

## Evaporitic sulfate concretions, Moodies Group (~3.2 Ga, Barberton Greenstone Belt, South Africa)

SAMI NABHAN<sup>1</sup>, CHRISTOPH HEUBECK<sup>1</sup>  
AND MARTIN HOMANN<sup>1</sup>

<sup>1</sup>Freie University Berlin, Institute of Geological Sciences,  
Malteserstr. 74-100, 12249 Berlin (sami.nabhan@fu-  
berlin.de; christoph.heubeck@fu-berlin.de;  
martin.homann@fu-berlin.de)

Quartz-rich sandstones of fluvial to supratidal facies in the Archean Moodies Group (~3223 Ma, Barberton Greenstone Belt, South Africa) include several regionally traceable beds with common to abundant nodular concretions of chert and megaquartz pseudomorphs after gypsum and barite. Electron microprobe analyses show remnants (<20 μm) of these minerals within the concretions but not in the host rock. Petrographic thin sections show characteristic mottled extinction of poikilotopic gypsum cement, now silicified.

Concretions reach up to 8 cm in diameter, are stratiform and commonly associated with aqueously reworked fine-grained tuffaceous sediment of rhyodacitic composition. Detailed geological mapping indicates a braided fluvio-deltaic setting, transitional to sandy supratidal flats which were colonized by microbial mats and occasionally underwent desiccation; the setting is clearly nonmarine. Gypsum pseudomorphs commonly grew inward into concentric hollow or fluid-filled cavities, suggesting mantling followed by dissolution of an unknown precursor mineral, but also grew displacively outward. Nodule growth apparently took place under early diagenetic conditions in unconsolidated sediment in the vadose zone dominated by frequent capillary rise of groundwater brine under mildly evaporative conditions. Partially reworked rhyodacitic tuffs may have delivered alkali cations such as Ca, Na, Ba, and K while carbonates were supplied by atmospheric silicate weathering of mafic to ultramafic volcanic rocks. The provenance of sulphate ions is unknown but may have included microbial and/or abiotic disproportionation of volcanic S or SO<sub>2</sub>.

Nodular concretions of the Moodies Group may represent the oldest terrigenous evaporites known to date. Their chemical and isotopic composition constrains the occurrence of sulfate in the atmo- and hydrosphere of the Early Earth, its interaction with the emerging biosphere, Archean weathering, possibly local climatic conditions, and vadose-zone hydrodynamics of the world's oldest well-preserved siliciclastic shoreline system.

## Petrosomatic Evolution of Montviel Alkaline System and Rare Earth Carbonatites, Abitibi, Canada

O. NADEAU\*, R. STEVENSON AND M. JÉBRAK

\*(correspondence: nadeau.olivier@uqam.ca) Geotop,  
Université du Québec à Montréal, Québec, Canada

Montviel is a Paleoproterozoic alkaline complex intruding the Archean TTG and volcanic rocks of the Northern Abitibi Zone, Quebec, Canada. It consists of a series of ultramafic to carbonatitic peralkaline bodies. According to field relations, intrusions of peridotites and pyroxenites were followed by melteigites / ijolites / urtites, syenites, sodic granite, and comagmatic silicocarbonatites, calciocarbonatites and ferrocarnatites [1]. The magmatic evolution appears to have ended with a major explosive event which formed carbonatite-bearing polygenic breccia. The carbonatites and the breccia are hosts of one of the largest rare earth element (REE) and niobium mineral deposits being developed in Canada [2]. Detailed petrographic work indicates primary mineralization was partly magmatic, hosted in carbocernaite (REE carbonate) and partly carbothermal, recrystallizing carbocernaite to cebaite and kukharenkoite (REE fluorocarbonates). A second carbothermal event enriched specific parts of the system in heavy rare earths, crystallizing ewaldite (heavy REE carbonate) and heavy REE-enriched qaqarsukite (a fluorocarbonate). A third metasomatic event preferentially remobilized the light REE, further enriching the heavy REE in the areas that were first enriched. Preliminary analyses suggest that the fluorocarbonic stages were followed by an aqueous, hydrothermal stage. The final explosion stage of mineralization preferentially remobilized the light REE enriching the breccia in heavy REE. Trace element concentrations and <sup>143</sup>Nd/<sup>144</sup>Nd ratios are used to investigate the petrogenesis of the system, trace the source(s) of the rare earths and study their behavior in this complex magmatic-carbothermal system.

[1] Goutier, J., 2005. Géologie de la région du lac au Goéland (32F15). Ministère des ressources naturelles et de la faune du Québec. Report RG 2005-05. 44 page. [2] Desharnais, G., Duplessis, C., 2011. Montviel Core Zone REE Mineral Resource Estimate, Professional Report 43-101, Quebec, Canada, 74 pp.

## Guyana: The Lost Hadean crust of South America?

S. NADEAU<sup>1\*</sup>, W. CHEN<sup>2</sup>, J. REECE<sup>1</sup>, D. LACHHMAN<sup>1</sup>,  
R. AULT<sup>1</sup>, T. FARACO<sup>3</sup>, L. FRAGA<sup>4</sup>, N. REIS<sup>5</sup>  
AND L. BETIOLLO<sup>6</sup>.

<sup>1</sup>Guyana Geology and Mines Commission, Georgetown,  
Guyana goldenserge@hotmail.com (\* presenting author)

<sup>2</sup>State Key Laboratory of Mineral Deposit Research, Nanjing,  
China: nmgchenwei@163.com

<sup>3</sup>CPRM Belém, Brazil: telma.faraco@cprm.gov.br

<sup>4</sup>CPRM Rio de Janeiro, Brazil: leda.fraga@cprm.gov.br

<sup>5</sup>CPRM Manaus, Brazil: nelson.reis@cprm.gov.br

<sup>6</sup>CPRM Boa Vista, Brazil: leandro.betiollo@cprm.gov.br

U-Pb age dating of zircons was conducted on eighteen rocks from Southern Guyana (Guiana Shield). These were collected by geologists of the geological surveys of Guyana and Brazil during a joint geological and geo-diversity mapping project along their common border. A total of 447 U-Pb age determinations in zircons were obtained by Laser ICP-MS at the State Key Laboratory of Mineral Deposit Research, Nanjing, China.

The rocks were taken from the three main stratigraphic units present in Southern Guyana, where little age dating existed and will be presented south to north:

1) The zircons of granitic rocks of the Southern Guyana Granite Complex (most southerly) yielded the youngest age ca 1925-1984 Ma. These rocks contain only a few older zircon xenocrysts clustering at ca 2086 Ma, ca 2138 Ma, ca 2261 Ma and ca 2297 Ma.

2) The metamorphic age of zircons from the Kanuku Complex (centrally located) is estimated at ca 1956-1968 Ma and obtained from one S-type granite and one paragneiss sample. Moreover, several paragneiss samples contain significant proportions of detrital zircons with older age values clustering at ca 2200-2269 Ma, ca 2450 Ma, ca 2520 Ma, ca 2635 Ma and ca 2707-2721 Ma.

3) The rocks of the Iwokrama Formation (most northerly) display the largest range of age due to the presence of numerous zircon xenocrysts. Minimum age of crystallization of the volcanic and subvolcanic granitic rocks is ca 1981-1986 Ma. Older zircon xenocrysts cluster at ca 2196-2202 Ma, ca 2395-2417 Ma, ca 2487-2489 Ma, ca 2852-2882 Ma, ca 2949 Ma, ca 3701 Ma, ca 3778 Ma and ca 4218 Ma. The oldest age obtained is from a zircon core with a concordant age of 4219 Ma +/- 19 (1s). A second zircon core determination from the same crystal yielded a slightly discordant age of 4210 Ma +/- 19 (1s). The rim of the same zircon gave an age of 3733 Ma +/- 23 (1s).

The zircon xenocrysts in the range ca 2520-3811 Ma in the Iwokrama Formation overlap with Archean age of rocks of the Imataca Complex in Venezuela and of the Amapa Complex of northern Brazil dated between ca 2500 and 3700 Ma. The subvolcanic granite and felsic volcanic rocks of the Iwokrama Formation appear to contain zircons from a "Lost Hadean Crust" representing the oldest component of the Guiana Shield and of South America.

## Hydrothermal magnetite from the Grasberg porphyry and Ertsberg East skarn Cu-Au deposits

PATRICK NADOLL<sup>1</sup> JOHN WALSHE<sup>1</sup> DAVID FRENCH<sup>2</sup> AND  
CLYDE LEYS<sup>3</sup>

<sup>1</sup>CSIRO, Australian Resources Research Centre, PO Box  
1130, Bentley, WA 6102, Australia

<sup>2</sup>CSIRO, Energy Technology, PO Box 52, North Ryde, NSW  
1670, Australia

<sup>3</sup>Freeport McMoRan Indonesia, Jakarta 12310 Indonesia

Recent years have seen an increased interest in the use of hydrothermal magnetite as a pathfinder mineral for exploration. Ongoing research puts further constraints on systematic compositional patterns in hydrothermal magnetite that can help to target deeply covered and remote deposits. We present preliminary data for hydrothermal magnetite from the Grasberg porphyry and the Ertsberg East Skarn System Cu-Au deposits. Both are among the biggest deposits of their types in the world and occur within the Ertsberg mineral district in Papua, Indonesia. Magnetite of igneous and hydrothermal origin is a widespread mineral phase in intrusive rocks and hydrothermal veins as well as in associated skarns. A total of 892 electron microprobe analyses of hydrothermal magnetite have been obtained. The main elements that can be used to characterize and discriminate hydrothermal skarn and porphyry magnetite are Mg, Al, V, Mn, and Zn. Titanium, Cr, Co, and Ni show little to no distinct variation between these two types of magnetite (Figure 1). Magnesium and Mn contents are comparable with concentrations found in hydrothermal magnetite from other skarn deposits. Titanium on the other hand appears to be characteristically enriched in hydrothermal skarn magnetite from the Grasberg deposit compared to skarn magnetite from other deposits.

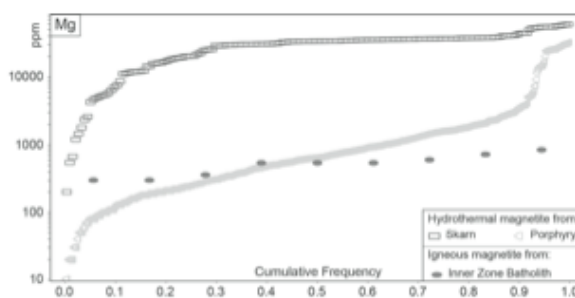


Figure 1 Probability plot for Mg concentrations in hydrothermal magnetite from the Grasberg deposit. Igneous magnetite from the Inner Zone Batholith, Japan is plotted as a reference.

## Large scale material transport in the protoplanetary disk and its relevance to the “planetary” oxygen isotopic composition

H. NAGAHARA<sup>1</sup> AND K. OZAWA<sup>2</sup>

<sup>1</sup>Dept. Earth Planet. Sci., The Univ. Tokyo, Hongo, Tokyo 113-0033, Japan. hiroko@eps.s.u-tokyo.ac.jp

<sup>2</sup> (ozawa @eps.s.u-tokyo.ac.jp)

Protoplanetary disk evolves basically due to the change of the accretion rate with time, of which most significant consequence is the change of temperature as a function of the location within the disk and time. Despite most physical models and astrophysical observations, meteoritic and planetary evidence strongly suggest the presence of high temperature stage at least in the early stage that resulted in isotopic homogenization of the inner solar system. Furthermore, the inner edge of the disk was faced to the proto-Sun for a long duration, where condensation /evaporation of planet-forming minerals should have occurred, and it is now well known that some of condensates were transported to the asteroid belt or even the comet regions. Oxygen isotope is one of the exceptions that retained isotopic heterogeneity in chondrites but approximate homogeneity in planets.

Large scale material transport was investigated by using the model by Ciesla (2011; ApJ 740) and the possibility of homogenization by oxygen isotopic exchange during drift of grains within the disk. The basics of the model is the radial advection and diffusion equation, where the stochastic diffusion term is introduced by the Monte Carlo method. The evolution of temperature and density radial profiles were described as a function of distance from the proto Sun, and therefore the trajectory of grains enables us to evaluate the thermal history. The disk is in a steady state, number of grains were 10000, oxygen isotope of dust formed in the inner edge is assumed to be -50 permils and ice from outside is +100 permils. We assume that  $T \sim 1000\text{K}$  is the boundary when grains exchange oxygen isotopes with the ambient gas.

The calculation results show that the average position moves inward with time, and grains larger than cm in order fell quickly to the Sun, but smaller grains remain in the disk, although large fraction of the grains fell into the Sun in  $10^6$  years with some grains experiencing  $T > 1000\text{K}$ . If the viscosity of the disk is as small as  $\alpha = 0.0001$ , most grains remain after  $10^6$  years. The results suggest that it is impossible to change oxygen isotopic composition of all the dust grains in the inner disk, and therefore, oxygen isotopes homogenization took place at the very early stage and that was retained through the disk evolution.

## Molybdenum Isotopic Compositions in Allende Chondrules

Y. NAGAI<sup>1\*</sup>, T. YOKOYAMA<sup>1</sup> AND W. OKUI<sup>1</sup>

<sup>1</sup>Department of Earth and Planetary Sciences, Tokyo Institute of Technology (Tokyo Tech), 2-12-1 Ookayama, Meguro, Tokyo 152-8551, Japan

(\*correspondence: yuichiro.nagai@geo.titech.ac.jp)

Chondrules are primordial materials formed in the early Solar system. They have various characteristics of the texture and petrography as well as  $\Delta^{17}\text{O}$  values that generally correlate with the classes of their host chondrites. It is argued that chondrules have formed in multiple reservoirs separated in time and space in the early Solar System. This is also supported by variable  $^{84}\text{Sr}/^{86}\text{Sr}$  ratios in chondrules from different chondrite groups [1]. However, there still remains unclear how individual chondrules have obtained the nucleosynthetic Sr isotope anomalies, nor is clear the linkage between isotope anomalies and the other characteristic properties of chondrules. In this study, we focus on Mo isotopes in chondrules to further constrain their formation processes. Molybdenum has seven isotopes produced by different nucleosynthetic processes (s-, r- and p-process). The Mo isotope anomalies recorded in bulk meteorites and CAIs would provide a clue to decode the material transport in the solar nebula [2], yet no Mo isotope data are available regarding chondrules.

Chondrules samples prepared by the freeze-thaw method. were dissolved using a mixture of HF-HNO<sub>3</sub> (3:1) in Teflon vessels at 180 °C. After drying at 120 °C, they were dissolved in 0.5M HF and centrifuged for several hours. Mo was purified by a two-step anion exchange column chemistry employing HCl-HF-HNO<sub>3</sub> (modified from [3]). Molybdenum isotopic compositions in the chondrules were measured by N-TIMS (TRITON *plus* at Tokyo Tech).

Allende chondrules are found to have Mo isotope anomalies (e.g.,  $\mu^{95}\text{Mo}/^{96}\text{Mo} = 94 \pm 27$  ppm) that are resolvable from those in bulk Allende [4] and Allende CAIs [2]. The anomalies in Allende chondrules are also distinctive from bulk Murchison [2,4], which has an s-process deficit in Mo isotopes. Thus, it is conceivable that chondrite matrices, CAIs and chondrules are formed from separated, isotopically distinctive reservoirs at least for Allende. Our result is consistent with Sr isotope anomalies observed in Allende meteorite [1].

[1] Okui & Yokoyama (2013). *LPSC*, **44th**, #2776. [2] Burkhardt *et al.* (2011). *EPSL*, **312**, 390-400. [3] Nagai *et al.* (2012). *Goldschmidt*, **22nd**, #4414. [4] Nagai & Yokoyama (2013). *LPSC*, **44th**, #2373.

## Development of Large-Scale Apparatus for Gas Production from Methane Hydrate Layer

JIRO NAGAO\*, YUSUKE JIN AND YOSHIHIRO KONNO

ProTech/MHRC, National Institute of Advanced Industrial Science and Technology (AIST), Sapporo 062-8517, Japan (correspondence: jiro.nagao@aist.go.jp)

### Background

To utilize methane hydrate as valuable natural gas resources, a suitable gas production technique and conditions should be established. Experimentally the production method and suitable conditions have been investigated using the core samples. The reproducible results on how methane hydrate dissociates under various conditions could be presented from core-sample experiments. Whereas a core-scale experiments in a laboratory can demonstrate the heat transport process, a dissociation of methane hydrates in an actual reservoir is dominated by the material flow process. In order to couple data obtained from core-scale experiments with the results of field-scale production tests, a large-scale gas production apparatus was conducted at the AIST [1], financially supported by MH21 Research Consortium.

### Certification of Apparatus

A large-scale production system for methane hydrate production tests can perform the dissociation experiments under the similar conditions of the actual reservoir under a deep sea floor. Developed large-scale apparatus is shown in Fig.1. The steel vessel has an inner diameter of 1000 mm, a height of 1500 mm and a volume of 1710 L. An overburden pressure of up to 16.5 MPa can be applied for sandy sample. The temperature of the vessel can be controlled from  $-5$  to  $20^{\circ}\text{C}$ . A production well of a steel pipe with a diameter of 100 mm and a length of 1000 mm with holes is connected to a gas and water separator. Holes in the side and bottom of vessel are provided to allow the insertion of gas, water and temperature/pressure sensors. Real-time observations of the rate of the production of gas and water can be performed.



Fig.1 Developed large-scale apparatus

[1] Nagao (2012) *Synthesiology* 5, 89-97.

