itrax™ Core Scanner as a quick screening tool for polluted coastal sediments

B. RUBIO *, D. REY, I. RODRÍGUEZ-GERMADE, P. ÁLVAREZ-IGLESIAS AND A.M. BERNABEU

Research group GEOMA. Departamento de Geociencias Marinas y Ordenación del Territorio, Universidad de Vigo, Vigo (Spain).
*Correspondence: brubio@uvigo.es

The traditional techniques for the study of chemical composition of sediment cores, are, among others, the X-ray fluorescence (XRF) and the spectrometry (ICP) applied on discrete samples. The development of non-destructive continuous analysis as the XRF scanners as the Itrax™ core scanner [1], which analyses humid core-sections with a millimetric resolution, have supposed a great advance in the study of sediments and rocks. These instruments are able to detect the majority of the elements from the Al to the U, in a low concentration, depending on the acquisition conditions. Until now, the majority of the works with these scanners have been focused on palaeoceanographic or palaeoclimatic reconstructions, both in marine and continental sediments, being much more scarce the studies based on discrimination of pollution.

We have analysed with the ITRAX from the University of Vigo and varying time-acquisition conditions, sediment cores from the inner Galician Rías Baixas (NW Spain). These are highly organic, but not very heavily polluted environments, however ITRAX was able to detect Hg concentrations lesser than 0.6 µg g⁻¹ and Cd concentrations in the order of 1 µg g⁻¹. These values were confirmed by total digestion and subsequent analysis by ICP and by conventional XRF of pressed pellets, obtaining a good relationship for most of the trace elements (Zn, Pb, Cu, etc.) and confirming the presence of Cd and Hg. Pollution by these elements was restricted to the upper 10-15 cm, approximately ranged between 30-50 yr based on ²¹⁰Pb and ¹³⁷Cs datings obtained by gamma spectrometry. Only Pb and Hg showed concentrations above the sediment quality guidelines that could be associated with measures of adverse effects. Several sequential extraction protocols (BCR and NWR) of selected samples were also applied in order to get information about the bioavailability of these elements. The data confirms the predominance of oxides and residual fractions in the case of Pb and oxidizable forms (organic-matter and sulphides) in the case of Hg. Our results confirms that ITRAX represent a fast and high-resolution tool for identify pollution in these environments not heavily affected.


Aerosol ageing and effect on their optical properties by a new broadband aerosols spectrometer

MICHEL FLORES¹, NIR BLUVSHEIN AND YINON RUIDCH¹*  

¹Department of Environmental Sciences, Weizmann Institute of Science, Rehovot, 76100 Israel  
(Flores@weizmann.ac.il, Nir.bluvshtein@weizmann.ac.il  
*correspondence: yinon.rudich@weizmann.ac.il)

The optical properties of complex aerosols, important in determining their radiative forcing in the atmosphere and, subsequently, their impact on climate, are extensively examined. There is an abundance of natural and anthropogenic organic compounds in the atmosphere that can be released as primary aerosols or form secondary organic aerosols (SOAs) via photochemical reactions with OH, NO₃, and O₃.

Aerosols can undergo further processing in the atmosphere with oxidizing species, changing the chemical, physical, and optical properties of the particles. Particle internal structure and composition have important implications for their optical properties. Despite their acknowledged importance, the internal structures of aerosols, mechanisms of formation, atmospheric aging, and heterogeneous reactivity remain poorly understood and yet their environmental role cannot be quantitatively determined.

In this talk we will describe new studies that investigate the changes in optical properties of different model aerosols. We will describe a new broadband aerosol spectrometer that can retrieve aerosol optical properties between 360 and 420 nm, a less explored wavelength range. As examples, we will present the effect of nitration of organic aerosols on aerosol absorption, and the effect of aging on the optical properties of SOA that form from the ozonolysis of biogenic and anthropogenic VOCs. The effect of structure on the optical properties, and how core/shell structure differs from homogenous structure will be demonstrated.
Glacial tills reveal temporal evolution of upper continental crust

ROBERTA L. RUDNICK1, RICHARD M. GASCHNIG1 AND WILLIAM F. MCDONOUGH1

1Dept. Geology, University of Maryland, College Park, MD 20782, U.S.A., rudnick@umd.edu

Defining the absolute composition of the continental crust, and its lateral and vertical variations, are essential parameters needed in extracting the geoneutrino signal from the mantle and thereby place constraints on the Earth’s present-day radioactive power. K, Th, and U are strongly concentrated in the upper continental crust (UCC) so refining its composition and deriving uncertainties is important to neutrino geoscience.

UCC estimates generally rely on reference suites of shales, pelites, and loess (e.g., Hu and Gao, 2008: HG08). Here we use modern to Archean glacial tills and tillites to determine the average UCC composition through time and then we compare them with HG08. Paleoproterozoic tillites are systematically enriched in transition metals (Sc, Cr, Co, Ni) relative to post-Archean tillites and average UCC, indicating more mafic contribution to the Archean upper crust (as previously documented in shales). However, in contrast to shale data, we find no systematic differences in Th/Sc as a function of age in tills, implying that Th is not systematically depleted in Archean UCC as sampled by the glaciers. Th/U of the tills correlates with their age: Th/U ~3 in modern tills, and Carboniferous and Paleoproterozoic tills, whereas Neoproterozoic tills and HG08 have Th/U ~6. The high Th/U of the Neoproterozoic tills can be linked to intense weathering (and U leaching) attending the snowball Earth glaciations. The lack of a significant difference in the abundances of heat producing elements in Archean and post-Archean average UCC may imply that the lower surface heat flow in Archean cratons compared to post-Archean regions may be related to differences in Moho heat flux.

Resolving gas transport through compacted sand/bentonite material by using noble gases

J. RUEEDI1, R. SENGER2, DONATELLA MANCA3, KARAM KONTAR4 AND P. MARSCHALL1

1NAGRA, 5430 Wettingen, Switzerland
2Intera Inc., 5408 Ennetbaden, Switzerland
3EPFL ENAC IIC LMS, 1015 Lausanne, Switzerland
4Solexperts, 8617 Mönchaltorf, Switzerland

Gases (hydrogen, methane, carbon dioxide) may accumulate in the emplacement caverns of a geological repository for low/intermediate-level waste due to the corrosion and degradation of the wastes. Nagra is evaluating the concept of an engineered gas transport system (EGTS), aimed at providing an additional transport pathway for gas release if overpressures were to be developed. Gas permeable tunnel seals are among the main design elements of the EGTS, consisting of sand/bentonite (S/B) mixtures with a bentonite content of 20% to 30%.