## Microbially mediated redox processes in lactate stimulation with sedimentary rock and groundwater

T. NAGAOKA<sup>1\*</sup>, T. NAKAMURA<sup>1</sup>, Y. SASAKI<sup>2</sup>, T. ASANO<sup>2</sup>, T. ITO<sup>2</sup>, Y. AMANO<sup>3</sup>, T. IWATSUKI<sup>3</sup> AND H. YOSHIKAWA<sup>2</sup>

<sup>1</sup>Bioengineering sector, Environmental Science Research Laboratory, Central Research Institute of Electric Power Industry, 1646 Abiko, Chiba, 270-1194, Japan (\*correspondence: nagaoka@criepi.denken.or.jp)

<sup>2</sup>Geological Isolation Research and Development Directorate, Japan Atomic Energy Agency, Tokai, Ibaraki, Japan

<sup>3</sup>Geological Isolation Research and Development Directorate, Japan Atomic Energy Agency, Horonobe, Hokkaido, Japan

It is significant to investigate the geochemical groundwater evolution around the nuclear waste repository, because geochemical condition could influence the radionuclide migration behavior and corrosion of barrier materials in the repository. Therefore, a laboratory jar experiment was conducted with deep subsurface sedimentary rock and groundwater, in order to assess the response of the geochemical and microbial communities toward redox processes. The redox process was induced by exposure to air and discontinuation to sediment suspension, which simulated the process occurring during operation of nuclear waste repositories, i.e., tunnel excavation, transport of waste containers, and final backfilling. During the experiments, redox potential, dissolved oxygen, and pH in the suspension were measured, and the concentrations of dissolved ions concentration, HCl-extractable iron, and also head space gasses in the jar were analyzed. Moreover, microbial DNA was extracted from the suspension, and PCR-DGGE analysis was performed to analyze the response of microbial communities toward the geochemical changes. As a results, after discontinuation of air exposure with lactate amendment, redox potentials decreased from ca.  $+100$  mV to  $-600$  mV (vs. Ag/AgCl), and some sequential terminal electron-accepting process (TEAPs) was observed with the reactions of aerobic respiration, iron reduction and hydrogen fermentation. The related species of the microbes along with TEAPs, e.g., *Pseudomonas sp.* for aerobic respiration and *Shewanella sp.* for iron reduction, was also detected. These results indicated that the microbial activities would affect the geochemical changes in nuclear repositories.

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## Mineralogy, petrology, O and Mg-isotope compositions of AOAs from CH carbonaceous chondrites

KAZUhide NAGASHIMA<sup>1</sup>, ALEXANDER KROT<sup>1\*</sup> AND CHANGKUN PARK<sup>1</sup>

<sup>1</sup>HIGP/SOEST, University of Hawai'i at Manoa, Honolulu, HI, 96822, USA. \*(kazu@higp.hawaii.edu)

Amoeboid olivine aggregates (AOAs) in CH chondrites are texturally and mineralogically similar to those in other carbonaceous chondrite groups. They show no evidence for thermal metamorphism or alteration in an asteroidal setting and consist of nearly pure forsterite (Fa<sub>23</sub>), anorthite, Al-diopside, Fe,Ni-metal, spinel, ±low-Ca pyroxene (Fs<sub>1</sub>Wo<sub>23</sub>) and CAIs. The CAIs inside AOAs are composed of Al,Ti-diopside, spinel, perovskite, melilite (Åk<sub>13-44</sub>), anorthite, hibonite, and grossite. The CH AOAs, including CAIs within AOAs, have isotopically uniform <sup>16</sup>O-rich compositions ( $\Delta^{17}\text{O} = -23.5 \pm 2.2\%$ ) and on a three-isotope oxygen diagram plot along ~slope-1 line. The only exception is a low-Ca pyroxene-bearing AOA that shows a range of  $\Delta^{17}\text{O}$  values, from  $-24.3\%$  to  $-15.2\%$ . Melilite, grossite, and hibonite in four CAIs within AOAs show no evidence for radiogenic <sup>26</sup>Mg excess ( $\delta^{26}\text{Mg}^*$ ). In contrast, anorthite in 5 out of 6 AOAs measured has  $\delta^{26}\text{Mg}^*$  corresponding to (<sup>26</sup>Al/<sup>27</sup>Al)<sub>0</sub> of  $(4.4 \pm 0.6) \times 10^{-5}$ ,  $(4.2 \pm 0.6) \times 10^{-5}$ ,  $(4.0 \pm 0.6) \times 10^{-5}$ ,  $(1.7 \pm 0.2) \times 10^{-5}$ , and  $(1.7 \pm 0.2) \times 10^{-6}$ . Anorthite in another AOA shows no resolvable  $\delta^{26}\text{Mg}^*$ : (<sup>26</sup>Al/<sup>27</sup>Al)<sub>0</sub> <  $2 \times 10^{-6}$ . We infer that CH AOAs formed by gas-solid condensation, aggregation of the condensates mixed with the previously formed CAIs, thermal annealing, and possibly melting to a small degree in a <sup>16</sup>O-rich gaseous reservoir during a brief epoch of CAI formation. The lack of resolvable  $\delta^{26}\text{Mg}^*$  in melilite, grossite, and hibonite in CAIs within AOAs reflects heterogeneous distribution of <sup>26</sup>Al in the solar nebula during this epoch. The observed variations of the inferred initial <sup>26</sup>Al/<sup>27</sup>Al ratios in anorthite of the mineralogically pristine and uniformly <sup>16</sup>O-rich CH AOAs could have recorded (i) admixing of <sup>26</sup>Al in the protoplanetary disk during the earliest stages of its evolution and/or (ii) closed-system Mg-isotope exchange between anorthite and spinel+forsterite+Al-diopside during subsequent prolonged (days-to-weeks) thermal annealing at T>1000°C and slow cooling rates (~0.01 K hr<sup>-1</sup>) that has not affected their O-isotope systematics. The proposed thermal annealing may have occurred in an impact-generated plume invoked for the origin of non-porphyratic magnesian chondrules and Fe,Ni-metal grains in CH and CB carbonaceous chondrites about 5 Ma after formation of CV CAIs.

## Rare-earth element speciation in ferromanganese oxides from the Indian Ocean

B. NAGENDER NATH<sup>1</sup>, T.C.VINEESH<sup>2</sup> AND G. PARTHIBAN<sup>3</sup>

<sup>1</sup>CSIR-National Institute of Oceanography, Goa-403004, India, nagender@nio.org

<sup>2</sup>Faculty of Maritime Studies, King Abdulaziz University, Jeddah, Saudi Arabia, vineeshtc@gmail.com

<sup>3</sup>CSIR-National Institute of Oceanography, Goa-403004, India, parthi@nio.org

Oceanic ferromanganese oxides are major sinks for rare-earth elements (REE); hydrogenous oxides being especially suitable for cerium enrichment. Deep-sea muds and ferromanganese nodules and encrustations are considered as potential future sources of REEs. There are differing views on the relative importance of two oxides of Fe and Mn as the REE carriers. Here we present results from sequential leaching experiments performed on different types of ferromanganese oxides from the Indian Ocean in order to quantify the amount of REE associated with the hydrous Mn oxides and Fe oxides. A four-step sequential leaching method is employed here, which is intended to selectively leach metals that are surface adsorbed/loosely bound, Mn-oxide bound, Fe-oxide hosted or held in aluminosilicate residue respectively. Results of this sequential extraction experiment work have revealed that nearly all REEs are closely associated (above 95%) with Fe-bearing phase. The shale-normalized patterns of iron-oxide bound fraction show a distinct similarity in shape and magnitude with the bulk REE patterns except for Ce. Similar magnitude suggests that much of the REEs are hosted by iron-oxyhydroxide phase. Likewise, ~90% of cerium is bound to iron oxide phase and this phase displays a positive Ce anomaly which is typical of low temperature ferromanganese oxides. In contrast, Mn-oxides exhibit a weak positive Ce fractionation. A pronounced positive cerium anomaly in the iron oxide phase suggests an important role of Fe-oxide in acquiring positive Ce anomaly. Enrichment of other tetravalent elements such as Zr, Th and Hf in this phase suggests that the Ce-oxidation must have taken place before the adsorption.

A distinct europium positive anomaly and depleted HREE is seen in the manganese oxide phase in many of the samples. Fractionation of Eu from other REEs and reduction of Eu<sup>+3</sup> to Eu<sup>+2</sup> can only occur at temperatures above 200–250°C and characteristic of hydrothermal plume particulates and seawater. This is interesting and may pose a question as to whether the hydrothermal sources are contributing Mn to the CIB nodules.

## Mollusc clumped isotope thermometry using a new approach

PRASANNA NAIDU K.<sup>1A</sup> AND PROSENJIT GHOSH<sup>2</sup>

<sup>1</sup>(prasanna@ceas.iisc.ernet.in)

<sup>2</sup>(pghosh@ceas.iisc.ernet.in)

We present a new approach of calibrating clumped isotope thermometry for mollusc. In our study we sampled growth bands from live mollusc specimens (*Villorita cyprinoides* var. *cochinensis*) collected from Cochin back water estuary in India. The growth bands represent seasonal carbonate deposition at different temperatures during a year. Simultaneous collection of water samples and co-existing carbonate allowed calculation of temperature using Epstein thermometry [1]. The temperature estimated using this approach showed seasonal range of 20° C to 42 °C.

The  $\Delta_{47}$  values are derived using the method described in Ghosh *et al* 2006 [2] where heated gas equivalent together with carbonate standards (like NBS-19 and MAR J1) are analysed. The approach in producing this calibration curve varies from Henkes *et al.*, 2013 [3] where bulk samples of mollusc species collected from natural marine setup across latitudes along with specimens grown under monitored conditions were analysed for  $\Delta_{47}$  using carbon dioxide equilibrium scale. Our relation obtained as a function of temperature (in kelvin) is

$\Delta_{47} = 0.055 \times 10^6/T^2 + 0.02$  ( $r^2 = 0.8996$ ), which matches well with the inorganic calcite precipitation curve. We are monitoring the similar specimens at laboratory condition at different temperatures to further evaluate the thermometry equation.

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## A first look at boron isotope based pCO<sub>2</sub> values from the eastern Arabian Sea for the last 22 kyr

S. S. NAIK<sup>1\*</sup>, P.D. NAIDU<sup>1</sup>, S. N. NAIK<sup>1</sup>  
AND G. L. FOSTER<sup>2</sup>

<sup>1</sup>CSIR-National Institute of Oceanography, Goa, India 403004  
(\*correspondence: sushant@nio.org)

<sup>2</sup>Ocean and Earth Science, National Oceanography Centre  
Southampton, University of Southampton, SO14 3ZH,UK  
(Gavin.Foster@noc.soton.ac.uk)

The Arabian Sea is an unique region with semi-annual reversal of surface water circulation between southwest (SW) and northeast (NE) monsoons. The pCO<sub>2</sub> in the Arabian Sea is always in excess of that in the atmosphere, and the EAS is found to serve as a significant source of carbon dioxide to the atmosphere [1]. However nothing was known up to today about the past pCO<sub>2</sub> variations of the EAS.

We present here for the first time pCO<sub>2</sub> values from the eastern Arabian Sea for the last 22 kyr. We have used planktonic foraminifera species *Globigerinoides ruber* (*sensu stricto*) from a sediment core AAS9/21, collected at 1807m water depth (14°30.539'N, 72°39.118'E). We have analysed boron isotopes on a MC-ICPMS at the University of Southampton, UK. pH and pCO<sub>2</sub> were calculated from the boron isotopic values. Results show that pCO<sub>2</sub> varied from ~200 to ~440ppmv during the study period. A comparison with atmospheric CO<sub>2</sub> data from Antarctic ice core [2] suggest that the EAS seems to have fluctuated between a source and sink of atmospheric CO<sub>2</sub> in the past, with significant excess (w.r.t. the atmosphere) during the deglacial. Further comparison with western Arabian Sea (WAS) pCO<sub>2</sub> values [3] for the similar period reveals that during most of the time the WAS pCO<sub>2</sub> values were much higher as a result of intense upwelling which brings CO<sub>2</sub>-rich sub-surface waters to the surface. The large variations in pCO<sub>2</sub> from the EAS are probably be due to a combination of physical processes such as moderate upwelling, influx of freshwaters from rain and rivers, and winter convective mixing processes.

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## Cerium stable isotope fractionation as a potential paleo-redox proxy

RYOICHI NAKADA<sup>1\*</sup>, YOSHIO TAKAHASHI<sup>1,2</sup>, AND  
MASAHARU TANIMIZU<sup>2,1</sup>

<sup>1</sup> Hiroshima University, Higashi-Hiroshima, Hiroshima, ryo-  
(nakada@hiroshima-u.ac.jp)

<sup>2</sup> Japan Agency for Marine-Earth Science and Technology  
(JAMSTEC), Nankoku, Kochi 783-8502, Japan

Cerium (Ce) has anomalously high or low concentrations relative to its neighboring elements, lanthanum (La) and praseodymium (Pr), because of its chemical properties; this phenomenon is known as the Ce anomaly. This redox-sensitive property of Ce allows the estimation of the redox state of paleo-ocean environments and the evolution of the atmosphere. However, a consideration of only the relative abundance of Ce may lead to an incomplete understanding of its oxidation process. In the current study, three important geochemical parameters, namely, abundance, stable isotope ratio, and chemical speciation, were obtained for Ce to derive more information from the Ce anomaly. Assuming equilibrium isotopic fractionation, the mean isotopic fractionation factors between the liquid and solid phases ( $\alpha_{L-S}$ ) of (i) Ce adsorbed on ferrihydrite, (ii) spontaneous precipitation of Ce, and (iii) Ce adsorbed on  $\delta$ -MnO<sub>2</sub> were 1.000145 ( $\pm 0.000022$ ), 1.000196 ( $\pm 0.000031$ ), and 1.000411 ( $\pm 0.000079$ ), respectively. These results indicate that the degree of isotopic fractionation of Ce between the liquid and solid phases becomes larger as the redox condition becomes more oxic in the following order: adsorption without oxidation < spontaneous precipitation < oxidative adsorption. Previously, the appearance of the Ce anomaly and/or XANES analysis constituted the only tool available for exploring the redox state. This study, however, suggests that the degree of mass-dependent fractionation of Ce can be used to clearly distinguish spontaneous precipitation from oxidative adsorption on  $\delta$ -MnO<sub>2</sub>, that occurs under more oxic conditions than the Ce(III)/Ce(IV) boundary. Our results suggest that the combination of the stable isotope ratio and chemical state of Ce can be used to classify the redox condition into the three stages based on Ce geochemistry, thereby offering a powerful tool for exploring redox conditions in paleo-ocean environments.

[1] R. Nakada, Y. Takahashi, and M. Tanimizu, Isotopic and speciation study on cerium during its solid-water distribution with implication for Ce stable isotope as a paleo-redox proxy. *Geochim. Cosmochim. Acta* 103 (2013) 49-62.

## Stable isotopes of heavy elements in the modern ocean

YUSUKE NAKAGAWA, SHOTARO TAKANO  
AND YOSHIKI SOHRIN\*

Institute for Chemical Research, Kyoto University, Gokasho  
Uji, Kyoto 611-0011, Japan (\*correspondence:  
sohrin@scl.kyoto-u.ac.jp)

Stable isotopes of heavy elements are now emerging as powerful tracers in the modern ocean and proxies in the paleocean (Tanimizu *et al.*, 2013). Mass fractionation of heavy elements in marine environments is expected to provide unique information on a number of processes. The isotopic compositions of dissolved heavy metals in seawater are fundamental data for stable isotope marine chemistry. However, the precise analysis of seawater is highly challenging (Boyle *et al.*, 2012). The target elements occur at nmol/kg to pmol/kg in seawater. For the precise isotopic ratio determination using MC-ICPMS or TIMS, we have to preconcentrate the analytes quantitatively with a 50-1000-fold enrichment factor from a kg scale sample. It is also important to chemically separate the analytes from interfering major and minor constituents. In addition, it is critical to avoid contamination of the analytes through the sampling, pretreatment, chemical separation, and measurement. Preconcentration using chelating resins seems promising for this purpose.

We have developed a new method for the precise determination of Mo isotope ratios in seawater on the basis of preconcentration using the TSK-8HQ chelating resin and measurement by MC-ICPMS (Nakagawa *et al.*, 2008). Using this method, we have analyzed 172 seawater samples obtained from the Pacific, Atlantic, and Southern Oceans, with an oxygen concentration of 16–373  $\mu\text{mol/kg}$  (Nakagawa *et al.*, 2012). The average isotope composition in  $\delta\text{Mo}$  (relative to a Johnson Matthey Mo standard solution) was as follows:  $\delta^{92/95}\text{Mo} = -2.54 \pm 0.16\text{‰}$  (2SD),  $\delta^{94/95}\text{Mo} = -0.73 \pm 0.19\text{‰}$ ,  $\delta^{96/95}\text{Mo} = 0.85 \pm 0.07\text{‰}$ ,  $\delta^{97/95}\text{Mo} = 1.68 \pm 0.08\text{‰}$ ,  $\delta^{98/95}\text{Mo} = 2.48 \pm 0.10\text{‰}$ , and  $\delta^{100/95}\text{Mo} = 4.07 \pm 0.18\text{‰}$ . These results demonstrate that Mo isotopes are uniformly distributed in the modern oxic ocean, strongly supporting the possibility of seawater as an international reference material for Mo isotopic composition.

Recently we have developed a new method for the isotopic analysis of dissolved Cu in seawater (Takano *et al.*). We are now studying the isotopic composition of Cu of the modern ocean. Our data suggest that the combination of concentration and isotopic composition of Cu would be useful to evaluate relative significance of biogeochemical processes.



## Nature of transition metals on fine and ultrafine particles and the cytotoxicity

Y. NAKAMATSU, T. AOKI AND S. UTSUNOMIYA

Dept. Chemistry, Kyushu University, Fukuoka 812-8581, Japan (utsunomiya.satoshi.998@m.kyushu-u.ac.jp)

Despite of mounting evidence indicting adverse health effects of ultrafine particle (UFP; <100 nm in diameter), it is difficult to appropriately evaluate the toxicity because of the small size, various shape, mixed chemical state and complicated crystal structure. Transition metals are known to be a factor that causes damage by inducing reactive oxygen species (ROS). The aim of this study is to systematically understand the nature of UFP associated with transition metals and the adverse health effects on lung cells based on the rigorous investigation of crystallo-chemical property of individual UFP in the urban atmosphere and the cytotoxicity assessment.

Inductively coupled plasma mass spectrometry (ICP-MS), X-ray absorption near-edge structure (XANES), scanning and transmission electron microscopy (SEM and TEM) have been employed to rigorously characterize particulate matters collected at urban areas of Fukuoka and Tokyo, and at remote area of Nagasaki. Epithelium cells and macrophage cells were exposed to 0.5-50 ug/ml of SRM 1649a, magnetite nanoparticle, and heavy metal ions, Fe, Mn, Ni and Cr, for 12 hours-26 days in a humidified atmosphere at 37 °C and 5% CO<sub>2</sub>. Cytotoxicity assessment was performed using WST assay. Statistic analysis was carried out based on analysis of variance (ANOVA).

All samples revealed that the dominant Fe speciation of the size fraction >1 µm was Fe-bearing aluminosilicate, while that in submicron-size fraction was ferric Fe oxides. In the urban UFP, major Fe species was spinel-structured Fe oxides such as magnetite or maghemite, and some of them were mixed with Mn, Cr and Ni. In addition, sulfate and SiO<sub>2</sub> coating were identified in some of those particles.

Both urban UFPs and magnetite nanoparticles did not reveal an acute health effects on the lung cells; however, an exposure to aqueous Mn<sup>2+</sup> significantly decreased the viability. Ni<sup>2+</sup> also revealed the cytotoxicity in less extent. These results suggest that the speciation of heavy metals in the solution determine their toxicity, and protein and amino acid may decrease the toxicity of heavy metals by forming complexes. Because Fe-bearing nanoparticles did not decrease the viability, the soluble species of the other toxic metals, namely Mn and Ni, are the primary factor determining the acute cytotoxicity. On the other hand, long life-time of magnetite nanoparticles in alveoli solution resulted in the phase transformation from spherical magnetite to needle-shaped oxyhydroxide, which may result in an increase in the toxicity.

## Non-ideal fluid geometry in the mantle and lower crust

M. NAKAMURA<sup>1\*</sup>, S. OKUMURA<sup>1</sup>, T. YOSHIDA<sup>1</sup>, O. SASAKI<sup>2</sup>, AND E. TAKAHASHI<sup>3</sup>

<sup>1</sup>Dept. Earth Sci., Tohoku University, Aobaku, Sendai 980-8578, Japan (\*correspondence: nakamm@m.tohoku.ac.jp)

<sup>2</sup>Tohoku University Museum, Aobaku, Sendai 980-8578, Japan (sasaki@museum.tohoku.ac.jp)

<sup>3</sup>Dept. Earth Planet. Sci., Tokyo Institute of Technology, Tokyo 152-8551, Japan (etakahas@geo.titech.ac.jp)

Fluid phases characterize the physical and chemical processes in subduction zones. The conventional view on grain-scale fluid distribution is based on dihedral angle between minerals and fluids in isotropic monomineralic rocks (i.e. ideal “equilibrium” geometry). Natural rocks are, however, composed of anisotropic multiple phases and undergo textural adjustment to minimize interfacial and strain energy such as grain growth and dynamic recrystallization, which results in microstructural complexity. To understand real fluid distribution in deep-seated rocks, we conducted an X-ray CT study of xenoliths from the lower crust and uppermost mantle from Ichinomegata-Maar, NE Japan. All the observed spinel lherzolite, hornblendite, and hornblend gabbro xenoliths contained upto a few vol% of intergranular pores, indicating that the rocks were saturated with a free-fluid phase (Figure 1). The imaged pore fluids are typically polyhedral and tens–hundreds of micrometers in scale; this suggests that they were formed via coalescence of smaller pore fluids. The fluids are localized in interphase boundaries (between different mineral phases), while most of the monomineralic triple junctions lack pore fluids. All these characteristics are consistent with the results of grain-growth experiments in a fluid-bearing bimineralic system[1]; in other words, the role of interfacial energy anisotropy and grain growth are crucial in determining fluid distribution in nature. The geometry, distribution and thus connectivity of fluids cannot be assessed simply from dihedral angles.

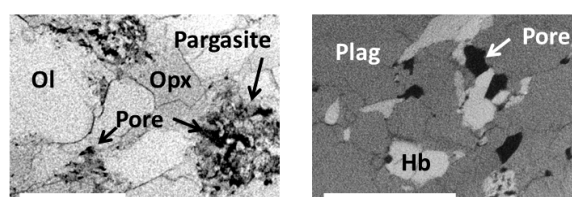


Figure 1: Typical CT images of pores in the lherzolite (left) and hornblende gabbro (right) xenoliths. Scale bars, 500 µm.

[1] Ohuchi and Nakamura (2005) *J. Geophys. Res.* **111**, B01201, doi:10.1029/2004JB003340.



## ***In situ* observation of electrical current generation in deep-sea**

HASHIMOTO<sup>4</sup> KEN TAKAI<sup>2,3</sup> AND HYDROTHERMAL ENVIRONMENTS RYUHEI NAKAMURA<sup>1</sup>, MASAHIRO YAMAMOTO<sup>2,3</sup>, KAZUMASA OGURI<sup>2</sup>, SHINSUKE KAWAGUCCI<sup>2,3</sup>, KATSUHIKO SUZUKI<sup>3</sup>, AND KAZUHIITO

<sup>1</sup>RIKEN Center for Sustainable Resource Science, Wako, Saitama 3510198, Japan, (ryuhei.nakamura@riken.jp)

<sup>2</sup>Institute of Biogeosciences, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Yokosuka, Japan

<sup>3</sup>Submarine Resources Research Project, JAMSTEC, Yokosuka, Japan

<sup>4</sup>Department of Applied Chemistry, School of Engineering, The University of Tokyo, Japan

Deep-sea hydrothermal vents discharge subsea floor hot and reductive fluids into cool and oxidative seawater. The inter-fluidal oxidation-reduction potential substantially drives various abiotic and biotic oxidation-reduction reactions and supports chemosynthetic ecosystems in the mixing zones. It is predicted that electric current is generated if the two solutions are connected by conductor with electrodes [1]. Here we conducted *in situ* electrochemical analyses of high temperature of hydrothermal fluids and ambient seawater. We succeeded in measurement of the oxidation-reduction potential as about -39mV at high temperature about 309°C in deep-sea hydrothermal fluid. The voltammetry analyses indicated that the open circuit voltage between the hydrothermal fluid and ambient seawater bridged by platinum electrodes was up to 0.74 V but the average current density generated in the seawater cathode was much lower than that in the hydrothermal-fluid-anode. By harvesting the natural setting of potential steep, we for the first time show proof of *in situ* generation of electricity in a newly developed fuel cell installed in deep-sea hydrothermal vents and witness light emitting diode lamp lighting in dark deep-sea environment. The results provide important clues not only to understanding of extracellular electron transports in the deep-sea vent microbial communities but also to future development of *in situ* electric power plants that will supply the electricity for the exploration of deep-sea resources and the following observatories of the deep-sea environments and ecosystems.

[1] R.Nakamura *et al.* *Angew. Chem.* 2010 **49**, 7692.

## **Millennial-scale wet and dry climate changes during the last glacial maximum in the south Siberia**

F.W. NARA<sup>1\*</sup>, T. WATANABE<sup>1\*</sup>, T. KAKEGAWA<sup>2</sup>, K. MINOURA<sup>2</sup>, S. YAMASAKI<sup>1</sup>, N. TSUCHIYA<sup>1</sup>, T. NAKAMURA<sup>3</sup> AND T. KAWAI<sup>4</sup>

<sup>1</sup>Graduate School of Environmental Studies, Tohoku University, Sendai 980-8579, Japan. (narafumi@m.tohoku.ac.jp)

<sup>2</sup>Department of Earth and Planetary Materials Science, Graduate School of Science, Tohoku University, Sendai, 980-8578, Japan

<sup>3</sup>Center for Chronological Research, Nagoya University, Nagoya, 464-8602, Japan

<sup>4</sup>Association of International Research Initiatives for Environmental Studies, Tokyo, Japan

To investigate the millennial-scale wet and dry climate changes in the south Siberian region for the last 33 kyr, the centennial scale analysis (less than 70 years) of the inorganic elements (e.g. K and Ti) for the Lake Baikal sediment core (VER99G12) were carried out. The fluctuation of the K/Ti ratio during the last glacial maximum period (LGM; 26–19 cal kyr BP) was observed (Fig. 1). Because of the susceptible to water leaching of K comparing to Ti in soil environment, this fluctuation indicates the millennial-scale wet and dry climate changes during the LGM in the south Siberian region. Also, the increase in the precipitation at the climate transition period between OIS2 and 1 (OIS2/1, 11.5 cal kyr BP) was indicated by the significant decrease in the K/Ti ratio. The result of the grain size distribution of the same core is also discussed as well.

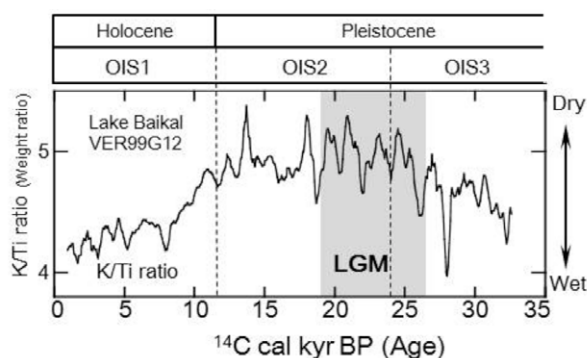


Figure 1. Vertical profile of the K/Ti ratio of the Lake Baikal sediment core (VER99G12). OIS; Oxygen isotope stage

## Mass-independent fractionation of sulfur isotopes for all S-bearing components of Archean sediments

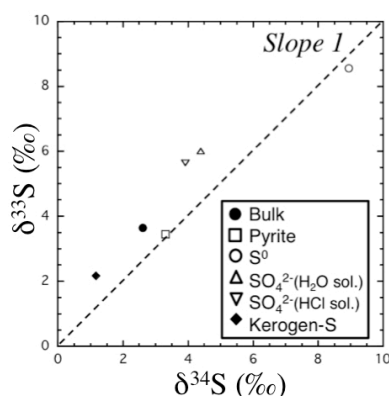
HIROSHI NARAOKA<sup>1</sup>, EMI MORIWAKI<sup>1</sup> AND SIMON R. POULSON<sup>2</sup>

<sup>1</sup>Dept. Earth & Planet. Sci., Kyushu Univ., Japan  
(naraoka@geo.kyushu-u.ac.jp)

<sup>2</sup>Dept. Geol. Sci. & Engineer., Univ. Nevada-Reno, USA  
(poulson@mines.unr.edu)

Mass-independent isotope fractionation of sulfur (MIF-S) signatures in Archean sediments have been often used to infer the presence of an O<sub>2</sub>-poor atmosphere, as UV photolysis of atmospheric SO<sub>2</sub> can produce MIF-S in the absence of an ozone layer [e.g. 1]. However, recent theoretical [2] and experimental [3,4] studies have shown that non-photochemical processes can also produce MIF-S. Hence, key factors controlling the production of MIF-S signatures in Archean sediments remain unclear. In this study, we performed  $\delta^{34}\text{S}$ - $\delta^{33}\text{S}$  analyses of S-bearing fractions and bulk samples of ~2.7 Ga black shales from drill core from the Jeerinah Formation, Western Australia. Elemental sulfur (S<sup>0</sup>), sulfate (water-soluble and HCl-soluble fractions), pyrite and organic-bound sulfur (kerogen-S) fractions were obtained by solvent extraction and gravity separation.

A slope of ~1 is observed for many bulk samples in a plot of  $\delta^{33}\text{S}$  vs.  $\delta^{34}\text{S}$ , but also for the S-bearing fractions (Fig. 1). The S-bearing fractions show large intra-sample heterogeneity (up to 8‰ for  $\delta^{34}\text{S}$ ), and positive  $\Delta^{33}\text{S}$  values for all fractions (up to 6‰). The presence of MIF-S for all S-bearing fractions indicates multiple sulfur sources throughout the Archean sulfur biogeochemical cycles, and suggest that possible modern weathering has had little impact upon S-isotope signatures.



**Figure 1.** Intra-sample  $\delta^{34}\text{S}$ - $\delta^{33}\text{S}$  heterogeneity in Archean sediment.

[1] S. Ono *et al.*, *EPSL* **213**, 15 (2003) [2] A.C. Lasaga *et al.*, *EPSL* **268**, 225 (2008) [3] Y. Watanabe *et al.*, *Science* **324**, 370 (2009) [4] H. Oduro *et al.*, *PNAS* **108**, 17635 (2011).

## Use of homogenized sediment in experimental set up: Re-stabilization of redox fronts and artifacts due to sieving methods

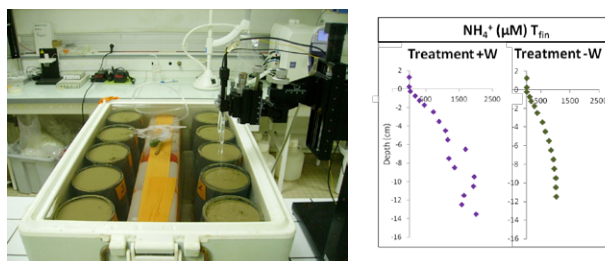
M.P. NARDELLI<sup>1\*</sup>, E. METZGER<sup>1</sup>, C. BARRAS<sup>1</sup>, F. JORISSEN<sup>1</sup> AND E. GESLIN<sup>1</sup>

<sup>1</sup> LUNAM University, Université d'Angers, UMR CNRS, 6112UMR, LPGN-BIAF, Angers, France.

(\*correspondence: mariapia.nardelli@univ-angers.fr)

In experimental microcosms where the addition of marine sediments is needed to mimic natural benthic systems, sieved and homogenized natural sediment is often used (e.g.[1]), but the consequences of sieving methods on early diagenetic processes and their possible effects on experimental results are often neglected.

Our experiment investigated the effects of two different sieving methods on organic matter concentration and mineralization, exchanges at water/sediment interface and geochemical steady state reaching times for the main chemical species (O<sub>2</sub>, Fe<sup>2+</sup>, PO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, ΣNO<sub>3</sub>, H<sub>2</sub>S, SO<sub>4</sub><sup>2-</sup>).



**Figure 1** Experimental set up

One set of sediment samples was sieved (<38μm) with natural seawater (+W). The other was sieved without additional water (-W). The results show that while oxygen penetration depth in both treatments is stable within 7 days, the other chemical species show higher concentrations and longer time to reach steady state after the -W sieving treatment compared to the other sieving method. This is suggested to be due to the removal of organic matter during the +W treatment.

[1] Koho *et al.* (2011), *FEMS Microbiol. Ecol.* **75**, 273–283.

## Granite compositions in a veined-lower mantle, as indicated by mineral inclusions in diamonds from Juína deposits, Brazil

NARDI, L.V.S.<sup>\*1</sup>; PLÁ CID, J.<sup>2</sup>; PLÁ CID, C.C.<sup>3</sup>; GISBERT, AND P.E.<sup>4</sup>; BALZARETTI, N.M.<sup>5</sup>.

<sup>1</sup>Instituto de Geociências, Universidade Federal do Rio Grande do Sul, Brazil. (lauro.nardi@ufrgs.br)

<sup>2</sup>Departamento Nacional de Produção Mineral (DNPM), Brazil. (jorge.pla@bol.com.br)

<sup>3</sup>Universidade Federal de Santa Catarina, Brazil.

<sup>4</sup>Facultad de Geología - Universidad de Barcelona, Spain. E-mail: (pedro@natura.geo.ub.es)

<sup>5</sup>Instituto de Física - Universidade Federal do Rio Grande do Sul, Brazil.

The mineral inclusions of diamonds are the only natural samples from lower mantle. Recent studies of the inclusions in the alluvial diamonds from Juina province, Brazil, which are believed to be formed in the lower mantle and in the transition zone, have shown the presence of K- and Na-bearing inclusions with structures corresponding to hollandite and composition equivalent to those of alkali feldspars. Compositional determinations were obtained with electron microprobe, and structural information from RAMAN microspectroscopy. Hollandites, stichovite, phengite, CAS-phase, titanite and Na-Ca-garnet/cpx are in composite inclusions with hydrous MgFeAl-perovskite and almandine-grossularite garnet; isolated inclusions of ferropericlaase, ilmenite and pigeonite-augite clinopyroxene were also observed. Na- and K-hollandite can also occur as isolated inclusions. K- and Na-hollandite + SiO<sub>2</sub> in the same diamond grains indicate the presence of melts crystallizing, at the lower mantle, products with compositions corresponding to granitic rocks. The association with abundant inclusions of ferropericlaase and MgFeAl-perovskite suggests a highly heterogeneous mantle, probably with a 'veined'-structure similar to that suggested by Foley<sup>(1)</sup>, but, with veins of granite composition. The growth of diamonds in the parts of mantle where melting occurred and these veins were formed, is consistent with high concentrations of volatiles, probably originated from subducted oceanic lithosphere.

<sup>(1)</sup> Foley, SF (1992) *Lithos* 28:435-453.

## Crystal-melt partitioning of REE and evolution of Martian melts

W. NASH<sup>1,\*</sup> AND B. WOOD<sup>1</sup>

<sup>1</sup>Department of Earth Science, Oxford University, Oxford, UK, (\*correspondence: william.nash@earth.ox.ac.uk)

REE concentrations in the SNC (Shergottite-Nakhilite-Chassignite) meteorites preserve information about the nature of their source regions, now widely believed to be the Martian mantle [1]. In particular, the influence of major phases on partial melting and fractional crystallisation can be inferred from REE concentrations in the meteorites, provided mineral-melt partition coefficients are known for each element under the appropriate conditions, and provided the REE concentrations (assumed chondritic) of the source region are known. Such information may then be combined with knowledge of the pressure-temperature-dependences of the inferred phase's stability to yield constraints on the depth of melting within the Martian mantle.