It is expected that material heterogeneities at repository scales will, at least to some extent, lead to a water saturation and a gas invasion behaviour that differs from those observed in small-scale lab experiments. Past applications of probabilistic two-phase flow models tried to assess the influence of material heterogeneities on water and gas transport in clay material. The models revealed complex two-phase flow patterns during gas imbibition and after gas breakthrough. It is thought that these patterns are mainly driven by the material properties and associated heterogeneity. However, there is little experimental evidence to constrain the large number of possible model realisations.

In 2010, a laboratory column was filled with a S/B mixture (80% sand and 20% MX80 bentonite) and compacted to a density of 1.5 g/cm³. The column was then saturated with distilled water for a few weeks and a hydro test was performed to determine the hydraulic permeability of the material and to confirm saturation. A gas test was performed by injecting N₂ at increasing pressures until breakthrough. After breakthrough the gas flow was kept constant and the N₂ gas was replaced by a gas mixture (N₂, He, Ar, Xe, SF₆) and the breakthrough pattern of the different gases was monitored continuously using a mass spectrometer. The choice of the gas tracers was made based on their different physical properties – i.e. solubility in water and diffusivity in both gas and liquid phases.

The observed partitioning of the different gas tracers provides unique experimental evidence for the determining the dominating transport processes within the partially saturated material and thus help constrain probabilistic models for two-phase flow and transport through S/B material.
Large Igneous Province Volcanism, Ocean Anoxia and Marine Mass Extinction

M. RUHL1,2,*, C. BJERRUM1, D.E. CANFIELD3, C. KORTE1, L. STEMMERICK4 AND R. FREI1

1Nordic Center for Earth Evolution (NordCEE), Copenhagen University, Oster Voldgade 10, DK-1350 Copenhagen, Denmark.
2Department of Earth Sciences, University of Oxford, South Parks Road, OX1 3AN, Oxford, UK.
3Nordic Center for Earth Evolution (NordCEE), University of Southern Denmark, Campusvej 55, 5230 Odense, Denmark.
4Geological Museum, Natural History Museum of Denmark, Copenhagen University, Øster Voldgade 5-7, DK-1350, Copenhagen, Denmark.

(* correspondence: micha.ruhl@earth.ox.ac.uk)

Past global marine mass extinction events are often linked to terrestrial Large Igneous Province (LIP) volcanism, but exact mechanisms driving extinction are often not well constrained.

We studied two of Earth’s largest mass extinction events, at the Triassic-Jurassic (~201.4 Ma) and Permian-Triassic (~252 Ma) boundaries, which coincide with Central Atlantic Magmatic Province (CAMP) and Siberian Trap volcanism, respectively. The Triassic-Jurassic mass extinction is often contributed to carbon release driven ocean acidification while the Permian-Triassic mass extinction is suggested to be related to widespread ocean anoxia.

We compare Permian-Triassic and Triassic-Jurassic ocean redox change along continental margins in different geographic regions (Permian-Triassic: Greenland, Svalbard, Iran; Triassic-Jurassic: UK, Austria) and discuss its role in marine mass extinction.

Speciation of iron ([Fe$_{red}$/ Fe$_{tot}$] and [Fe$_{cy}$/ Fe$_{cy+}$]) and redox-sensitive trace element concentrations (e.g. Mo, V etc.) show that the Triassic-Jurassic marine mass extinction directly coincides with a rapid shift to anoxic and euxinic conditions at the onset of CAMP volcanism and increased atmospheric $p$CO$_2$. Biotic recovery after the extinction event only commences when redox-conditions return from a euxinic to a ferruginous state and stabilization of marine ecosystems only commences after decreasing atmospheric $p$CO$_2$ and a return to more oxic marine conditions.

Iron-speciation at both the Triassic-Jurassic and Permian-Triassic mass extinctions however shows 2 phases of euxinia along continental margins, with an initial short peak at the onset of volcanism followed by a shift to ferruginous conditions, possibly due to a strongly diminished ocean sulphate reservoir because of massive initial pyrite burial. D$^{34}$S$_{pyrite}$ suggests that following prolonged (several 100kyr) euxinic conditions only commence when the ocean sulphate reservoir is replenished by the release of sulphur from volcanism.

Geochemistry of cassiterite and wolframite from quartz veins in Central Iberian Zone (Spain)

CASILDA RUIZ1,* AND CONCEPCIÓN FERNÁNDEZ-LEYVA2

1Technical University of Madrid (UPM). Spain
(*correspondence: casilda.ruiz@upm.es)
2Geological Survey of Spain. Madrid 28003
(c.fernandez@igme.es)

Sn- and Sn-W-bearing quartz veins in the Central Iberian Zone mainly cut across the granites. Some of these veins were mined during the last century. The paragenetic sequence corresponds to two oxide-silicate stages and a sulfide stage in that order. Massive crystalline quartz is the main mineral of the three stages. Stage 1 consists of muscovite, cassiterite and arsenopyrite, stage 2 of wolframite and arsenopyrite, and stage 3 of small amounts of sulfides: arsenopyrite, pyrite, pirrotite, sphalerite and chalcopyrite.

Cassiterite from Sn- and Sn-W-bearing quartz veins shows Ti$>$ Fe$>$ Mn content, and Ti replaces Sn. The chemical variation of cassiterite crystals is controlled by the direct substitution of Sn$^4+$ by Ti$^4+$. Cassiterite generally shows lighter and darker zones, and Nb content is higher in darker than in the lighter zones. Wolframite consists almost entirely of FeO, MnO, and WO$_3$, with less than 1% Ta$_2$O$_5$, Nb$_2$O$_5$, and TiO$_2$. It shows Mn and Fe substitution. Wolframite individual crystal shows a decrease in the hübnerite component from core to rim. Likewise, Nb increases toward the rim of the wolframite crystal. Ta content of cassiterite and wolframite is generally higher than Nb content. Cassiterite has a higher Nb and Ta content than wolframite [1].