We have experimentally determined mineral-melt partition coefficients for a wide range of trace elements, between a synthetic Martian primary melt [2] and each of the conjectured major mantle-forming minerals (olivine, orthopyroxene and clinopyroxene) [3]. Experiments were conducted in a piston-cylinder apparatus at 15 kbar pressure, 1340°C, in graphite capsules. The  $fO_2$  conditions approximate those anticipated during melting of Mars' mantle [4]. The new data have relevance for questions concerning the degree of relatedness among the SNC meteorites, and by extension the extent of heterogeneity within the Martian mantle.

In addition to their application to Mars specifically, these new partitioning data provide a test of the Wood and Blundy partitioning model [5] for iron-rich systems, and of its extension to similar situations for which experimental data are not currently available. Data for clinopyroxene in particular show close agreement with the model (for trivalent cations occupying the M2 site), with a maximum partitioning value ( $D_o$ ) of 0.31, and an ideal radius ( $r_o$ ) 0.97Å similar to the values reported for terrestrial clinopyroxenes under similar conditions [5].

[1] Treiman *et al* (2000). *Planetary and Space Science*, 48(12-14), 1213-1230. [2] Bertka and Holloway (1993a). *Contributions to Mineralogy and Petrology*, 115(3), 313-322. [3] Bertka and Holloway (1993b). *Contributions to Mineralogy and Petrology*, 115(3), 323-338. [4] Filiberto, *et al* (2010). *Geophysical Research Letters*, 37(13). [5] Wood and Blundy (1997). *Contributions to Mineralogy and Petrology*, 129(2-3), 166-181.

## Geochemical modelling of salt systems: Case study Sebkhia Om lekhalate

NASRI N.<sup>1</sup>, BOUHLILA R.<sup>2</sup>, SAALTINK M. W.<sup>3</sup> AND GAMZO P.<sup>4</sup>

<sup>1</sup>Laboratory of Modelling in Hydraulic and Environment National School of Engineering of Tunis, (nasri.hydro@gmail.com)

<sup>2</sup>National School of Engineering of Tunis, (bouhlila.rachida@enit.rnu.tn)

<sup>4</sup>GHS, Dept Geotechnical Engineering and Geosciences, Universitat Politècnica de Catalunya, UPC- Barcelona,

<sup>3</sup>Water Department, University of the Republic, Uruguay

The process of evaporation constitutes very important phenomena in formation of salt system in arid environment [1]. Based in hydrogeochemical modeling, CHEPROO and PROOST using data base Pitzer [2] elaborate the evolution of the salt sequence minerals according to the time and along the distance.

The center of sabkha in characterized by enrichment in mirabilite ( $\text{Na}_2 \text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) and depletion of calcium in clay formation.

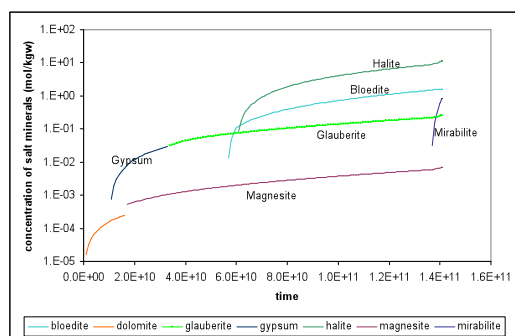


Fig. Salt minerals according to the time

[1] Bouhlila 1999 thesis ENIT. [2] Pablo *et al.* 2011 Journal of Hydrology **401** 154–164

## Chromium mobility in Tuscan serpentinite bodies: Inferences from rodingitization and carbonation

C. NATALI<sup>1\*</sup>, C. BOSCHI<sup>1</sup>, I. BANESCHI<sup>1</sup>, A. DINI<sup>1</sup>, AND L. CHIARANTINI<sup>1</sup>

<sup>1</sup>CNR-Istituto di Geoscienze e Georisorse, Pisa, Italy

(\*correspondence: c.natali@igg.cnr.it)

The natural heavy metal enrichment of Tuscan ultramafic rock bodies and derived soils represents an important environmental concern for the area in which they outcrop. Moreover, most of them are superficial aquifers due to their high level of fracturing, thus representing an ideal study case to evaluate the mobility of heavy metal. Despite a comparable whole rock geochemistry, the heavy metal content of spring waters outpouring from the various ophiolitic outcrops reveals significant differences. The highest level of total chromium are detected in spring waters circulating in naturally carbonated serpentinites whereas very low chromium amount is recorded in non-carbonated serpentinite aquifers. Moreover, beside the total chromium content, also the CrVI in the most enriched waters exceed the maximum allowed from the Italian regulation and has therefore monitored and evaluated [1]. The key factors controlling both chromium mobility and carbonation potential have to be referred to the different oceanic history of these rock bodies that led in some occurrences to the alteration of the primary Cr-bearing phases. In particular, in the ophiolitic outcrop of Montecastelli Pisano (PI), serpentinitisation and subsequent modal Ca-metasomatism affecting serpentinite promoted the spinel re-equilibration and Cr transfer from Mg-Al-chromite (and chromite) to adjacent newly formed silicate phases (Cr bearing garnet and Cr-chlorite) whose are significantly more sensible to weathering. The intense Fe-brucite (and serpentine) vein crosscutting the whole serpentinites should provided a viable pattern for the CO<sub>2</sub>-rich fluids circulating in these rocks to leach out Cr, and other elements, from alteration minerals. The carbonation of the serpentinite body, mainly affecting Fe-brucite vein, led to an increase of the porosity and therefore enhancing the mineral weathering. In addition, the massive Fe-brucite dissolution controlling carbonation, led to the formation of Mg-Fe-carbonates and Mg-Fe-Layered Double Hydroxydes (LDH) in the carbonated veins, in which CrIII can substitute FeIII and potentially oxidized to CrVI [2].

[1] Chiarantini *et al.*, (2013) *Geo. Res. Abs.* **15**, EGU2013-8839. [2] Radha & Vishnu Kamath (2004) *Bul. Mater. Sci.* **27**, 355–360.

## High precision determination of the terrestrial $^{40}\text{K}$ abundance

M.O. NAUMENKO<sup>1\*</sup>, K. MEZGER<sup>1</sup>, T.F. NÄGLER<sup>1</sup> AND I.M. VILLA<sup>1,2</sup>

<sup>1</sup>Universität Bern, Institut für Geologie, Baltzerstrasse 3, CH-3012 Bern, Switzerland. (correspondence: naumenko@geo.unibe.ch)

<sup>2</sup>Università di Milano Bicocca, Piazza della Scienza 4, 20126 Milano, Italy

$^{40}\text{K}$  is one of the important constituents of the age equation used for K-Ar and K-Ca dating systems. The main sources of the uncertainty in K-Ca, K-Ar and  $^{39}\text{Ar}$ - $^{40}\text{Ar}$  ages are the branching ratio of the  $^{40}\text{K}$  decay, the total decay constant and the abundance of  $^{40}\text{K}$ . The most recent reports [1] imply that the least precisely known term in the K-Ar age equation is the abundance of  $^{40}\text{K}$ . A  $^{40}\text{K}$  abundance of  $(1.1672 \pm 41) \times 10^{-4}$  was measured on terrestrial material [2], which is to this day the basis of the IUPAC recommendation of the terrestrial K isotope composition. Its uncertainty of 0.35% is much higher than the goal of the EARTHtime initiative, i.e. a total absolute uncertainty of 0.1% on the absolute age.

In order to improve on this situation we measured the abundances of the K isotopes in terrestrial standards NIST SRM 918b and 985 by thermal ionisation mass-spectrometry on a Finnigan TRITON instrument. Three measurement protocols combined with two amplifier set-ups were applied: (A) dynamic measurement with in-run normalisation to the IUPAC value  $^{41}\text{K}/^{39}\text{K}=0.072168$ ; (B) a simple total evaporation procedure; (C) the "NBL-modified" total evaporation [3]. Two loading techniques and two types of filaments (tantalum and rhenium) were tested. The total ion yields (ionisation+transmission) were tested for the evaporation procedures (B) and (C) and ranged up to 48%. Isobaric interferences of Ca on K were tested and were not observed.

The results all agree with the terrestrial  $^{40}\text{K}/^{39}\text{K}$  ratio recommended by IUPAC, but have much higher precision. The most reliable results were obtained with the total evaporation protocol with an amplifier configuration that uses  $10^{10}$ ,  $10^{11}$  and  $10^{12}$   $\Omega$  resistors on Faraday cups. The uncertainty of K-Ar and K-Ca dating systems contributed by the uncertainty of the  $^{40}\text{K}$  abundance are now reduced from 0.35% to 0.05%.

[1] Renne P.R. *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 5349-5367. [2] Garner E.L. *et al.* (1975) *J. Res. Natl. Bur. Stand.* **79A**, 713-725. [3] Richter S., Goldberg S.A. (2003) *Int. J. Mass Spect.* **229**, 181-197.

## Re-Os isotope systematics of sulfides from Olympiada gold deposit (Yenisei Rige, Russia)

NAUMOV E.A.,<sup>1\*</sup> TESSALINA S.,<sup>2</sup> BORISENKO A.S.<sup>1</sup>, NEVOLKO P.A.,<sup>1</sup> AND KOVALEV K.R.<sup>1</sup>

<sup>1</sup> Institute of geology and mineralogy SB RAS, Novosibirsk, Russia, 630090, (\*correspondence: naumov@igm.nsc.ru)

<sup>2</sup> John de Laeter Centre, Curtin University, Perth, Australia

The Olympiada Au deposit is located within the Yenisei Ridge in Central Siberia, along with a number of other Au and Au-Sb deposits. The Olympiada deposit occurs in metasedimentary terrigenous-carbonate rocks of Paleoproterozoic to Mesoproterozoic age, metamorphosed to amphibole-epidote greenschist facies. This deposit contains about 550–600 t of Au with the average grade of 3–4 ppm Au in primary sulfide ores and 10 ppm in supergene ores.

The Au mineralisation occurs in the contact zone between quartz-mica and carbonate-quartz-mica schists, and is controlled by a district-scale anticline, incorporating bedding-subparallel fractures and transverse fault zones. The orebodies are composed of carbonate-quartz-mica metasomatites containing 3–5 vol% sulfides (mostly arsenopyrite, pyrite, pyrrhotite, stibnite) and scheelite. Minor chalcopyrite, sphalerite, galena, tennantite-tetrahedrite and Bi-minerals are locally present.

Arsenopyrite is the main Au-bearing mineral and can be subdivided into 2 types according to mineralogical and chemical specific features: coarse-crystalline (Type 1) and acicular aggregates (Type 2), which represent distinct ore forming events differing by Au contents. First type is characterized by elevated contents of Au averaging 330 ppm, whereas Type 2 arsenopyrite contains only about 30 ppm of Au.

Both type of arsenopyrite were studied for isotopic composition of Re and Os. Type 1 arsenopyrite contains 3 ppb of Os and 20 ppb of Re and characterised by high  $^{187}\text{Os}/^{188}\text{Os}$  ratio up to 14. Type 2 arsenopyrite has lower Os and Re contents up to 0.5 ppb and 5 ppb correspondingly, together with low  $^{187}\text{Os}/^{188}\text{Os}$  ratio of 0.3.

This difference implies different sources for these 2 stages of ore-forming process. Ore-forming fluids which forms gold-bearing arsenopyrites of the first type possibly have some crustal source. Origin of arsenopyrite of the second productive stage requires a source with mantle-like Os isotope signatures.

## CO<sub>2</sub> induced geochemical reactions at the pore scale

NAVARRE-SITCHLER, A.<sup>1,2</sup>, MOUZAKIS, K.<sup>2</sup>, ROTHER, G.<sup>3</sup>, BANUELOS, J.L.<sup>3</sup>, WANG, X.<sup>4</sup>, KASZUBA, J.<sup>5</sup>, AND MCCRAY, J.<sup>2</sup>

<sup>1</sup>Department of Geology and Geological Engineering, Colorado School of Mines, (asitchle@mines.edu)

<sup>2</sup>Hydrologic Sciences and Engineering, Colorado School of Mines

<sup>3</sup>Chemical Sciences Division, Oak Ridge National Laboratory

<sup>4</sup>Chinese University of Petroleum

<sup>5</sup>Geology and Geophysics, University of Wyoming

In many geologic systems pore space is conceptualized as a containment and delivery system for fluids, not unlike a pipe network that delivers water through a city. However, in rocks exposed to reactive fluids, pore networks are not static. The pore network undergoes constant reshaping as minerals dissolve and precipitate. Despite the importance of pore network structure on many fundamental geologic processes, the physical characteristics of pore networks in rocks are poorly understood, in part due to their dynamic nature. Sub-micron sized pores in fine-grained rocks, such as shales and mudstones, require advanced techniques for quantification and characterization. Small angle neutron scattering, a technique that provides statistical data on the topology and architecture of pore networks, was combined with high-resolution imaging, and gas sorption measurements to characterize and quantify the pore network structure in 5 fine-grained rocks. In these rocks a large fraction (up to 80%) of the pore volume and surface area is contained within pores <20 nm in diameter. When two of these rocks were reacted with CO<sub>2</sub> under conditions relevant to CO<sub>2</sub> sequestration or enhanced oil recovery, mineral dissolution and precipitation changed the structure of the pore network with an overall loss of pore connectivity. This study demonstrates the application of neutron scattering to the study of pore networks in fine-grained rocks and the reshaping of these pore networks by mineral reaction.

## The Río Mundo dolostones (Spain): Implications for MVT and hydrocarbon formation

D. NAVARRO-CIURANA<sup>1\*</sup>, R. CODINA-MIQUELA<sup>1</sup>, E. CARDELLACH<sup>1</sup>, E. VINDEL<sup>2</sup>, D. GÓMEZ-GRAS<sup>1</sup>, A. GRIERA<sup>1</sup>, L. DANIELE<sup>1</sup> AND M. CORBELLA<sup>1</sup>

<sup>1</sup>Dept. de Geologia, Universitat Autònoma de Barcelona, Campus UAB, Edifici C, 08193, Bellaterra, Spain.

(\*correspondence: didac.navarro.ciurana@gmail.com)

<sup>2</sup>Dpt. de Cristalografía y Mineralogía, Facultad de Ciencias Geológicas, Universidad Complutense de Madrid UCM, 28040, Madrid, Spain.

Dolomitic rocks constitute a potential natural resource as they may host base-metal and hydrocarbon deposits. The study of the dolomitization associated with a Zn-(Pb) Mississippi Valley-type (MVT) deposit in the Río Mundo area (Albacete, SE Spain) may be a breakthrough for mining and hydrocarbon companies, as it is an excellent example to unravel relationships between dolomitization, fluid flow, fractures, host-rock porosity, ore deposition and hydrocarbon accumulation. Petrographical and C/O stable isotope data from carbonates (dolomites and calcites) have been used in order to study these associations. The MVT mineralization consists of sphalerite with hydrocarbon fluid inclusions, galena, pyrite and marcasite. It is hosted by Middle Jurassic dolostones, which are found below Upper Cretaceous age rocks. The hydrothermal dolomitizing event was essential for the ore genesis as it increased the rock porosity up to ~25%. Host limestones have δ<sup>18</sup>O values between +27.55 and +27.83‰ (SMOW) and δ<sup>13</sup>C from +2.32 to +3.16‰ (PDB). Pervasive dolomitization resulting from interaction with hydrothermal fluids have δ<sup>18</sup>O values between +25.07 and +26.89‰ and δ<sup>13</sup>C from -0.53 to +0.61‰. The limited δ<sup>18</sup>O shift may be explained by interaction of regional limestones with a <sup>18</sup>O-enriched dolomitizing fluid at low fluid/rock ratio and constant temperature. δ<sup>13</sup>C values indicate that hydrothermal fluids were enriched in <sup>12</sup>C, compatible with the presence of hydrocarbons trapped in sphalerite and porosity-filling organic matter. Although part of the ore is disseminated within dolostones (δ<sup>18</sup>O: +25.85 to +26.34‰; δ<sup>13</sup>C: -2.31 to -0.15‰), most massive brown to reddish sphalerite zoned crystals appear associated with vein-dolomite (δ<sup>18</sup>O: +25.13 to +26.93‰; δ<sup>13</sup>C: -0.75 to +0.59‰) filling fractures. The overlap of the different dolomite isotopic signature ranges suggests an isotopic resetting or the occurrence of a single dolomitizing event. The mineralization and hydrothermal dolomitization event must have occurred during Upper Jurassic to Lower Cretaceous times.



## The compared reactivity of different organic matters and clay in the whole soil and at the microscale: Unraveling the reactivities by combining chemical analysis and physical fractionation

A. NAVEL<sup>1</sup>, L. SPADINI<sup>1\*</sup>, I. LAMY<sup>2</sup>, E. VINCE<sup>1</sup> AND JEAN M.F. MARTINS<sup>1</sup>

<sup>1</sup>LTHE Laboratory, UMR5564 CNRS, University of Grenoble 1, France (\*correspondence: lorenzo.spadini@ujf-grenoble.fr) (aline.navel@ujf-grenoble.fr, , jean.martins@ujf-grenoble.fr)

<sup>2</sup>INRA, UR251, PESSAC Physico-chemistry and ecotoxicology of soils from contaminated agrosystems - RD10 -F78026 Versailles Cedex, France (isabelle.lamy@versailles.inra.fr)

Organic carbon is one of the most reactive, often the most reactive component of common soils. Despite this, describing inside a complex soil matrix the reactivities of the different habits of organic matter (bioclasts, bacteria, degraded solid and dissolved organic matter) and the relative contribution to reactivity of mineral compounds is still a challenging task. The study focus on the reactivity determination of metals, protons, and generally complexing compound. A procedure is presented based on 'soft' granulometric fractionation separating coarse soil aggregates (>250 and 250-63 $\mu$ m), silty (63-20  $\mu$ m) and fine (20-2 and <2  $\mu$ m) soil fractions. The whole-fraction reactivity toward protons and Cu(II) (taken as example of complexing trace elemental cations) is compared to the fraction-specific total organic carbon ( $T_{OC}$ ) and aqua regalis extracted Al ( $E_{Al}$ ) content.  $T_{OC}$  varies in the soil fractions dependent on 20 years lasting organic amendments in the studied silty-loam soil.  $E_{Al}$  content represents the acid, and consequently the relative water accessible clay content in each fraction. Combining linearly these reactivities descriptors allows accessing to the reactivity contribution of different soil organic matters, soil clay and a residual phase. The comparison with referenced reactivity knowledge shows that this method allows accessing representative reactivities of studied components. With this method the soil aggregates are preserved. They are known to represent specific microbial habitats. This opens interesting perspectives relative to the study of biogeochemical site effects in the complex soil matrix.

## Thermodynamic Constraints on Stability of Ceramics under Extreme Conditions – Phase Change and Amorphization from Chemical Effects of Radioactive Decay

ALEXANDRA NAVROTSKY<sup>123</sup>

(<sup>1</sup>anavrotsky@ucdavis.edu)

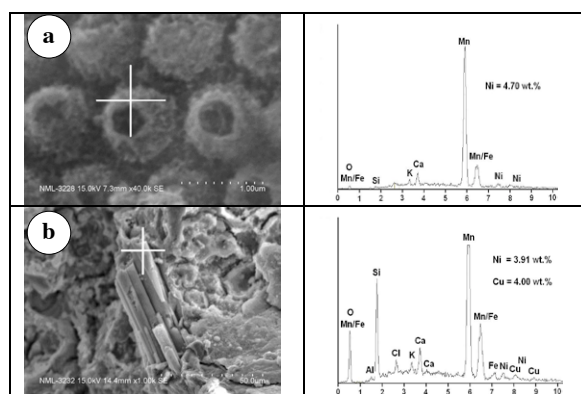
In addition to radiation damage, ceramics in a nuclear reactor or waste form undergo chemical changes as a result of fission and radioactive decay. Because ceramics are typically ionic solids with stringent requirements to maintain appropriate cation size and charge balance on various sublattices, and such transmutations change both the size and charge of ionic species, one can expect phase change, exsolution, and/or vitrification arising from these chemical changes as well as from radiation damage. Two examples are discussed: the incorporation of rare earth fission products in UO<sub>2</sub> and the effect of the decay of Sr to Y to Zr and of Cs to Ba in titanate waste forms incorporating these short-lived fission products. In the former case, rare earths are accommodated by creation of oxygen vacancies, which change ionic and thermal conductivity and, in many cases, stabilize the fluorite phase. In the latter, using perovskite, pollucite, and fersnoite as examples, a general trend of destabilization is seen, with exsolution of new phases and extensive vitrification arising from the violation of charge balanced substitution within the initial structures. Such behavior has the potential to diminish waste form durability

## Bio-influence on the metal precipitation in ferromanganese nodules of the Central Indian Ocean Basin

B. NAYAK\*, S.K. DAS AND P. MUNDA

CSIR National Metallurgical Laboratory, Jamshedpur-831007, INDIA (\*correspondence: brn69@rediffmail.com)

In deep-sea ferromanganese nodules metals can precipitate by chemical oxidation and/or by microbial enzymatic processes [1-4]. Using high resolution FEG-SEM we have documented varieties of ultra-microfossils in the ferromanganese nodule samples of the Central Indian Ocean Basin (CIOB) (e.g., Fig. 1).



**Figure 1:** Fossilized microbes with their corresponding EDAX analysis at marked cross points; (a): clumpy microbes; (b): rod-shaped bacteria.

These fossilized microbes are mostly protozoa belonging to varieties of bacteria, diatoms and foraminifera. The chemical compositions of these ultra microfossils indicate a high-level of manganese precipitation in and around them. While clumpy microbes are enriched with Ni, the rod shaped bacteria are rich in Cu. Up to 4.7 wt.% Ni and 5.3 wt.% Cu have been recorded in the fossilized microbe bodies. The high abundance of ultra-microfossils and their chemical compositions indicate that microbes played a major role in the precipitation of metallic elements in the ferromanganese nodules of the CIOB.

[1] Graham & Cooper (1959), *Nature* **183**, 1050-1051. [2] Greenslate (1974), *Nature* **249**, 181-183. [3] Roy (2006), *Earth Sci. Rev.* **77**, 273-305. [4] Wang *et al.* (2009), *Mar. Biotech.* **11**, 99-108.

## Characterization of Diagenetically Altered Carbonate Reservoirs, Asmari Formation, Dezful embayment, SW Iran

P. NAZARIAN SAMANI<sup>1\*</sup>, M. MORADPOUR<sup>1</sup> AND S. A. MOALLEMI<sup>1</sup>

<sup>1</sup> Research Institute of Petroleum Industry-14665, 137-Tehran-Iran (\*correspondence: samanip@ripi.ir)

The Oligocene-Miocene Asmari carbonate Formation is wellknown as a major hydrocarbon reservoir in southwestern Iran. Determining the Asmari Formation reservoir quality based on defining diagenetic evolution were deduced from microscopic description of thin sections. Development of reservoir quality appears to be controlled effectively by diagenesis. Investigations reveal that diagenetic factors including compaction, cementation (by anhydrite, calcite and dolomite), dolomitization, dissolution and their effect on porosity changed the reservoir quality. Compaction and significantly cementation reduced the porosity however; this effect was healed by later dissolution and leaching processes. Dolomitization in this Formation enhanced the original porosity in depositional textures and protracted dolomitization created intercrystalline porosity, creating the best reservoir facies in SW Iran [1]. Two kind of distinct dolomitic textures involve fine to medium dolomite crystals (20-100 $\mu$ ) increased the intercrystalline porosity while the other, coarse mosaic of dolomite crystals (>100 $\mu$ ) especially associated with mud residuals are shown degradation effect on reservoir quality. It will be appeared that rock-water interaction lead to dissolution and dolomitization phenomenon which are the most important processes fortify pore spaces and controlling the reservoir quality in the Asmari Formation of SW Iran.

[1]Aqrawi *et al.* (2006) *Journal of Petroleum Geology*, **29**, 381-401.

## Synchrotron FTIR on melt inclusions, clinopyroxene and olivine from Mt Etna recent explosive eruptions

SABRINA NAZZARENI<sup>1</sup>, MASSIMO POMPILIO<sup>2</sup>, HENRIK SKOGBY<sup>3</sup>, ANDERA PERUCCHI<sup>4</sup> AND PAUL DUMAS<sup>5</sup>

<sup>1</sup>Dip. Fisica e Geologia, Università di Perugia, Italy  
(sabrina.nazzareni@unipg.it)

<sup>2</sup>Istituto Nazionale di Geofisica e Vulcanologia, Sez. di Pisa, Italy

<sup>3</sup>Dept. of Geosciences, Swedish Museum of Natural History, Stockholm, Sweden

<sup>4</sup>SISSI, Elettra, Trieste Italy

<sup>5</sup>SMIS, Soleil synchrotron, Paris, France

The volatile budget of magmas from active volcanoes are crucial in developing volcanological models. The solubility of H<sub>2</sub>O in silicate melts is, on the whole low, and strongly dependent on pressure. As a consequence magmatic melts reaching the surface have lost most of their original volatile contents.

We studied the volatile content of recent eruptions of Mount Etna (the 3930 BP picritic eruption and Cono del piano - 2001 and 2002 eruptions), to reconstruct a model for the ascent and degassing of these magmas. We determined the volatiles content by FTIR techniques measuring the hydrogen content of clinopyroxene phenocrysts and the H<sub>2</sub>O and CO<sub>2</sub> contents of melt inclusions entrapped in the same clinopyroxenes (cpx) as well as in olivine (ol) phenocrysts.

Synchrotron FTIR experiments were conducted at SMIS (Soleil, Paris) and SISSI (Elettra, Trieste) beamlines. FTIR spectra were collected in the 900-8000 cm<sup>-1</sup> range with 4 cm<sup>-1</sup> resolution using scanning areas of variable size (200-400 μm-long and 200-400 μm-wide) following a regular grid of square-aperture dimension of 10 μm. Thus we measured high resolution chemical maps of H<sub>2</sub>O and CO<sub>2</sub> distribution and speciation on melt inclusions to study the diffusion of H between the inclusions and cpx- or ol-host mineral. Line transect across chemical zonations in cpx (from the outer edge to the core of the crystal) showed details on the H<sub>2</sub>O distribution with a more water rich core (PDL2001: 214 ppm H<sub>2</sub>O; TEF2002-2:204 ppm H<sub>2</sub>O ) and a more "dry" (PDL2001: 138 ppm H<sub>2</sub>O; TEF2002-2: 109 ppm H<sub>2</sub>O) rim as detected by polarised FTIR spectra of oriented single-crystals. The water content of the Etna cpx phenocrysts is quite high suggesting a water rich magmatic system and showed only minor variations from the different eruptions: 254 ppm H<sub>2</sub>O for 3930 BP picritic eruption; 214 ppm H<sub>2</sub>O for 2001 eruption; 161-254 ppm H<sub>2</sub>O for 2002 eruption.

## Amber and amber-like materials on the Romanian market

ANTONELA NEACȘU<sup>1\*</sup>, DELIA GEORGETA DUMITRAȘ<sup>2</sup>, MIHAELA ELENA CIOACĂ<sup>2</sup> AND ANGELA MARIA ANASON<sup>2</sup>

<sup>1</sup>University of Bucharest, Faculty of Geology and Geophysics, 1, N. Bălcescu Ave., 010041 Bucharest, Romania.

(\*correspondence: antonela.neacsu@gmail.com)

<sup>2</sup>Geological Institute of Romania, 1, Caransebes Str., Bucharest, Romania, RO-012271.

Amber is a natural fossil resin with a controversial paleobotanical origin and is a mineraloid for mineralogists. The final internal structure and chemical composition of amber depend on light and oxygen exposure, on temperature and humidity differences, also on the biologic agents that characterized the environment, including the geological one, after resinosis (a large, unrepeatably secretion of resin by some Conifers and flowering trees, during Cretaceous and Tertiary periods). The oxidizing processes into the depositional context are important for the gemological properties of amber (color, cracks and transparency).

There are few amber varieties used for manufacturing, including jewelry: the Baltic amber with its variety succinite (Poland, Russia, Baltic Countries, Ukraine, Germany), the amber of Dominican Republic, the Chinese amber, the Burma amber (burmite), the amber from the Romanian Carpathians (rumanite or romanite). In Romania amber is treated as gemstone, including the risk of fake industry, that uses both natural substances (e.g., actual resins, copal and pressed amber), and synthetic polymers (glass and plastics). A distinction between amber and imitations could be made applying Fourier-transform infrared spectroscopy (FTIR) and X-ray diffractometry (XRD) targeting the natural inclusions or proving an internal organizing tendency of material. FTIR curves of amber-like samples found ourdays in gem exhibitions organized by the Geological Institute of Romania are similar to those of romanite samples are similar to those of romanite, succinite, Dominican amber, burmite and copal. On the contrary, plastics, synthetic resins and modern resin of Rosaceous are found on the Romanian market, used as imitations or sometimes sold as genuine amber.

## The effect of AFC processes and source oxidation on Fe isotopes in evolved Banda Arc lavas

O.NEBEL<sup>1</sup>, R.J.ARCULUS<sup>1</sup>, M.WILLE<sup>2</sup> AND P.Z.VROON<sup>3</sup>,

<sup>1</sup>Research School of Earth Sciences, The Australian National University, Canberra, Australia

<sup>2</sup>Mineralogie und Geodynamik, Eberhard Karls Universität Tübingen, Germany

<sup>3</sup>Department of Petrology, VU University Amsterdam, The Netherlands

Igneous rocks, ranging in composition from mafic to felsic, show resolvable variations in their stable Fe isotope compositions [1]. These variations are closely related to the oxidation state of Fe in igneous systems, i.e., Fe<sup>2+</sup> and Fe<sup>3+</sup>, with heavy Fe isotope compositions predominately associated with the more oxidized species. Reported Fe isotope variations ( $\delta^{57}\text{Fe}$  relative to IRMM-014) in island arc basalts (IAB) span a range from negative to positive values [2], and are on average systematically lighter than those reported for mid ocean ridge basalts (MORB) [3], a fact that is seemingly opposing their expected oxidation state.

Here we present the stable Fe isotope composition of 13 IAB and 8 subducting sediments sampled along the active Banda Arc (East Indonesia). All samples are well characterised for their Sr-Nd-Pb-Hf-O isotope composition, which record progressive sediment melt contribution along the arc from NE to SW. We find that crystal fractionation increases  $\delta^{57}\text{Fe}$  and identify this process as the dominant factor controlling the Fe isotope composition of this evolved arc suite. The opposite effect is observed upon magnetite saturation at ~4 wt.% MgO. Arc crust assimilation has also a strong influence driving the IAB towards heavier Fe isotopes. Sediment melting appears to have little or no effect on the Fe isotope composition in contrast to signatures for most radiogenic isotope tracers.

We imply that Fe in the sediment melt fully equilibrates with the mantle wedge either prior to or during wedge melting. As a consequence, if it is assumed that sediment melts carry more Fe than aqueous fluids, the slab agent has little or no effect on the redox state of IAB sources. Instead we propose that progressive wedge depletion has the potential to harvest Fe<sup>3+</sup> and this lowers  $f\text{O}_2$  (and  $\delta^{57}\text{Fe}$ ). If  $\delta^{57}\text{Fe}$  monitors the redox conditions of evolving arc rocks, then crystal fractionation is the driving force in elevating  $f\text{O}_2$  in subduction zones.

[1] Dauphas and Rouxel, Mass Spectrometry Reviews, 2006;

[2] Dauphas *et al.*, EPSL, 2009, [3] Teng *et al.*, GCA 2013

## Geochemical features of granitoid Central Siberia magmatism in the Permian-Triassic

T.S. NEBERA, AND N.N. BOROZNOVSKAYA

Tomsk State University, Tomsk, Russia (tsnebera@mail.ru)

The granitoids of the Kolyvan-Tomsk folded zone, part of the western segment of the Altai-Sayan region, are the youngest magmatic formations of Late Hercynian tectogenesis. Developing the geochemical criteria of granitoid classification is an important perspective for geodynamic interpretation of the granitoids. The studied rocks are characterized peraluminiferous and have converged features granite S-and I-types. I-granites have a more mafic composition with a high content of calcium amphibole and accessors in the form of magnetite and allanite. They are characterized by a high oxidation of iron and oxygen fugacity, appreciable concentrations of Ba (~ 800-1200 g / t), Sr (~ 1200-2000), and calcium. Derived from the granite-granodiorite -granosyenite series, geochemically similar to rocks of I-type. They can be attributed to the products of latite-type magmatism with  $\text{K}_2\text{O} > \text{Na}_2\text{O}$ , high the K/ Rb ratios, Mg, high Ni concentrations. Breed from leucogranit series are rather consistent with S-type characteristics. They have a relatively high concentration of Rb in the background of a sharp decrease in the content Ba (up to ~ 120 g / t) and Sr (up to ~ 40 g / t) are enriched in Be and Cs, which makes them similar to Li-F granites. The results of luminescent analysis of the granitoids studied (intensive X-ray luminescence of Fe<sup>3+</sup> in feldspars) indicates also that they were formed from a high-alkaline melt. The geochemical differences (characteristics) discovered for the granitoids allow us to assume that they were formed under complicated geodynamic conditions from the high alkalinity melt. This study was funded by the Russian Ministry of Education and Science (projects 5.3143.2011, 14.B37.21.0686, 14.B37.21.1257).

## Cadmium sorption by green rust

S. NEDEL\*, K.N. DALBY, K. DIDERIKSEN,  
B.C. CHRISTIANSEN, AND S.L.S. STIPP

Nano-Science Center, Department of Chemistry, University of  
Copenhagen, Denmark (\*correspondance:  
sorin@nano.ku.dk)

Cadmium pollution, released into soils from agricultural and industrial activities, is considered a potential threat to biota. As with other pollutants, Cd mobility and bioavailability in soils largely depend on sorption-desorption processes at the interface between soil solution and mineral surfaces. Fe (oxyhydr)oxides are ubiquitous in soils. They have a large surface area and can adsorb and incorporate metals, meaning that these minerals are likely to affect Cd migration. The interaction of Cd with soil minerals has been investigated thoroughly but we know of no study on Cd interaction with green rust (GR). GR consists of brucite like layers of Fe(II),Fe(III) hydroxide separated by interlayers of water molecules and anions. These minerals are highly redox active, can form both by biotic and abiotic processes, and are likely to be present in soils and groundwater. The aim of this work was to determine if Cd can be sorbed and effectively immobilized by GR.

GR was synthesised at circumneutral pH by two methods: transformation of ferrihydrite in an Fe(II) solution and oxidation of an Fe(II) solution. Cadmium was added, at a series of concentrations either in the initial Fe(II) solution or in suspensions with preformed GR. X-ray diffraction (XRD) and transmission electron microscopy (TEM) showed that Cd<sup>2+</sup> was not reduced by preformed GR nor incorporated in freshly forming GR. However, GR<sub>504</sub> partially sorbed the divalent heavy metal, with higher sorption occurring at lower Cd concentrations. Upon oxidation of GR, Cd<sup>2+</sup> remained associated with the Fe(III) solid. X-ray photoelectron spectroscopy (XPS) showed that it was sorbed by newly formed lepidocrocite.

These results contribute to fundamental understanding of contaminant interaction with green rust and can be implemented in current reactive transport models. We also demonstrated that Cd<sup>2+</sup> mobility will be affected to some extent by sorption to GR, which can be present naturally in soil and form from iron corrosion, for example in permeable reactive barriers or pipes.