Tungsten is carried as H$_2$WO$_4$, WO$_2$- [2] and wolframite can be precipitated by the cooling of an Fe-W-bearing fluid, without wall rock reaction [3]. Mineralizing fluid deposits cassiterite, associated with muscovite selvages in the paragenetic stage 1. This fluid evolves and precipitates wolframite, mainly within quartz veins in stage 2. Tungsten shows different behavior from that of tin and consequently, cassiterite is generally not associated with wolframite.


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Geochemical modelling of Sn and W in granites from Central Iberian Zone (Spain)

CASILDA RUIZ 1* AND CONCEPCIÓN FERNÁNDEZ-LEYVA 2
1Technical University of Madrid (UPM). Spain
(*correspondence: casilda.ruiz@upm.es)
2Geological Survey of Spain. Madrid 28003
(c.fernandez@igme.es)

Field and petrographic observations of the quartz veins mineralization in relation with granites in Central Iberian Zone (CIZ) [1], show that cassiterite and wolframite occur in quartz veins principally. It seems that quartz deposition is before the cassiterite one and wolframite is deposited after cassiterite. Processes that form mineral deposits associated with granitic rocks can have a close relationship with magmatic processes. Geochemical calculations applied to Sn and W have been performed to investigate if magmatic processes have been the mechanism by which the mineralisation was generated in the (CIZ).

Complex linear mixing models show that Sn and W increase their concentration in the fractionation stages while modal extracted muscovite is reduced. Sn and W are concentrated in the residual liquid when the modal quantity of extracted muscovite is ≤ 5%. Starting from an initial leucogranitic composition, concentrations of Sn can reach up values over 100 ppm after high degrees of fractionation. On the other hand, the calculated W concentrations are much lower. The same results suggest models for equilibrium and fractional crystallisation [2]. Complex linear mixing models show that crystallisation processes generated mineralizations by concentrations of Sn, whereas W does not reach the levels required for generating ones.


The pH influence on barite nucleation and growth

CRISTINA RUIZ-AGUDO 1, CHRISTINE PUTNIS 2 AND ANDREW PUTNIS 3
1c_ruiz02@uni-muenster.de
2putnisc@uni-muenster.de
3putnis@uni-muenster.de

Barite (BaSO4) scale formation is a problem in many industrial processes, especially in oilfields where mixing sea water with reservoir water can result in solid layers of barite scale that can completely block pipes. Organic compounds (e.g. organophosphonates) have been used as inhibitors for barite precipitation. The effectiveness of these compounds is pH-dependent, usually more effective at high pH where they are highly deprotonated. Thus to be able to determine the performance of organic additives as barite scale inhibitors, we have first studied the influence of pH on barite nucleation and growth.

To determine the influence of pH on growth, AFM observations of barite growth on a barite cleavage surface were carried out under conditions of constant supersaturation, temperature, Ba/So4 ratio and ionic strength but changing growth solution pH.

The effect of pH on nucleation was studied with turbidimetry and conductivity experiments complemented with FESEM observations to determine changes in morphology and size of the barite precipitated. Induction times were determined by monitoring the variation in absorbance due to barite precipitation and this enabled the estimation of potential changes in interfacial tension. Conductivity experiments allowed us to determine the onset of nucleation (i.e. induction time) as well as the supersaturation reached at that point and how both parameters vary with pH.

It was found that increasing the pH of the growth solution results in shorter induction times and lower values of interfacial tension. These changes can be explained considering the effect of increasing hydroxyl ion concentration on barium hydration.
Porosity development during carbonation reactions

ENCARNACIÓN RUIZ-AGUDO¹, CHRISTINE V. PUTNIS²
AND ANDREW PUTNIS²

¹Department of Mineralogy and Petrology, University of Granada, Granada, Spain. encaruiz@ugr.es
²Institut für Mineralogie, University of Münster, Münster, Germany. putnisc@uni-muenster.de

The reduction in industrial emissions of CO₂ is one of the major challenges of this century. Anthropogenic CO₂ capture and injection into geological formations is considered a promising strategy for the permanent storage of this greenhouse gas. This process is based on the dissolution of silicate rocks in contact with CO₂-rich fluid and the precipitation of carbonates, so that CO₂ is trapped as a stable mineral phase. The generation of product layers on the surface of the carbonating material occurs by an interface-coupled dissolution-precipitation reaction (Putnis, 2009). The study of the processes of dissolution and carbonation of portlandite, Ca(OH)₂, is crucial due to the great potential of this reaction for CO₂ capture and storage, as well as for understanding the carbonation behavior of artificial mineral associations such as mortars or cements.

A critical aspect to consider in mineral replacement processes described above is the porosity evolution. The porosity created depends on the difference between the molar volumes of reagent and the product as well as the relative solubility of the two phases in the reaction fluid. The generation of product layers on the surface of the carbonating material occurs by an interface-coupled dissolution-precipitation reaction (Putnis, 2009). The study of the processes of dissolution and carbonation of portlandite, Ca(OH)₂, is crucial due to the great potential of this reaction for CO₂ capture and storage, as well as for understanding the carbonation behavior of artificial mineral associations such as mortars or cements.

This work is aimed at determining how certain physicochemical parameters of the solutions (hydrodynamic conditions, pH or composition) may affect the development of porosity during replacement reactions. Geochemical modelling and experimental studies of the replacement of wollastonite (CaSiO₃) and portlandite by calcite (CaCO₃) are used for illustrating the influence of such parameters.


Toxic element balances in small scale wood combustion systems

H. RUPPERT* AND T. SEIDEL

Geosciences Center & Interdisciplinary Center for Sustainable Development, University of Goettingen, Goldschmidtstr. 3, D-37077 Goettingen, Germany (*correspondence: hrupper@gwdg.de)

In Europe, wood combustion in stoves and boilers is widely applied for residential heating. In Germany, approximately 15 million of 40 million households own small-scale wood-burning furnaces, which deliver 7% of Germany’s heat consumption. Using state-of-the-art small-scale combustion systems, we investigated how the air quality changes due to the emissions of harmful elements and organic pollutants during the combustion of wood and straw.

Beside the fuel, we analysed all the originating ashes – grate ash, heat exchanger ash, and fly ash – to reconstruct element fluxes. As the input/output balance calculations show, some elements – such as cadmium, zinc, tin, thallium, lead, bismuth and antimony – may also be retained within the cooler zones of the furnace, in the chimney, or in the refractory lining material where samples could not be taken (Fig. 1). The elements collected by filters correspondent to the element amount in the flue gas, which is emitted into the ambient air. At most, these element portions represent 30 percent of the amount contained in the fuel [1, 2].