## Zircon U-Pb-ages, Hf isotope and trace element composition in the evolution of the IVAC Complex (Urals, Russia)

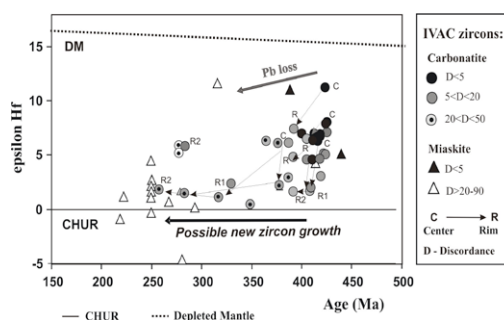
I.L. NEDOSEKOVA<sup>1\*</sup>, E.A. BELOUSOVA<sup>2</sup>,  
B.V. BELYATSKY<sup>3</sup> AND N. PEARSON<sup>2</sup>

<sup>1</sup>Zavaritsky IGG UB RAS, Ekaterinburg, Russia  
(\*correspondance: vladi49@yandex.ru)

<sup>2</sup>GEMOC/CCFS, Macquarie University, Sydney, Australia  
(elena.belousova@mq.edu.au)

<sup>3</sup>IPGG RAS, St.Petersburg, Russia (bbelyatsky@mail.ru)

It has been widely accepted that Hf isotope composition of zircon is relatively stable and is not affected by significant alteration due to influence of the hypogenic processes [1]. We have studied Hf isotope composition (coupled with U-Pb-age) in different populations of zircon from Ilmeny-Vishnevorsky Alkaline Complex (IVAC), Uralian Fold Belt.



**Figure:** Hf isotope composition of the IVAC zircons (calculated for individual zircon ages) plotted against U-Pb ages, where D presents percentage of their age discordance.

The results indicate that the early zircons I from IVAC carbonatites and miaskites form concordant age cluster (U-Pb-age 410-424 Ma, D<5) and displays moderately depleted isotope Hf composition ( $\epsilon_{\text{Hf}}=11.7-4.7$ ), where variations plausibly reflect primary heterogeneity of the magma source(s). The outer zones of the zircon I grains are characterized by disturbed U-Pb systems ( $5 < D < 20$ ) and lower  $\epsilon_{\text{Hf}}$  values (shifting by 3-4 units in regard to the central parts of grains). These shifts do not correspond to the lines of Hf isotope evolution of zircons compositions or radiogenic Pb loss trends (Figure). The later newforming zircons II dated at T=250-320 Ma (frequently  $D > 50-90$ ,  $\epsilon_{\text{Hf}} = -5$  to +11).

Both, the disturbance of U-Pb-system and formation of zircons with distinct, less radiogenic Hf-isotope composition could be related to the later ca 250 Ma metamorphic event.

[1] Patchett *et al.* (1981) *ContrMinPet* **78**, 279-297.

## Biological fractionation of molybdenum isotopes: Lake Mývatn, Iceland

REBECCA NEELY\*<sup>1</sup>, CHRISTOPHER SIEBERT<sup>2</sup>,  
KEVIN BURTON<sup>3</sup>, EYDÍS SALOME EIRIKSDÓTTIR<sup>1</sup> AND  
ÁRNI EINARSSON<sup>1</sup>

<sup>1</sup>\* Institute of Earth Sciences, Sturlugata 7, 101 Reykjavík, Iceland (correspondence: ran6@hi.is)

<sup>2</sup>GEOMAR, Helmholtz Centre for Ocean Research, Germany

<sup>3</sup>Department of Earth Sciences, Durham University, UK

Molybdenum (Mo) is an essential enzyme cofactor in nearly all organisms and has been known to be of biological importance for some time [1]. Such biochemical ubiquity may come as a surprise given the relative scarcity of Mo at the Earth's surface. However, its unreactive, conservative behaviour in oxygenated, aqueous solutions makes it the most abundant transition metal in the oceans.

Laboratory based studies have shown that certain soil bacteria and cyanobacteria all favour light isotopes during Mo assimilation, thus causing measurable fractionations [2]. This study aims to bridge the gap between these laboratory experiments and the natural environment. Lake Mývatn is an ideal location to investigate these processes. Located on young, porous lava of the Icelandic rift zone it is almost exclusively sourced by groundwater flow and has only one riverine output, making it a perfect natural "box-model". Groundwater and outlet samples were analysed for Mo isotopes over the course of one growing season.

There are two distinctive groundwater inputs;  $\delta^{98}\text{Mo}_{\text{hot}}$ : 0.57 ‰ and  $\delta^{98}\text{Mo}_{\text{cold}}$ : 0.35 ‰ (0.1 2s.d.). The Mo concentration of the lake waters is described by simple, proportional mixing of these inputs. However, the Mo isotope value of the lake is heavier than the mixed inputs, consistent with a preferential uptake of light Mo isotopes by *Anabaena* (cyanobacteria), known to bloom in the lake in the summer months. Over the course of the year the outlet varied systematically between  $\delta^{98}\text{Mo}$  0.36 ‰ and  $\delta^{98}\text{Mo}$  0.66 ‰ with a signal predicted by a concentration driven model and biological fractionation of between - 0.2 ‰ and - 0.4 ‰. These results represent the first measurements of biological fractionation of Mo in the natural environment and have implications for our understanding of Mo systematics and its potential as a proxy in a geological context.

[1] Howarth & Cole (1985) *Science* 229. 653-655. [2] Zerkle, Scheiderich, Maescam, Liermann & Brantley (2011) *Geobiology* 9 (1): 94-106

## XAFS analysis of C-S-H formed by cement-bentonite interaction

KUMI NEGISHI<sup>1</sup>, HIROYUKI SKAMOTO<sup>1</sup>, TOMOKO ISHI<sup>2</sup>,  
DAISUKE HAYASHI<sup>2</sup>, NAOKI FUJII<sup>2</sup>, HITOSHI OWADA<sup>2</sup>,  
AND HIROAKI NITANI<sup>3</sup>

<sup>1</sup>Taiheiyō Consultant Co., Chiba pref., 285-0802, Japan

<sup>2</sup>RWMC, Tokyo, 104-0052, Japan

<sup>3</sup>KEK, Ibaraki pref., 305-0801, Japan

The analysis of long-term alteration of engineered barriers to be used for the disposal of TRU waste predicted precipitation of calcium silicate hydrate (C-S-H) minerals in the bentonite along the interface with the cement. In order to quantitatively measure the C-S-H predicted to form as a secondary mineral in the bentonite, the authors used XAFS analysis technique. The XAFS analysis which provides information around the concerned element regardless of the crystallinity of the mineral was assumed to be an effective mean to analyze poorly crystallized C-S-H. The local structural environment of calcium in the C-S-H with different Ca/Si ratio was also evaluated based on the EXAFS spectra in this study.

A test piece prepared by contacting a compacted bentonite and a hardened cement paste was immersed in the simulated fresh, reducing and high pH (FRHP) groundwater. The calcium K-edge XAFS measurement was conducted for the compacted bentonite. A synthetic C-S-H with high Ca/Si ratio was prepared and dissolved to generate low Ca/Si ratio C-S-H. These C-S-H minerals were subjected to the XAFS analysis.

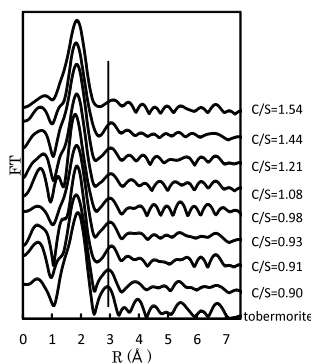


Fig.1 Radial structure function of C-S-H

The XAFS measurement allowed for evaluation of the variation of the quantity of the C-S-H in the bentonite. No significant difference was observed in the EXAFS spectra and conditions around the calcium among C-S-H minerals with different Ca/Si ratio. Conditions around the calcium in the C-S-H were similar to those in the tobermorite (Fig. 1).

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## A new model for biomineralization and trace-element signatures of foraminifera tests

G.NEHRKE<sup>1\*</sup>, N KEUL<sup>2</sup>, G. LANGER<sup>3</sup>, L. DE NOOIJER<sup>4</sup>, J. BIJMA<sup>1</sup> AND A. MEIBOM<sup>5</sup>

<sup>1</sup>Alfred Wegener Institute, Bremerhaven, Germany

(\*correspondence: gernot.nehrke@awi.de)

<sup>2</sup>Lamont-Doherty Earth Observatory, Columbia University, Palisades, New York, USA (nkeul@ldeo.columbia.edu)

<sup>3</sup>Department of Earth Sciences, Cambridge University, Cambridge, UK (gl345@cam.ac.uk)

<sup>4</sup>Department of Marine Geology, Royal Netherlands Institute of Sea Research, Horntje, The Netherlands (Lennart.de.Nooijer@nioz.nl)

<sup>5</sup>Laboratory for Biological Geochemistry, School of Architecture, Civil and Environmental Engineering (ENAC), Ecole Polytechnique Fédérale de Lausanne. CH-1015 Lausanne, Switzerland (anders.meibom@epfl.ch)

The Mg/Ca ratio of foraminifera calcium-carbonate tests is used as proxy for seawater temperature and widely applied to reconstruct global paleo-climatic changes. However, the mechanisms involved in the carbonate biomineralization process are poorly understood. The current paradigm holds that calcium ions for the test are supplied primarily by endocytosis of seawater. Here, we combine confocal-laser scanning-microscopy observations of a membrane-impermeable fluorescent marker in living benthic species *Ammonia tepida* with dynamic <sup>44</sup>Ca-labeling and NanoSIMS isotopic imaging of its test. We infer that Ca for the test in *A. tepida* is supplied primarily via trans-membrane transport, but that a small component of passively transported (e.g. by endocytosis) seawater to the site of biomineralization plays a key role in defining the trace-element composition of the test. Our model accounts for the full range of observed Mg/Ca and Sr/Ca benthic foraminifera test compositions and predicts the effect of changing seawater Mg/Ca ratio.

## Re-Os-PGE constraints on the evolution of backarc oceanic mantle

WENDY R NELSON<sup>1</sup> JONATHAN E SNOW<sup>1</sup> ALAN D BRANDON<sup>1</sup> YASUHIKO OHARA<sup>2,3</sup> AND CIN-TY LEE<sup>4</sup>

<sup>1</sup>Dept of Earth and Atmospheric Sciences, University of Houston, Houston, USA (wrnelson2@uh.edu, jesnow@uh.edu, abrandon@uh.edu)

<sup>2</sup>Hydrographic and Oceanographic Dept of Japan, Tokyo, Japan (yasuhiko.ohara@gmail.com)

<sup>3</sup>Japan Agency for Marine Earth Science and Technology, Yokosuka, Japan

<sup>4</sup>Dept. of Earth Science, Rice University, Houston, USA (ctlee@rice.edu)

Our direct understanding of the evolution of oceanic mantle during backarc extension is limited to exposures of abyssal peridotite and ophiolites. Few direct comparisons of ophiolite and backarc peridotite have been made due to the small number of documented exposures and limited in situ samples from backarc settings. Here we report Re-Os and PGE data for backarc abyssal peridotites from the Godzilla Megamullion (GM), a massive ~9000 km<sup>2</sup> oceanic core complex located in the Parece Vela Basin (Philippine Sea). The distal portion of GM records early, magmatically productive extension marked by moderately depleted spinel peridotites. This transitions into a less melt-productive medial region characterized by more fertile peridotite. The proximal region represents the most recently exhumed portion of the megamullion. Isotopically, the regions are indistinguishable, with whole rock <sup>187</sup>Os/<sup>188</sup>Os = 0.1174-0.1704. Elevated <sup>187</sup>Os/<sup>188</sup>Os values correlate with MgO loss, suggesting the influence of sea floor weathering. While spinel grains in proximal samples record high TiO<sub>2</sub> and Cr# indicative of melt-rock interaction, PGE abundances are not strongly affected; distal samples record stronger depletions in Pt-Ru-Pd than proximal samples, consistent with higher degrees of melt extraction. In all samples, Re abundances are low (2-107 ppt) and are positively correlated with TiO<sub>2</sub> abundances in spinel, suggesting that Re is mildly influenced by melt-rock interaction. However, <sup>187</sup>Os/<sup>188</sup>Os ratios are not correlated with Re concentration, demonstrating that modest Re addition occurred recently. As a whole, the <sup>187</sup>Os/<sup>188</sup>Os data suggest that the backarc oceanic mantle in this region did not experience significant ancient melt depletion. Instead, the geochemical and isotopic signatures of the GM were generated during backarc extension associated with the Izu-Bonin-Mariana subduction zone.

## Evolution of the Lower Crust in the Point of View of Fluid-Rock Interaction Under the Bakony-Balaton Highland Volcanic Field

BIANCA NÉMETH<sup>1,2</sup>, KÁLMÁN TÖRÖK<sup>1</sup>,  
ISTVÁN KOVÁCS<sup>1</sup> AND CSABA SZABÓ<sup>2</sup>

<sup>1</sup> Geological and Geophysical Institute of Hungary, H-1143, Srefánia út 14, Budapest, Hungary

<sup>2</sup> Lithosphere Fluid Research Lab, Institute of Geography and Earth Sciences, Eötvös University, Budapest, Hungary, H-1117, Pázmány Péter sétány 1/c

Plio-Pleistocene alkali basalt hosted mafic garnet granulite xenoliths were studied from the Bakony-Balaton Highland Volcanic Field (Hungary). Two particular samples were chosen for analyses (optical microscopy, microthermometry, major and trace element geochemistry, Raman and IR spectroscopy), which contain primary silicate melt inclusions (SMI) in the rock-forming minerals. The samples have non-equilibrium texture in contrast with majority of known mafic garnet granulite xenoliths. SMI were observed in plagioclase, clinopyroxene and ilmenite in both xenoliths. The major element geochemistry of the glass of SMI suggests the presence of a silica rich melt at relatively high temperatures (830-920 °C). The origin of the melts could have been derived by the melting of biotite-gneiss or quartz-amphibolite. Our data suggest that the SMI derived from partial melting of different lower crustal rocks having mafic and metasedimentary origin with an occasional presence of C-O-H±S±N fluids. Petrography suggests at least five fluid events in the lower crust. The IR study of the water content in the rock-forming minerals and in the host minerals, including SMI and fluid inclusions, suggest that the acidic melt contained relatively high amounts of water. The observed SMI and fluid inclusions locally rehydrated the originally dry minerals.

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## When do insoluble particles act as good CCN?

A. NENES<sup>1,2\*</sup>

<sup>1</sup>School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta GA, USA (correspondence: athanasios.nenes@gatech.edu)

<sup>2</sup>School of Chemical And Biomolecular Engineering, Georgia Institute of Technology, Atlanta GA, USA

The ability of dust particles to serve as CCN under atmospherically relevant supersaturations depends on their mineralogy, size, morphology, and atmospheric processing. Most studies to date focus on the soluble fraction of aerosol particles when describing cloud droplet nucleation, and overlook the interactions of the hydrophilic insoluble fraction with water vapor. A new approach to include such interactions is presented, by combining multilayer Frenkel-Halsey-Hill (FHH) physical adsorption isotherm, Kohler theory and curvature (Kelvin) effects.

The importance of adsorption activation theory (FHH-AT) is demonstrated by measurements of CCN activity of mineral aerosols generated from clays, calcite, quartz, and desert soil samples from Northern Africa, East Asia/China, and Northern America. Based on the dependence of critical supersaturation with particle dry diameter, it is found that the FHH-AT is a better framework for describing fresh (and unprocessed) dust CCN activity than classical Köhler theory (KT). Ion Chromatography (IC) measurements performed on fresh regional dust samples indicate negligible soluble fraction, further supporting FHH-AT.

The results presented reshapes the conventional model of CCN activity, as it demonstrates that dust particles do not require deliquescent material to serve as atmospheric cloud nuclei. A droplet parameterization framework for large scale models that includes the new CCN activation physics is also developed and constrained by laboratory measurements. The framework accounts for aging of dust (via deposition of hygroscopic material), and is included within a global model framework to assess the impact of dust on warm cloud droplet number.

## Crystallographic relationships between diamond and its olivine inclusions. An update

F. NESTOLA<sup>1\*</sup>, P. NIMIS<sup>1</sup>, S. MILANI<sup>1</sup>, R. ANGEL<sup>1</sup>,  
M. BRUNO<sup>2</sup> AND J.W. HARRIS<sup>3</sup>

<sup>1</sup>Dipartimento di Geoscienze, Università di Padova, Italy  
(\*correspondence: fabrizio.nestola@unipd.it,  
paolo.nimis@unipd.it, sula.milani@studenti.unipd.it,  
rossjohn.angel@unipd.it)

<sup>2</sup>Dipartimento di Scienze della Terra, Università di Torino, Italy (marco.bruno@unito.it)

<sup>3</sup>School of Geographical and Earth Sciences, University of Glasgow, UK (Jeff.Harris@glasgow.ac.uk)

We have investigated the crystallographic relationships between olivine inclusions and their diamond hosts by in-situ single-crystal X-ray analysis. We studied 21 diamonds, all from the same kimberlite source (Udachnaya, Yakutia), containing a total of 51 olivine inclusions with diamond-imposed morphology. Each diamond contained up to nine individual olivines. On a statistical basis, no preferential orientation could be found. In particular, only 3 olivines showed an orientation comparable to that found by Mitchell & Giardini [1], i.e. (101)oli // (101)dia and (010)oli // (111)dia, which is believed to be the most favourable in the case of epitaxy. Based on our data, such orientation cannot be considered as “typical” of olivines included in diamonds. Although olivines in different diamonds showed random crystallographic orientations, multiple olivines within the same diamond often showed very similar orientations. Up to three sets of iso-oriented inclusions have been found within a single diamond. Our unprecedented data set clearly refutes the long assumed existence of a systematic crystallographic relationship for olivine inclusions in diamonds [1, 2]. The implications in terms of syngensis vs. protogenesis of the inclusions will be discussed.