Figure 1: Element recovery rates with and without electrostatic precipitator ESP (combined element amounts in all ashes divided by the amounts contained in the combusted wood)

The pollutants are bound in fine (< 1 µm) particles or gaseous compounds and may enter the lungs’ alveoli and contaminate the body. Clearly, effective emission reduction measures are necessary.

The architecture of the intermediate-sized Quizapu magma system

PHILIPP RUPRECHT1*, GEORGE BERGANTZ2, KARI COOPER3 AND OLIVIER BACHMANN4

1LDEO of Columbia University, Palisades, NY, USA, (*correspondence: ruprecht@ldeo.columbia.edu)
2Dept. of Earth and Space Sciences, University of Washington, Seattle, WA, USA
3Dept. of Geology, University of California, Davis, CA, USA
4Inst. für Geochemie und Petrologie, ETH Zürich, Switzerland

While high melt fraction magma chambers may be transient features in the crust, magmatic mashes represent the long-lived counterparts of the crustal magmatic factory. Together they source largely variable andesitic to dacitic composite volcanic cones and stratovolcanoes and manifest the continuous presence of silicic magma in the crust above convergent margins. Silicic magmas are ultimately fed and their eruption triggered by magmas generated in the mantle. How intermediate-sized (tens of km³) magmatic systems are assembled and what kind of crustal-scale architecture results from that assembly, requires an integrated approach of crystal-scale geochemistry, petrology, and fluid dynamics.

Utilizing such a combined approach provides tight constraints on the magmatic architecture beneath Volcán Quizapu (Chile), a magmatic system that produced two ~5km³ large historic eruptions. The shallowest part of the Quizapu system is dominated by high-melt fraction dacites with minimal evidence for hybridization. This eruptible dacite lense is generated by crystal-melt separation from an andesitic mush of intermediate temperature. Hybridization – common for arc systems – is limited to the andesitic mush, while hot recharge magmas interact only in rare cases directly with the shallow dacite magma [1]. Such mafic recharge leads to mixing and eruption and diffusion modeling of elemental zonation in phenocrysts at Quizapu (e.g., Mg in plagioclase) suggests that recharge, mixing, and eruption occurred within days to a few weeks [2]. Moreover, we consider the thermal effects on the mixing and eruption dynamics associated with hot mafic recharge and find (i) that overall mixing efficiency for the erupted volume is set early during the recharge events – limiting the extent of hybridization [1] – and (ii) that short-term reheating leads to significant viscosity reduction in the resident dacite magma. We argue that late-stage reheating may reduce the potential for Plinian eruptions as water-saturated dacites degas efficiently during ascent [3].


Are long-lived stratovolcanos low-pass filters for magma transport?

PHILIPP RUPRECHT1* AND TERRY PLAN1

1LDEO of Columbia University, Palisades, NY, USA, (*correspondence: ruprecht@ldeo.columbia.edu)

Arc stratovolcanoes localize magmatic activity for 10s to 100s kyr, leading to self-cannibalization and the emergence of polybaric subvolcanic magma storage regions. Partial melts accumulate within mush zones and sills at various levels in the crust. Dense primitive mantle-derived magmas that ascend from mantle source regions encounter those density barriers on their way to the surface, leading to stalling and an evolution to more buoyant magmas through fractionation, mixing, and assimilation. It is therefore not surprising and well-known through geochemical and isotopic studies that primitive magma compositions typically do not reach the surface within voluminous arc magma systems. This view suggests that long-lived arc stratovolcanoes act as low-pass filters for primitive magmas from the mantle, where the frequency of magma addition from the mantle is converted in the crust to a slower integrated ascent rate as magmas stall, evolve and accumulate. Isotope and geochronology studies on crystal cargo provide evidence for such prolonged magma processing. While some stalling and processing in the crust is commonly agreed upon, magma transit times at middle to lower crustal levels are particularly unconstrained. A contrasting view is that magmas rise rapidly (potentially adiabatically), resorb any crystal cargo upon ascent, and crystalize at shallow depth.

Combining geochemical data from primitive crystals (e.g., Fo90), observations of upward earthquake migration beneath long-lived volcanic centers, and thermal constraints on magma transport in the crust, we show that slow processing (low-pass filtering) may not be as ubiquitous as it is assumed for large stratovolcanoes [1]. Instead, a second mode of fast magma transit from the mantle to the surface must coexist. Some phenocrysts in arc magmas record in their crystal zoning mixing episodes of primitive magmas at Moho depth (e.g., >1000 ppm Ni variations in olivines of constant Fo), and provide an upper limit on ascent rates of primitive magmas. In fact, thermal models for dike transport and trace element diffusion calculations for Ni zoning constrains integrated Moho-to-surface ascent rates for the fast mode to ~ 0.1-1 km/day, well in line with seismic observations from migrating earthquake swarms. Such ascent rates require primitive magmas to bypass or transit effectively most middle to lower crust magma storage regions.


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Hydrothermal-sedimentary lithogenesis

V.YU. RUSAKOV

V.I. Vernadskiy Institute Geochemistry and Analytical Chemistry, RAS (rusakov@geokhi.ru)

The model of the hydrothermal-sedimentary lithogenesis rests on data of suspended and settled matter of ‘black smokers’, proximal and distal metalliferous sediments (MS), as well as the Paleozoic hydrothermal-sedimentary deposits. Recent hydrothermal fields (Broken Spur (<1 kyr), TAG (~40-50 kyr), Krasnov (~120 kyr), Semenov ore cluster (~37-124 kyr)) and ancient VMS deposits of the Urals (Modolezhnoye, Yaman-Kasy, Safiyanovskoe) was selected as an illustration of the model. Moreover, the manganiferous deposits of the Urals (Kyzil-Tash, South-Faizulinskoe, Bikkulovskoe) was also included in this model as an ancient prototype of distal hydrothermal-metalliferous sediments.

On the basis of study of sediment strata on the Krasnov field [Rusakov et al., 2011; 2012] and Semenov ore cluster [Rusakov et al., 2013 in press] was found that epicenter part of the hydrothermal-sedimentary strata in form of ore-bearing sediments, covered ore-bodies, reflects a zone of interrelation between ore-bearing solutions (infiltration-metasomatic processes) and seawater (halmyrolysis). At the distance of the zone the ore-bearing sediments are transformed into proximal MS, ore part of which is completely presented by Fe-oxyhydroxides. Main part of Mn is precipitated on great distance from the hydrothermal field from non-buoyant plumes.

On the basis of study of ferruginous rock around VMS deposits enable to reveal main stages of the meta-sediment formation: (1) sedimentation, (2) infiltration-metasomatic, (3) halmyrolysis, (4) lithification. The infiltration-metasomatic impact of hydrothermal solutions and oxidizing action of seawater leads to copper redistribution within sediment strata and formation of secondary minerals (pyrite is replaced by chalcopyrite, chalcopyrite is replaced by siderite, as well as formation of secondary calcite and chlorites). The main mechanism of lithification of MS is sediment dehydration, expressed in replacement of Fe-oxyhydroxides by hematite and silica by quartz. In spite of such transformations, original lateral zoning of rock is remained indicating on effect of hydrothermal-sedimentary genesis.

Origin of Earth’s Earliest Continental Crust: A Combination of Partial Melting and Fractional Crystallization?

T.RUSHMER1* AND J. ADAM1

1Department of Earth and Planetary Sciences, Macquarie University, Sydney, AUS (*Tracy.Rushmer@mq.edu.au)

The origin of tronialite-trondhjemite-granodiorite (TTG) plutonic complexes continues to be a major focus of research as these suites make up a majority of Earth’s earliest continental crust. Partial-melting experiments were conducted (at 900-1100 °C and 0.5-3.0 GPa) on two greenstones from the Nuvvuagittuq Complex, Quebec, Canada and on PC-103, a 3.66 Ga tonalite that encloses the mafic rocks of the Nuvvuagittuq Complex. At 1.5-3.0 GPa and 950-1100 °C, the experimentally produced melts are compositionally similar to Archaean TTGs (including PC-103). But the degree of melting needed to produce these melts is high (> 30 %) and so the relative concentrations of most incompatible elements in the melts are similar to those of their greenstone parent rocks. These greenstones have compositional affinities with modern subduction zone magmas. Thus, arc-like mafic rocks appear to have been selectively involved in TTG formation, implying the involvement of crustal recycling in TTG genesis. The results of experiments on the tonalite PC-103 suggest either equilibrium of its original magma with a garnet pyroxenite residue at ~1050 °C and 3.0 GPa, or compositional control by the plagioclase-pyroxene cotectic at ~ 900 °C and < 1.0 GPa. The latter option is more consistent with the compositional trends of Archaean TTGs. In either case, a high degree of inheritance is involved implying a role for early crustal recycling.
Green River CO₂ natural analogue, Utah: insights into Fe mobilisation from jarosite fracture mineralisation.

J. C. Rushton, D. Wagner, G. Purser, J. M. Pearce and C. A. Rochelle

British Geological Survey, Environmental Science Centre, Keyworth, Nottingham NG12 5GG. jere1@bgs.ac.uk

Outcrop samples of the Jurassic Entrada Sandstone in the Green River area of Utah, USA, have been studied as part of a CO₂ storage natural analogue study (CRIUS consortium). These rocks are locally bleached, the pattern of which is enigmatic but commonly associated with sub-vertical fractures. In some locations these fractures are pathways to recent carbonate travertine deposits. Of key interest is the fate of Fe, whose reduction and mobilisation is implied by the host rock bleaching patterns and which is present in travertine of Fe, whose reduction and mobilisation is implied by the host rock bleaching patterns and which is present in travertine deposits. Of key interest is the fate of Fe, whose reduction and mobilisation is implied by the host rock bleaching patterns and which is present in travertine deposits.

Petrographic analysis has revealed a complex and unusual textural and mineralogical assemblage in the fractures. Jarosite (KFe₃(SO₄)₂(H₂O)₆) has been identified; its formation is typically associated with oxidative alteration of sulphide minerals and acid mine drainage. Cubic pseudomorphs mostly comprising goethite, centrally concentrated in the fractures and containing rare pyrite relics, suggest pyrite was the primary fracture mineralisation, and may indicate that S-bearing reducing fluids are responsible for the host rock bleaching patterns.

Expansive textures associated with the jarosite suggest that it formed with minimal overburden, and that the oxidative fluids were a near-surface episode. Zones of complete and then partial dissolution of diagenetic carbonates in the host sandstones adjacent to the fractures, associated with Al oxide / hydroxide mineralisation, are consistent with low pH fluids resulting from sulphide oxidation. Gypsum- and calcite-cemented fractures cross-cut the jarosite mineralised textures; these later events relate to current CO₂-rich fluid movements since they can be observed to form part of the feeder system linking directly to travertine deposits at some locations. This paragenesis shows that the same fracture flowpaths have been used by several generations of fluids.

Petrographic observations, together with an experimental study of Fe mobilisation from the Entrada Sandstone, suggest that dissolved Fe in the modern regional CO₂-rich fluids is largely derived from the fracture mineral assemblage, rather than through current alteration and bleeding of the host rock.


Observed Aerosol Effects on Eastern Pacific Stratocumulus Clouds


1Scripps Institution of Oceanography, UCSD, La Jolla, CA (correspondence: lmrussell@ucsd.edu).
2California Institute of Technology, Pasadena, CA.
3University of Arizona, Tucson, AZ.
4Georgia Institute of Technology, Atlanta, GA.
5Rosenstiel School of Marine Sciences, Miami, FL.
6Center Interdisciplinary Remotely-Piloted Aerosol Studies.
7Environment Canada, Toronto, Canada.
8Harvey Mudd College, Claremont, CA.