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## Colloid-associated iron and arsenic transport in streams

ELISABETH NEUBAUER<sup>1</sup>, FRANK VON DER KAMMER<sup>1</sup>,  
KLAUS-HOLGER KNORR<sup>2</sup>, STEFAN PEIFFER<sup>2</sup>,  
MARTIN REICHERT<sup>2</sup>, STEPHAN J. KÖHLER<sup>3</sup>,  
HJALMAR LAUDON<sup>4</sup> AND THILO HOFMANN<sup>1</sup>

<sup>1</sup>University of Vienna, Department of Environmental Geosciences, Austria (elisabeth.neubauer@univie.ac.at)

<sup>2</sup>University of Bayreuth, Department of Hydrology, Germany

<sup>3</sup>Swedish University of Agricultural Sciences, Department of Aquatic Sciences and Assessment, Uppsala, Sweden

<sup>4</sup>Swedish University of Agricultural Sciences, Department of Forest Ecology and Management, Umeå, Sweden

Significant correlations between concentrations of arsenic (As), iron (Fe), and natural organic matter (NOM) are often observed in wetland draining streams. However it is not yet understood how the transport of Fe and As along with NOM and iron hydroxide colloids is affected under variable hydrological and hydrochemical conditions.

Analysis with Flow Field-Flow Fractionation coupled to UV-Vis spectroscopy and inductively coupled plasma mass spectrometry revealed that As was associated with NOM and, if present, Fe-organo-mineral colloids in the size range below 25 nm.

The colloid composition in the studied streams was highly variable on a temporal and spatial level: Short-term groundwater level fluctuations affected the release of Fe, NOM and As, and colloid composition with respect to NOM and Fe-hydroxides changed within hours. This is due to changing flow paths of the groundwater that feeds the stream as well as the chemical composition of the hydraulically active soil layers. Under all conditions, 25 to 50% of the total As was associated with NOM. However, the mass of As exported per mass of NOM was considerably higher under baseflow conditions.

The colloid composition was also affected when stream water moved from first order, acidic streams to more basic, larger streams. Fe was mainly transported as Fe-NOM complexes in acidic first order streams. In contrast, in the more basic higher order streams, Fe-hydroxide colloids and particles were present. The amount of colloid-associated As decreased from 75% to 26% with increasing pH, and As in the colloidal size range was mainly associated with NOM.

There is growing interest in quantifying the riverine fluxes of Fe to the oceans. Association with NOM enhances the Fe mobility in streams. Concentrations of NOM bound Fe in the studied catchments were high compared to literature data. In conclusion, wetland-draining catchments are of special importance for riverine Fe and trace element transport.

## Nickel and methanogens

A. NEUBECK<sup>1\*</sup> AND M. IVARSSON<sup>2</sup>

<sup>1</sup>Department of geological sciences, Stockholm University, Stockholm, Sweden

<sup>2</sup>Department of Paleobiology and the Nordic Center for Earth Evolution (NordCEE), Swedish Museum of Natural History, Stockholm, Sweden

Methanogens require Ni for their growth and as a consequence the microbial fractionation of Ni isotopes can be used as a biomarker for activity of methanogenic communities [1]. Anaerobic laboratory experiments were performed using methanogens to investigate methanogenic growth in a modified nutrient media [2] with olivine Fo91 (5g/l) added as an additional mineral nutrient source and as the only H<sub>2</sub> provider. One of the investigated methanogens showed an increased growth in the experiments with added olivine. There was also a close relationship between the mobilized Ni and the growth of the methanogen. This is the first experimental evidence of a close methanogen-mineral interaction. Ni is an element that previously has been neglected in the study of fossilized microorganisms and their interaction with mineral substrates and, thus, there are no records or published data of Ni in association with microfossils. However, we have detected enrichments of Ni in fossilized microorganisms and ichnofossils, respectively, from three separate locations. Ni is not present in the host rock in none of the samples, thus, it is more probable that the Ni content is primary, a remnant of the live microorganisms. More extensive analysis is required to understand the uptake, preservation and fractionation of Ni by methanogens as well as the preservation and magnitude of Ni in microfossils.

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[2] Westerholm M, Roos S, Schnürer A. *Syntrophaceticus schinkii* gen. nov., sp. nov., an anaerobic, syntrophic acetate-oxidizing bacterium isolated from a mesophilic anaerobic filter. *FEMS Microbiology Letters*. 2010.

## Characterization of microbial diversity of a geothermal plant after long-term shutdown periods

DOMINIK NEUMANN<sup>1</sup>, DARIA MOROZOVA<sup>1</sup>,  
JULIA SCHEIBER<sup>2</sup>, SEBASTIAN TEITZ<sup>1</sup>  
AND HILKE WÜRDEMANN<sup>1\*</sup>

<sup>1</sup> Helmholtz Centre Potsdam GFZ, International Centre for Geothermal Research, Hermannswerder 15, 14473 Potsdam, Germany. \*(Correspondence: [Wuerdemann@gfz-potsdam.de](mailto:Wuerdemann@gfz-potsdam.de))

<sup>2</sup> GEIE Exploitation Minière de la Chaleur, Kutzenhausen, France.

The geothermal plant in Soultz-sous-Forêts, located at the western part of the Upper Rhine Graben, is running as an EGS, including four wells ranging to a depth of 5 km. By long-term circulation of deep brines in the reservoir geothermal fluids with a total dissolved solid content of 97 g/L, a temperature around 160°C and a pH around 4.5 are produced. In order to characterize the microbial diversity and its potential involvement in scaling and corrosion processes after long-term shutdown periods, a series of fluid samples from the production well GPK2, taken during two plant restarts, were analyzed. Characterization of the microbial community was done by genetic fingerprinting (PCR DGGE) and qPCR.

Results indicate a diverse microbial community in the fluid of the production well after shutdown periods. In both sampling campaigns a clear shift in the Bacteria community composition was visible after the restart, which could be explained by the increasing temperature and the increasing amount of reservoir fluid. The diversity of the Archaea was not affected.

Sulfate reducing Bacteria (SRB), as indicated by the presence of their 16S rRNA gene and *dsr* genes, were found only until a produced fluid volume of 260 m<sup>3</sup> (Two borehole volumes) during the first sampling campaign. This indicates the growth of these microorganisms and biofilm formation on the well casing during the shutdown period and their removal after restart of the fluid production. Preliminary quantification results underline this assumption: highest levels of DNA, 16S rRNA gene copies and *dsr* gene copies were found in the first samples after the restart, while in later samples values were lower or below the detection limit.

The results, as well as further analyzes like the creation of clone libraries or the detection of cell numbers will contribute to characterize the potential involvement of the found microorganisms in corrosion processes and enhance the understanding of the microbial community associated with geothermal plants.

## Effect of Al/B substitution on structure and properties of silicate glasses and melts

D. R. NEUVILLE

CNRS-IPGP, Géochimie&Cosmochimie, Paris Sorbonne Cité,  
1 rue Jussieu, 75005 Paris, France.

The relationship between physical properties and structure of glasses and melts in the system  $MO-T_2O_3-SiO_2$  (with  $M=Na_2, Ca$  and  $T=Al, B$ ) are technologically and geologically important, in particular to understand the microscopic origin of the configurational thermodynamic properties. The connection of these network former is fundamental to understand the physical properties of magmatic liquids.

The configurational properties of melts and glasses provide fundamental information needed to characterize magmatic processes. A principal difficulty, however is to link the "macroscopic" configurational entropy with the structure of melts. This has been done by combining viscometry with Raman and NMR spectroscopy studies. From the viscosity measurements at low and high temperatures, we have obtained the configurational entropy,  $S_{conf}$  ( $\log \eta = Ae + Be/TS_{conf}$ , where  $\eta$  is the viscosity,  $T$  the temperature and  $Ae, Be$  two constants).

Silicon, aluminum, and boron are 3 network formers playing different role on the silicate network, whereas Si is the strongest network former in coordination 4, 5 or 6 as a function of  $T, P$ ; Al can play different function as a network former in 4- or 5-fold coordination and probably as a network modifier in 6 fold coordination. Boron observed in 3 or 4 fold coordination is always a network former but for very "fragile" glasses.

For the glass the Al/B substitution produce a small decrease of the molar volume while this substitution produced a strong decrease of viscosity and glass transition temperature while the fragility of the network is less affected by this chemical change. Raman spectra show significant change in the D1 and D2 bands. NMR spectroscopies show also significant change as a function of chemical change and temperature. All this observations will be discussed and interpreted in order to link microscopic versus macroscopic changes.

## Historical deposition of Polycyclic Aromatic Hydrocarbons in an Amazon estuary

P.A. NEVES\*<sup>1</sup>, S. TANIGUCHI<sup>1</sup> AND M.C. BÍCEGO<sup>1</sup>

<sup>1</sup>Laboratório de Química Orgânica Marinha, Instituto Oceanográfico da Universidade de São Paulo, 05508-120, São Paulo, Brazil. \*(correspondence: ticinev@yahoo.com.br)

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitously distributed in the aquatic environments, coming from natural and anthropogenic sources. PAHs can accumulate in sediments and their historical deposition can show source alterations throughout time. The study area, Guajará Bay, is located in northeastern Amazon and Belém (one of Amazon's biggest cities) is located in its margins. To evaluate the temporal changes of PAHs in Guajará Bay a sediment core was collected in 2010. Total PAH concentration ( $\Sigma PAH$ ) ranged from 46.9 to 595  $ng\ g^{-1}$  (dry weight) along the core. The core can be divided in two periods regarding PAHs sources to the area. In the first period, corresponding from 1900's to the early 1960's,  $\Sigma PAH$  remained constant, with an average of 79  $ng\ g^{-1}$  (d.w.), possibly characterizing base levels of PAHs for this region. Composition of individual PAH showed a predominance of alkyl-PAH over its parental compound such as methylphenanthrene over phenanthrene. Usually, these PAHs are associated with petrogenic inputs, however, there is no evidence of oil during this period in the region. Thus, the higher proportions of alkyl-PAHs could be related to natural sources, such as organic matter diagenetic transformation or biogenic synthesis. During the second period, which starts in the late 1960's,  $\Sigma PAH$  increases, reaching its maximum value at the top of the core. Diagnostic ratios showed a predominance of pirolitic PAH in the area, suggesting that this input is probably related to the intensification of the urban and industrial development, encouraged by the government since 1950's. The variation of PAH contents was closely related to the changes in the environment of the Amazon area evaluated.

## Establishment of euxinic oceanic conditions following the Lomagundi Event

L. NGOMBI-PEMBA<sup>1\*</sup>, D. E. CANFIELD<sup>2</sup>,  
E. U. HAMMARLUND<sup>2,3</sup>, S. BENGTSON<sup>2,4</sup>,  
A-C. PIERSON-WICKMAN<sup>5</sup>, F. GAUTHIER-LAFAYE<sup>6</sup>,  
O. ROUXEL<sup>7</sup> AND A. EL ALBANI<sup>1</sup>

<sup>1</sup>UMR 7285, Univ. Poitiers, 86022 Poitiers, France  
(\*lauriss.ngombi.pemba@univ-poitiers.fr)

<sup>2</sup>Nordic Center for Earth Evolution (NordCEE), Box 50007,  
105 05 Stockholm, Sweden

<sup>3</sup>Southern University of Denmark, Institute of Biology,  
Campusvej 55, Dk-15 5230 Odense M, Denmark

<sup>4</sup>Swedish Museum of Natural History, Department of  
Palaeozoology

<sup>5</sup>Département Géosciences, UMR 6118, Université de  
Rennes, 35042 Rennes, France

<sup>6</sup>Laboratoire d'Hydrologie et de Géochimie de Strasbourg,  
UMR 7517-UdS-CNRS, 67084 Strasbourg, France

<sup>7</sup>IFREMER, Département Géosciences Marines, 29280  
Plouzané, France

Following the great oxidation event (GOE), the isotope record of marine carbonate rocks suggests a massive burial of organic carbon in an event known as Lomagundi excursion (LE). It is estimated that during this period atmospheric oxygen attained levels much higher than during GOE [1]. It is proposed that as the LE declined, oxygen dropped to lower levels [1, 2], but the direct geochemical evidence for the state of atmospheric and ocean oxygenation both during and after the LE is missing. This time window is also represented by the 2.2-2.0 Ga Francevillian group of Gabon, well known for the earliest large colonial organisms [3]. In order to investigate the nature of marine water-column chemistry, samples representing the entire section were subjected to multielement (C, S, Fe, Mo, U) biogeochemical study.

Geochemical data show deep water oxic conditions during deposition of the lower part of the section in agreement with the LE. Nevertheless the interlayered Mn deposits occurred in ferruginous anoxic conditions reflecting sea-level changes. The upper part of the section reflect euxinic conditions, and together with  $\delta^{98}\text{Mo}$  values, these data confirm a significant decrease in the oxygenation of ocean water in the aftermath of the Lomagundi Event.

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## Hydration, structure and mobility of Cs<sup>+</sup> and Sr<sup>2+</sup> in montmorillonite and muscovite clay minerals

BRICE F. NGOUANA W.<sup>1\*</sup>, NARASIMHAN L.<sup>1</sup> AND  
ANDREY G. KALINICHEV

Laboratoire SUBATECH (UMR-6457), Ecoles des Mines de  
Nantes, 4 Rue Alfred Kastler, La Chantrerie, 44307,  
Nantes Cedex 3, France (\* ngouana@subatech.in2p3.fr)

Clay minerals used as natural and engineered barriers in geological nuclear waste repositories are able to considerably reduce the mobility of radionuclides in the environment. The radionuclide retention happens through a combination of various physical and chemical processes taking place at the clay-water interface, but their molecular mechanisms are still insufficiently understood.

To obtain detailed microscopic scale information on the structure, dynamics, and energetics of Cs<sup>+</sup> and Sr<sup>2+</sup> ions at the surfaces of model illite and smectite clays (muscovite and montmorillonite, respectively) we have performed a series of classical molecular dynamics (MD) computer simulations using the CLAYFF force field [1]. New sets of structural models with different degrees of compositional disorder in the octahedral and tetrahedral layers of clay were constructed and investigated in order to quantify the effects of such disorder on the properties of the adsorbed ions.

The structural properties were probed in terms of the atomic density distributions in the direction normal to the clay surfaces, along the planes parallel to the clay surfaces, atom-atom pair correlation functions, and coordination numbers. The 2-dimensional and 3-dimensional diffusion coefficients were calculated to probe the ionic mobility at the clay surfaces and in the interlayer space. In the case of montmorillonite (a swelling clay), the hydration energetics was also systematically investigated by determining the hydration and immersion energies [2].

The atomic density profiles vary with the charge and size of the ions and show a significant layering at the interfacial regions of both studied clays. Pair correlation functions and coordination numbers indicate only one stable adsorption site for cations on the basal surface of muscovite (ditrigonal) in contrast to two adsorption sites on a similar montmorillonite surface (ditrigonal and triangular). Cs<sup>+</sup> and Sr<sup>2+</sup> mobility is considerably reduced by substrate adsorption, but the diffusion coefficients tend to get closer to bulk solution values when the ions are removed from the surface.

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## Constraining OH diffusivity in silicate melts

HUAIWEI NI<sup>1,2</sup>, ZHENGJIU XU<sup>3</sup> AND YOUXUE ZHANG<sup>3</sup>

<sup>1</sup>CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China (\*Correspondence: hwni@ustc.edu.cn)

<sup>2</sup>Bayerisches Geoinstitut, Universität Bayreuth, 95440 Bayreuth, Germany

<sup>3</sup>Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI 48109, USA

The transport of water in silicate melts is mostly dominated by molecular H<sub>2</sub>O (H<sub>2</sub>O<sub>m</sub>) diffusion. Diffusivity of hydroxyl (OH), the other water species, has not been well quantified. It has been previously assumed that OH diffusivity is close to the Eyring diffusivity (i.e., inversely proportional to melt viscosity), or essentially approaches zero. However, in our experimental study of water diffusion in an Fe-free andesitic melt, we found that these assumptions do not hold.

Diffusion experiments were performed at 1 GPa in a piston-cylinder apparatus using a double diffusion couple technique. One couple contained a dry glass (with 0.01 wt% water) and a hydrous glass (with ~3 wt% water), and the other contained the same dry glass and a different hydrous glass (with ~6 wt% water). Both couples experienced the same pressure and thermal history, which is crucial for constraining the dependence of H<sub>2</sub>O diffusivity on water content. Diffusion profiles preserved in the quenched products were analyzed with both FTIR and confocal Raman microspectroscopy. Nearly identical profiles were obtained from the two methods for profile length > 1 mm (produced at 1619-1842 K), but for profile length < 0.1 mm (produced at 668-768 K) FTIR analysis showed marked convolution effects due to its spatial resolution being inferior to that of Raman.

Previous models neglecting OH diffusivity cannot satisfactorily reproduce the measured profiles. We developed a new fitting procedure that simultaneously fits both diffusion profiles from a single experiment and also accounts for the role of OH diffusion. With the new model, OH diffusivity is constrained to be 10%-20% of H<sub>2</sub>O<sub>m</sub> diffusivity at 1619-1842 K as total water content approaches zero. The obtained OH diffusivity is much higher than the Eyring diffusivity, indicating that in melt structure OH is not necessarily bonded with network-forming cations, such as Si. On the other hand, OH diffusivity is close to reported F diffusivity (both the size and the valence of OH and F are comparable).