Aerosol particles in the marine boundary layer include primary organic and salt particles from sea spray and combustion-derived particles from ships and coastal cities. The Eastern Pacific Emitted Aerosol Cloud Experiment (E-PEACE) 2011 was a targeted aircraft campaign to assess how different particle types nucleate cloud droplets. Particle sources included shipboard smoke-generated particles with 0.05-0.2 μm diameters (which were measured in a variety of conditions with droplets containing both organic and sulfate components) [1]. Three central aspects of the collaborative E-PEACE results are: (1) the size and chemical composition of smoke particles compared to cargo ship emissions as well as background marine particles, (2) the characteristics of cloud track formation for smoke and cargo ships, as well as the role of multi-layered low clouds, and (3) the implications of these findings for quantifying aerosol indirect effects. For comparison with the E-PEACE results, the preliminary results of the Stratocumulus Observations of Los-Angeles Emissions Derived Aerosol-Droplets (SOLEDAD) 2012 provided evidence of the cloud-nucleating roles of both marine organic particles and coastal urban pollution, with simultaneous measurements of the effective supersaturations of the clouds in the California coastal region.

Analogue experiments on volatile escape from crystal-rich magmas

A. RUST\textsuperscript{1}, K. CASHMAN\textsuperscript{1}, J. OPPENHEIMER\textsuperscript{1} AND I. BELIEN\textsuperscript{2}

\textsuperscript{1}School of Earth Sciences, University of Bristol, UK
glkvc@bristol.ac.uk
\textsuperscript{2}Exxon Mobil Upstream Research, Houston, TX

The low water content of granitoid bodies requires effective escape of the volatile phase during crystallization of mushy magma. We explore the physical mechanisms for volatile migration in crystal-rich magmas with experiments on three-phase analogue mixtures of syrup, solid particles and gas. The liquid+particles was either placed in a vertical tube or sandwiched between two glass plates; gas was injected into the suspension, or generated throughout the suspension by chemical reaction or by decompression. The proportions of phases, syrup viscosity, particle sizes, and rate of gas injection/expansion were varied. Experiments were videoed and monitored with gas pressure data.

Comparisons with crystal-free experiments indicate that crystals in mushes strongly inhibit buoyancy-driven bubble migration, but can facilitate the formation of temporary connected gas pathways, allow degassing of permeable gas flow at much lower volume fractions of gas than the crystal-free system. The experiments with parallel glass plates facilitate visualization of the gas phase. Three regimes are identified by gas distribution patterns, and are found to be related to the volume fraction of solids: (1) At low particle concentrations the gas forms smooth fingers that intrude steadily; (2) At ~55% particles, the gas penetrates the suspension in bursts, and forms thin “fractures”; (3) At solid fractions sufficient to lock the particles in place, the gas pushes liquid out through the particle network.

In all three regimes the measured gas pressure increases smoothly and does not decrease until, or shortly before, the gas reaches the edge of the liquid+particle mixture. In the fracturing regime, the pressure increase is steady even during bursts of motion; this indicates that the ductile but sudden fracture formation rearranges the gas phase but does not create episodes of pressure buildup and release. Once a fracture has released gas to the outside, however, there are subsequent fluctuations in pressure as the initial fracture heals (viscously) and closes the system until a new fracture reaches the suspension boundary, at which point the process is repeated in a new location (because in heterogeneous suspensions fractures preferentially propagate into areas with relatively high solid contents). This mechanism would allow effective open-system degassing of crystallizing volatile-saturated magma, without leaving textural evidence of the volatile phase.


JAMES R. RUSTAD\textsuperscript{1}

\textsuperscript{1}University of California, Davis, Davis, CA 995615
(correspondence: jrrustad@ucdavis.edu)

Calculation of mass-dependent isotope fractionation in geochemical systems is probably the single most successful application of computational chemistry to geochemistry. The accuracy of these calculations is highly system dependent. For heavy isotopes with fractionations on the 1-2 permil level, first principles calculations are highly challenging, and computational requirements differ considerably between anionic and cationic systems. Aquo ions need large basis sets, particularly anions, which require basis sets of aug-cc-pVTZ (or better) quality. Aquo cations can be represented using continuum solvent models beyond the second shell, while aquo anions cannot. When density functional theory is used, the choice of the exchange-correlation functional has a strong effect on the results. This exchange-correlation variation, together with the basis set variation, can easily result in steps taken through basis-SET XC functional that vary over a range of more than ~3 permil, with no apparent consensus on which functionals work best. Thus while past success has often been impressive, reliable prediction of fractionation at the sub-1 permil level will remains a highly challenging, though not unattainable, goal. Examples are taken from BOH\textsubscript{3}(aq)-BOH\textsubscript{4}-(aq), Mg\textsuperscript{2+}(aq)-calcite, Ca\textsuperscript{2+}(aq)-calcite, Fe\textsuperscript{3+}(aq)-hematite, (H)CO\textsubscript{3}-(aq)-carbonate, perovskite-ferropericlase, chlorophyll, and amino acid systems.
Polyoxoions as Model Systems for Mineral Surface Chemistry

JAMES R. RUSTAD¹

¹Corning Incorporated, Sullivan Park Research Center, Corning, NY 14831, USA
(correspondence: rustadjr@corning.com)

Polyoxometalate ions (POMs) have structures similar to condensed oxide phases and can be used as representative molecular models of the oxide/water interface. Oxygen atoms in POM exchange with water molecules at different rates. At present there is no basis for predicting how the coordination environment and metal substitution influences rates and mechanisms. Lability of oxygen in POMs is governed by low-energy metastable configurations that form from the breaking of weak bonds between metals and underlying highly coordinated oxygen atoms, followed by facile hydroxide, hydronium or water addition. The mediation of oxygen exchange by these stuffed structures suggests a new view of the relationship between structure and reactivity at the oxide/solution interface that de-emphasizes local bond ruptures and activated transition states. Reaction rates are governed by pathways for the formation and destruction of oxygen-stuffed intermediate states, not specific oxygen site chemistry, as has long been assumed. These intermediates form from ring-opening reactions that allow isotopic exchange and, by extension, dissociation and dissolution. As for the Keggin-type polyoxocations, the common feature of these intermediates is the breaking of a weak bond between a surface metal and the deeper, highly coordinated oxygen. The relative energies of the intermediate structures are similar across the range of substituted decaniobates, supporting the experimental observation that metal substitution at a specific site does not change the relative order of reactivity of the different types of oxygen atom. Unlike the Keggin-type polyoxocations, metal substitutions in the decaniobate POMs affect rates mainly by modifying the Broensted acid/base properties of the molecule.

Combining geochemistry with thermal infrared remote sensing to characterize glacial weathering

A.M. RUTLEDGE*, P. CANOVAS, E. SHOCK AND P.R. CHRISTENSEN

School of Earth and Space Exploration, Arizona State Univ., Tempe, AZ 85281 USA
(*correspondence: allie.rutledge@asu.edu)

Subglacial and englacial weathering of geologic materials contributes to the solute flux in meltwater, provides feedback in the global carbon cycle, and is a potential source of energy to chemotrophic microbes [1]. Thermal infrared (TIR) remote sensing has been used to identify geologic materials and study weathering processes [2]. In this study, we characterize the weathering processes occurring in a glaciated silicate-carbonate system by linking Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER) infrared spectroscopy to in-situ rock and sediment samples, and compare our results with aqueous geochemical data. Our major objective is to link in situ samples with remote sensing capabilities.

Robertson Glacier (115°20’W, 50°44’N) drains the northern flank of the Haig Icefield in Peter Lougheed Provincial Park, Kananaskis Country, Alberta, Canada. The glacier rests on Upper Devonian impure limestones, dolostones, and shales [3]. Samples of glacially altered rock and sediments were collected at the glacier in 2010 and 2011. TIR laboratory spectroscopy was used to determine the composition and abundance of minerals present. Ice and water samples were also collected at similar locations and analyzed for major and minor elements. TIR imagery of the region was collected with the ASTER satellite instrument.

Dissolved Ca²⁺ and SO₄²⁻ increase downstream in the outflow channel. This is consistent with earlier studies of this system – these increases are interpreted to be due to acid hydrolysis of calcite fuelled by CO₂ dissolution and by pyrite oxidation [4], which is likely to be microbially mediated. Both ASTER- and lab-scale spectroscopic analyses show evidence for calcite leaching. Lab TIR analyses demonstrate the presence of calcite-depleted weathering rinds on hand samples. ASTER analyses show similar spectra on a regional scale; freshly revealed glacial till is seen to be depleted in calcite relative to the surrounding bedrock. This TIR remote sensing method has wide application to studies of glacial weathering, especially those focusing on less accessible regions of the world.


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Monitoring the 40Ar/39Ar irradiation parameter ‘J’ without using geological age standards

DANIEL RUTTE*1, SEPP UNTERRICKER2, JÖRG A. PFÄNDER1 AND RAYMOND JONCKHEERE1

1Institut für Geologie, TU Bergakademie Freiberg, Germany, [≡daniel.rutte@geo.tu-freiberg.de]
2Institut für Angewandte Physik, TU Bergakademie Freiberg, Germany

One of the major error components in 40Ar/39Ar geochronology is the irradiation parameter J. Its associated error is based on the accuracy of the independent age of the geological age standard and the inhomogeneity of the neutron fluence in the irradiation channel. To tackle both problems, we included independent fluence monitors (Ni and Co foil) in two of our irradiation containers, one irradiated under Cd-shielding in the research reactor Geesthacht FRG1 (Germany), the other without Cd-shielding in the research reactor Řez LVR-15 (Czech Republic). The irradiation containers were placed in rotating positions. Based on the activation reaction 58Ni(n,p)58Co, gamma-spectroscopy of the resulting decay of 58Co to 58Fe provided the means to calculate absolute fast neutron fluences. The relative variation of the calculated fast neutron fluence at different points in the irradiation container is in agreement with the J-values measured from geological age standards within 1 sigma errors. For the irradiation in the research reactor LVR-15, the calculated neutron fluence varied systematically by 2.5% over an axial distance of 6 cm and by 1.9% over a radial distance of 3 cm. From the calculated absolute fast neutron fluences we calculated J-values, independent of geological age standards. In a first approach, the calculated J-values are about 12% higher than the J-values determined using geological age standards. The relative 1 sigma errors of the calculated J-values are on average 0.15%, as determined by a Monte Carlo method, as well as counting statistics of the gamma-spectrometer.

Halogen Systematics of the Manus Spreading Center.

L. RUZIÉ1*, D. CHAVRIT1, R. BURGESS1, P. CLAY1, B. JOACHIM1, D. R. HILTON2, J. M. SINTON3 AND C.J. BALLENTINE1

1University of Manchester, UK
*lorraine.ruzie@manchester.ac.uk
2Scripps Institution of Oceanography, California, USA
3University of Hawaii, Honolulu, USA

The incompatibility of the heavy halogens (Cl, Br, I) combined with relatively high concentrations and distinct elemental compositions in surface reservoirs makes the halogens good tracers to detect the recycling processes in the different mantle sources. However, the halogen systematics in mantle reservoirs remains poorly constrained mainly because of their very low abundance in materials of interest. An innovative analytical technique, involving neutron irradiation of samples to convert halogens to noble gases then measured using conventional noble gas mass-spectrometry, provides detection limits unmatched by any other technique [1].

We focus on the halogen contents in the glassy margins of basalts erupted along the Manus Spreading Center (MSC), which lies in a back-arc basin setting. Samples consist of both MORB-type lavas and back-arc basin basalts (BABB) [3]. The major and trace elements, as well as 3He/4He ratios, water concentrations and δD have already been determined [2].

The halogen concentration range is between 160 and 1500 ppm Cl, 600 and 5700 ppb Br and 10 and 60 ppb I. The lower concentrations found in MORB-type samples are similar to E-MORB contents from Central Indian Ridge [4]. The higher concentrations are found in BABB samples. A strong negative correlation is apparent between I/Cl and both H2O/Ce and δD:

1) the lower I/Cl wt. ratios measured in BABB (4.1 ±1.4 x10⁻⁵) are associated with the higher H2O/Ce ratios (2,150 ±580) and δD (-52 ±15‰),
2) the higher I/Cl wt. ratios measured in MORB-type lava (7.2 ±2.5 x10⁻⁵) are associated with lower H2O/Ce ratios (750 ±130) and δD (-94 ±11‰).

From these results, we infer that our suite of samples from MSC are explained by mixing a seawater-derived component of the actual slab and the Manus underlying mantle. Considering both the MSC distance to the arc (240 km) and the slab slope, we conclude that a seawater-derived component can be preserved below 100 km depth.


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Ge and Ge-bearing mineral phases in gabbrodolerites of Mt. Ozernaya trap intrusion (Siberian platform)

V.V. RYABOV 1 AND L.V. AGAFONOV 1
1V.S.Sobolev of Institute Geology and Mineralogy SB RAS, Novosibirsk, 630090, Russia; e-mail: trapp@igm.nsc.ru

Native iron(-platinum) ores [1] are associated with the Mt. Ozernaya trap intrusion, which is a part of the large volcano tectonic structure. Small (5-25 µm) isometric grains and subhedral crystals of Ge and Ge-bearing oxygen-free and oxygen-containing mineral phases are observed in interstices of olivine-bearing gabbrodolerites of this intrusion. The phase composition was determined on LEO 143OVP scanning microscope and on GEOL JXA-8100 electron-microprobe. Because of small sizes of the grains, it was not possible to determine X-ray parameters of the mineral phases. The element composition in Ge and Ge-bearing mineral phases varies within the wide range: Ge (1.0-37.6%), Ni (24.8-72.2%), Co (0.9-5.1%), Fe (1.3-42.9%), Sb (0-20.2%), As (0-39.8%), and S (0-15.7%). Individual grains contain Cu (0.6-5.9%), Pd (4.5-19.9%), and Sn (10.7-18.0%). The ideal formulas of mineral phases are Ni2Ge, Ni2(Ge,Sb), Ni2(S,Ge), and Ni2(Ge,As).

Three analyses of the oxygen-containing Ge mineral phases show the variation: 41.41, 40.65 and 40.94 GeO2, 56.98, 51.84 and 51.62 FeO; 0.00, 4.33 and 4.94 MgO; 1.61, 1.65 and 1.61 NiO: 0.00, 0.38 and 0.55 Co; 0.00, 1.12 and 1.08 CuO, respectively. The sums are 100, 99.97 and 100.74, respectively. Their ideal formula is Fe2GeO4.

In association with the Ge and Ge-bearing phases, the following constituents are observed in interstices of gabbrodolerites: graphite, iron, cobalt, camacite, taenite, awaruite, NiCoFe-intermetallic compounds, silver, wustite, hercynite, chalcopyrite, cubanite, bornite, pentlandite, heazlewoodite, troilite, acantite, maucherite, nickeline, as well as fayalite, biotite, hastingsite, garnet, demidovskite, breakdown solid solution structure Wo2En47Fs51 - Wo40En42Fs18, and circon.

Formation of the mineral phases is assumed to occur under highly-reductive conditions involving organoelement compounds. [2]


Variations in modes and rates of long-term denudation in carbonate terrains under Mediterranean to hyper-arid climates

U. RYB 1*, A. MATMON 1, Y. EREL 1, I. HAVIV 2 AND L. BENEDETTI 3
1The Fredy and Nadine Herrmann institute of Earth Sciences, Admon J. Safra Campus, Givat Ram, Jerusalem, 91904, Israel. (*correspondance: uri.ryb@mail.huji.ac.il) 2Ben-Gurion University of the Negev, Be’er-Sheva 84105, Israel 3Aix-Marseille Université, CNRS-IRD-Collège de France, UM 34 CEREGE, Technopôle de l’Arbois, BP80, 13545 Aix-en-Provence, France

Using 36Cl measurements in >100 carbonate bedrock and sediment samples we calculate long-term denudation rates in two drainage basines that drain the western and eastern flanks of the Judean mountain range (central Israel). A sharp climatic gradient from Mediterranean to hyper-arid conditions characterizes the transition from the western to the eastern flank of the range, due to rain shadow effects. Moving from the Mediterranean to the hyper-arid climate zones, denudation rates of interfluves drop by an order of magnitude from ~20 to 1-3 mm kyr⁻¹ and are linearly dependent on precipitation, indicating that carbonate dissolution is the dominant erosional process. Conversely, denudation rates become increasingly dependent on hillslope gradient only in the dryer climate zone, and thus delineate the dominant control of mechanical processes on denudation within this zone. We demonstrate that the transition between chemically-controlled denudation to mechanically-controlled denudation occurs between mean annual precipitation values of 100 and 200 mm yr⁻¹. The growing contribution of mechanical processes to hillslope erosion is also evident in the increase of denudation rates calculated from sediments, collected from the eastern drainage, between the Mediterranean (16-18 mm kyr⁻¹) and the hyper arid (30-48 mm kyr⁻¹) regions. This study demonstrates that carbonate terrains have the capacity to switch between mechanical and chemical weathering regimes in response to changes in precipitation. Similar transitions in response to changes in temperature or the level of tectonic activity have been reported in the past. It is suggested that the abrupt nature of such transitions is a reflection of the competition between surface and subsurface drainage systems in carbonate terrains, derived from the congruent nature of carbonate dissolution processes.

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Sub-sea tailings deposition leach modeling

P. RZEPKA1*, I.F. WALDER1, P. BOŻĘCKI2
AND G. RZEPA2

1Kjeøy Research & Education Center, Kjeøy, 8412 Vestbygd, Norway;
(*correspondence: przemyslaw.rzepka@gmail.com)
2AGH University of Science and Technology, Department of
Mineralogy, Petrography and Geochemistry, al. Mickiewicza 30, 30-059 Kraków, Poland.

The sub-sea/deep sea tailings deposition is a controversial method for disposing of mine wastes. Hazardous chemicals used during processing and deposited metal sulfides may dissolve, affecting the sea environment.

The overall objective for this project is to evaluate the copper leaching potential from tailings on the example of the proposed submarine tailing disposal in Repparfjorden discharged from 2 deposits - Nussir and Ulveryggen, mined by Nussir ASA. This experiment gives better understanding of the reactivity of sulfide minerals in saline system during sub-sea deposition.

Several kinetic tests were run based on recirculation of the leachate (batch experiments) using a constant flow rate over the tailings material of 1-2 m/h. The columns were run at approximately 10 °C (Fig. 1).

There is a distinct increase in copper concentration during the experiments; while other hazardous elements (like Se, As, Ni) do not reveal changes. Copper leaching is a two-stage process: (1) initial rapid dissolution of secondary minerals formed from sulfide oxidation, related to the tailings material disposing period, and (2) long term slow leaching of available surface material of tailings settled on the bottom. Copper concentrations reached 0.02 mg/l after 100 days. Towards the end of experiments (from 70-100 days) the leaching rate leveled off (approximately 2.8 mg/m²/year) with time. Cu content data indicated that there were no further increase or leaching. These experiment results are potentially overestimating sub-sea tailings deposition natural conditions.