## Research on heavy metal environmental geochemistry in urban soils in Haikou, China

QIAN NI<sup>1</sup>, ZHENGYU BAO<sup>2</sup> AND CHUNYAN WANG<sup>3</sup>

<sup>1</sup> State Key Laboratory of Biogeology and Environmental Geology, (niq1981@163.com)

<sup>2</sup> Faculty of Material science and Chemistry, (zybao@263.net)

<sup>3</sup> Faculty of Engineering, (1239901602@qq.com)

China University of Geosciences, Wuhan 430074, China

Soil heavy metals constitute serious environmental hazards from the point of view of polluting the soils and adjoining streams and rivers. Therefore, a series of investigations were performed to provide heavy metal signatures of urban soils and to evaluate pollution level. Concentrations of Cd, Zn, Ni, Cr, Cu, Pb, Hg and As were measured on 70 topsoil samples and 16 deep-soil samples collected from green areas in Haikou city, capital of Hainan province. The results indicate that, in comparison with Chinese Environmental Quality Standard II for Soils (CEQSSII), urban soils in Haikou have lower metal concentrations as a whole, especially Hg, As, Cu, Pb and Zn (except one maximum) lower than the Chinese Environmental Quality Standard II (CEQSSI). These concentration levels are comparable to those in other studies, such as London, Hong Kong, Shanghai, and so on, we found that these values are lower in Haikou except Cr and Ni. Histograms of distributions of these concentrations show "double peak" or "long tailed", which may be related to soil parent material types and anthropic contributions. Pollution evaluations of single factor index and comprehensive index indicate that soils in study area are unpolluted by most heavy elements, except that Hg and Cd are medium polluted elements which should be noticed. Speciation analyses show that Zn, Ni, Cr, Cu, Pb and As are mainly in the residual and Fe-Mn oxide phases, while Hg is associated with the organic, humic and residual fractions. The high exchangeable Cd (about 24%) in urban soils need further investigation for ecological and health implications.

Keywords: Heavy metals, Urban soils, Pollution evaluation

## Alteration at bentonite-cement interfaces – An experimental approach

CLAUDIA NICKEL<sup>1,2</sup>, ANDRE BALDERMANN<sup>1</sup>, MARTIN DIETZEL<sup>1</sup>, GEORG H. GRATHOFF<sup>2</sup>  
AND LAURENCE N. WARR<sup>2</sup>

<sup>1</sup>Institute for Applied Geosciences, Graz University of Technology, Rechbauerstraße 12, 8010 Graz, Austria; (claudia.nickel@tugraz.at)

<sup>2</sup>Institute for Geography and Geology, Ernst-Moritz-Arndt Universität Greifswald, Friedrich-Ludwig-Jahn-Str. 17a, 17487 Greifswald, Germany

The identification of alteration processes at the interface of clay and contacting cement is crucial for ensuring the long-term stability of underground nuclear waste repositories, i.e. the Aspö field test site (Sweden).

In order to investigate alteration features directly at the bentonite-cement interfaces, three flow-through laboratory experiments were realized. Differences in the water uptake behavior and related changes in the mineralogy and chemistry of Portland cement clinker and air-dried MX-80 bentonite were monitored using wet-cell X-ray diffraction (XRD) and transmission electron microscopy analyses, covering an experimental period of 1 year.

The water uptake rate was ~44-times higher in the clay-cement experiments than that of the pure MX-80 bentonite reference experiment, and the steady state was reached after ~22 and ~963 h, respectively. XRD data display progressive hydration of the Na-montmorillonite interlayer sites, as expressed by the stepwise increase of the water layers (WL) from 12.4 Å (1 WL) and 15.7 Å (2 WL) to 18.6-19.1 Å (3 WL). *CALCMIX* modeling of the montmorillonite revealed 65 ± 2% 3 WL and 35 ± 2% 4 WL at the steady state, suggesting complete hydration of the cement and bentonite was reached in the less altered zone. In contrast, cation exchange of Na<sup>+</sup> (0.36 to 0.08 a.p.f.u.) for Ca<sup>2+</sup> (0.08 to 0.12 a.p.f.u.) was recognized in the montmorillonite interlayer sites close to the clay-cement contact, corresponding with a general depletion in CaO of the contacting Portland cement by a factor of 2.5. In addition, various of original cement phases were preserved, and only minor proportions of C-S-H phases were found.

Cation exchange within the clay and the preservation of original cement phases suggests that intense alteration processes occurred at the bentonite-cement contact. The Ca for Na substitutions strongly reduced the smectites swelling pressure and inhibited the formation of stable cement phases, by quantitative removal of CaO. These processes destabilized the clay-cement buffer and need further investigation for long-term nuclear waste disposal in sustainable underground repository sites that require clay-cement sealings.

## Coupled spectromicroscopic investigations for improved conceptual models of soil carbon cycling

PETER S. NICO<sup>1</sup>, MARCO KEILUWEIT<sup>1,2,3</sup>,  
JENNIFER PETT-RIDGE<sup>2</sup>, PETER WEBER<sup>2</sup>  
AND MARKUS KLEBER<sup>3</sup>

<sup>1</sup>Earth Sciences Division, Lawrence Berkeley Laboratory, One Cyclotron Rd, Berkeley CA 94720

<sup>2</sup>Chemical Sciences Division, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore CA 94550

<sup>3</sup>Crop and Soil Science, Oregon State University, Corvallis, OR 97331

Useful numeric models can only be constructed from accurate conceptual models. Biogeochemical interfaces or hotspots result from the spatial and temporal convergence of two or more different materials or processes. A comprehensive understanding of interfaces requires analytical techniques that complement each other in spatial, temporal, and elemental sensitivity. Our team has built expertise in the application of multiple (spectro)microscopic techniques to laboratory investigations of soil carbon cycling. We have sought to understand the interface between inorganic mineral phases, organic compounds, and biological organisms occurring at the micron scale. We have made particular use of synchrotron based (spectro)microscopic techniques such as SR-FTIR, STXM/NEXAFS, hard X-ray microprobe, and X-ray microtomography as well as high resolution secondary ion mass spectrometry (NanoSIMS). This presentation will include technical considerations and challenges associated with sample preparation and handling required for successful application of multi-modal imaging analysis. In addition, the specific findings from several different investigations and the associated insights will be presented. The data shown will illustrate the challenges associated with obtaining statistically robust and quantitative measurements with this approach along with its' power for improving conceptual mechanistic models.

## Leucosome formation by disequilibrium melting and melt loss: Perspectives from the South Marginal Zone (SMZ) of the Limpopo Belt, South Africa

G. NICOLI<sup>1\*</sup>, G. STEVENS<sup>1</sup>, J-F MOYEN<sup>2</sup>, AND J. TAYLOR<sup>1</sup>

<sup>1</sup>Stellenbosch University, PB X1, Matieland 7602, South Africa (\*correspondence: gnicoli@sun.ac.za)

<sup>2</sup>UMR 6524 CNRS, Université Jean Monnet, 23 rue du Dr Michelon, 42023 Saint-Etienne, France

This study investigates the details of the anatexis process which result in the formation of dm- to m-scale, markedly low K<sub>2</sub>O content leucosomes during biotite incongruent melting.

Two hypotheses exist for the origin of such leucosomes; that they represent the products of fractional crystallization of plagioclase and quartz [1]; and, the redistribution of K<sub>2</sub>O and H<sub>2</sub>O from the segregated melt back into the residuum [2]. Evidences from metapelites in the SMZ do not support either hypothesis. The peritectic assemblage is well preserved in zones of residua adjacent to leucosomes [3]; leucosomes are characterised by strong positive Eu anomalies, whilst the gneisses from which they were derived have insignificant Eu anomalies; Na:Ca ratios in the leucosomes are similar to those in their source rocks; field-based XRF profiles of K<sub>2</sub>O content across leucosomes and their hosting gneisses does not show substantial K<sub>2</sub>O enrichment in the gneisses adjacent to the leucosomes. In addition, leucosomes formed by biotite + sillimanite melting are shown to have become rheologically solid prior to the occurrence of biotite melting in the absence of sillimanite at higher temperature.

These findings suggest that the leucosomes formed by biotite fluid-absent melting involving disequilibrium behaviour of plagioclase. Such a mechanism fits with the entire spectrum of field, textural and chemical data from the SMZ and open new perspectives on the role played by disequilibrium processes during S-type granite genesis. The results argue that the melt leaves the source instantaneously, that individual leucosomes are constructed incrementally; that leucosome volumes do not represent the volume of melt present at any time; and the leucosomes in such granulites constitute part of the residuum after partial melting.

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## Changes of magma geochemistry at Mt. Etna during the last 45ka due to sampling of a variegated mantle

EUGENIO NICOTRA<sup>1,2\*</sup>, MARCO VICCARO<sup>2</sup>, RENATO CRISTOFOLINI<sup>2</sup> AND SANDRO CONTICELLI<sup>3</sup>

<sup>1</sup>Università della Calabria, Via P. Bucci 15/B, 87036, Arcavacata di Rende (CS), Italy, (eugenio.nicotra@unict.it)

<sup>2</sup>Università di Catania, Corso Italia 57, 95129 Catania, Italy

<sup>3</sup>Università di Firenze, Via G. La Pira 4, 50121, Firenze, Italy

Mt. Etna magmas show long- and short-term variations especially for K contents, some LILEs and HFSEs as well as Sr-Nd-Pb-Hf isotope ratios, a feature increasingly more evident during the last four decades of activity. Nonetheless, magma source characteristics are still debated. Contributions to this discussion arise from focusing the attention on volcanic products of Etna of the last 45 ka of activity, belonging to the “*Ellittico*” and “*Recent Mongibello*” volcanic successions. Incompatible trace elements for mantle-equilibrated compositions of the most basic products reveal that the Etnean magmas under consideration can be produced by rather low partial melting degrees of a peridotite variably enriched by metasomatic phases such as amphibole and/or phlogopite. Sr-Nd-Pb-Hf isotopes suggest that recycled and altered oceanic lithosphere is a dominant component in the Etnean mantle source. A dominant FOZO reservoir has been inferred [1], although not sufficient to satisfactorily explain the observed isotopic variations. Addition of variable proportions of an EM1-type component (up to 10%) has been then suggested. Hf isotopes provide further evidence that the enriching component at Mt. Etna could be related to the metasomatizing action of high-T fluids (i.e., silicate melts), which may be frozen in the form of pyroxenite veins at mantle conditions. Our calculations confirm that involvement of variable amounts of this enriched component in magma genesis is able to explain the long- and short-term geochemical and isotopic variations observed throughout the last 45 ka.

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## Gas geochemistry of spring waters along the Alpine Fault, NZ

S. NIEDERMANN<sup>1</sup>, M. ZIMMER<sup>1</sup>, J. ERZINGER<sup>1</sup>, S.C. COX<sup>2</sup>, C.D. MENZIES<sup>3</sup> AND D.A. TEAGLE<sup>3</sup>

<sup>1</sup>Deutsches GeoForschungsZentrum GFZ, Telegrafenberg, D-14473 Potsdam, Germany (nied@gfz-potsdam.de)

<sup>2</sup>GNS Science, Private Bag 1930, Dunedin 9054, New Zealand

<sup>3</sup>School of Ocean and Earth Science, University of Southampton, Southampton SO14 3ZH, United Kingdom

The Alpine Fault on the South Island of New Zealand is one of the longest, straightest, and fastest-moving transform faults, with oblique-slip at rates that accommodate over half of the Australia-Pacific plate motion and cause rapid uplift of the Southern Alps. No major earthquakes have occurred on the fault in historic time, but it last ruptured around 1717 AD and is thought to fail in large moment magnitude ( $M_w > 7$ ) to possibly great ( $M_w > 8$ ) earthquakes at ~330 yr recurrence intervals. Rocks southeast of the Alpine Fault are exhumed at rates faster than they can cool, resulting in a 63°C/km geothermal gradient, convective circulation and warm springs without related volcanic activity. Because the seismic cycle is fundamentally controlled by fluids, improved knowledge of fluid circulation in the shallow crust is paramount to understanding earthquake processes on the Alpine Fault.

In the context of the Deep Fault Drilling Project (DFDP), we have investigated gas compositions and noble gas isotopic abundances in spring waters from the vicinity of the fault. Free gas was sampled at four springs, while nine other springs provided water samples that were degassed in the lab. N<sub>2</sub> is commonly the most abundant gas, CO<sub>2</sub> concentrations vary widely from <0.1% to >96%, and CH<sub>4</sub> contributes up to 13%. He concentrations are up to ~500 ppm. <sup>3</sup>He/<sup>4</sup>He ratios are generally highest (up to 0.81 Ra) close to the fault and decrease to radiogenic values (<0.04 Ra) towards the southeast at distances of a few kilometers from the fault, with two exceptions: Copland Spring (0.42 Ra) is located ~12 km from the fault and exhibits the highest gas flow and the highest CO<sub>2</sub> content of all springs studied in this work. Kotuku Spring, the only location available for sampling on the Australian plate, yields a particularly high <sup>3</sup>He/<sup>4</sup>He ratio of ~3.1 Ra despite low gas flow and ~17 km distance from the fault. Obviously, mantle fluids can penetrate the thick crust beneath the Southern Alps directly at the fault and may be diverted away from it only where major passageways through the crust exist. It remains to be seen whether the high <sup>3</sup>He/<sup>4</sup>He ratio of Kotuku indicates a distinct fluid origin on the northwest side of the fault in general or is just a local feature.

## Calcium and Oxygen Isotope Fractionation during Precipitation of Calcium Carbonate Polymorphs

A. NIEDERMAYR<sup>1,2</sup>, A. EISENHAEUER<sup>3</sup>, F. BÖHM<sup>3</sup>, B. KISAKÜREK<sup>3</sup>, I. BALZER<sup>1</sup>, A. IMMENHAUSER<sup>1</sup>, S.J. KÖHLER<sup>4</sup> AND M. DIETZEL<sup>2</sup>

<sup>1</sup>Institute of Geology, Mineralogy and Geophysics, Ruhr University Bochum, Germany (andrea.niedermayr@rub.de).

<sup>2</sup>Institute of Applied Geosciences, TU Graz, Austria.

<sup>3</sup>GEOMAR, Helmholtz Centre for Ocean Research Kiel, Germany.

<sup>4</sup>Department of Aquatic Sciences and Assessment, University of Agricultural Sciences Uppsala, Sweden.

Different isotopic systems are influenced in multiple ways and amounts by the crystal structure, surface properties, hydration and dehydration processes, deprotonation, adsorption, desorption, isotope exchange and diffusion processes. Herein we studied the structural and kinetic effects on fractionation of stable Ca- and O-isotopes during CaCO<sub>3</sub> precipitation in order to evaluate processes controlling their fractionation.

Calcite, aragonite and vaterite were precipitated using the CO<sub>2</sub> diffusion technique<sup>1</sup> at a constant pH of 8.3, but various temperatures (6, 10, 25 and 40°C) and precipitation rates (10<sup>1.5</sup> to 10<sup>5</sup> μmol h<sup>-1</sup> m<sup>-2</sup>).

The precipitation rate effect on fractionation of Ca-isotopes is mainly influenced by the precipitated polymorph. The calcium isotope fractionation between calcite/vaterite and aqueous Ca<sup>2+</sup> increases with increasing precipitation rate. In contrast the fractionation of Ca-isotopes between aragonite and aqueous Ca<sup>2+</sup> decreases with increasing precipitation rate. Hence, the influence of precipitation rate on the fractionation of calcium isotopes of aragonite is reverse compared to that of calcite and vaterite. The fractionation of <sup>18</sup>O/<sup>16</sup>O between CaCO<sub>3</sub> and H<sub>2</sub>O decreases with increasing precipitation rate. The latter behaviour is - in contrast to calcium isotope fractionation - similar for all three polymorphs.

Vaterite formation induces lower fractionation of calcium isotopes ( $\Delta^{44/40}\text{Ca}_{\text{CaCO}_3\text{-aq}} = -0.10$  to  $-0.55$  ‰) compared to calcite ( $-0.69$  to  $-2.04$  ‰) and aragonite ( $-0.91$  to  $-1.55$  ‰). In contrast the fractionation of oxygen isotopes is highest for vaterite, followed by aragonite and calcite at similar precipitation rates and temperatures. Although fractionation of oxygen isotopes is mainly dominated by temperature in our experiments with constant pH, whereas fractionation of calcium isotopes is dominated by polymorphism and kinetic processes.

<sup>1</sup>A. Niedermayr, S.J. Köhler and M. Dietzel (2013), *Chemical Geology*, 340, 105-120.

## How sandstone mineral surfaces interact with $\text{Ca}^{2+}$ and $\text{Cl}^-$ ions

A.R. NIELSEN\*, K.N. DALBY, N. BOVET, AND S.L.S. STIPP

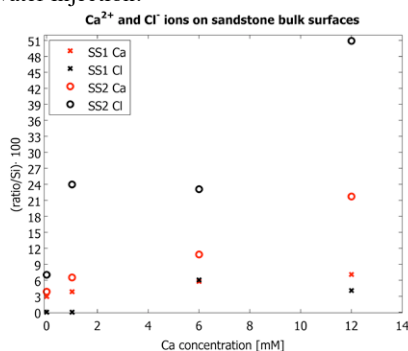
Nano-Science Center, Department of Chemistry, University of Copenhagen, Denmark (\*skrupsax@hotmail.com)

Sandstone oil reservoirs form an important global resource. Production with the highest possible yield would extend the resources that are currently accessible with existing infrastructure and postpone the need for developing more risky deep water and high Arctic fields. Enhanced oil recovery (EOR) methods, including flooding with low salinity water, have increased oil recovery rates for sandstone reservoirs, even though the mechanisms responsible are not yet fully understood. Linking reservoir scale studies with investigations carried out at the molecular scale would increase our understanding of such mechanisms and allow EOR methods to be optimised.

In this work, we examined the change in surface composition of two natural sandstones (SS1 and SS2) and the associated extracted clay, during exposure to calcium chloride ( $\text{CaCl}_2$ ) solutions at a variety of concentrations. For investigating surface uptake, we used X-ray photoelectron spectroscopy (XPS) on fast frozen samples [1] The sandstones and extracted clay have been thoroughly characterised with X-ray powder diffraction (XRPD) and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDXS).

The ratio of  $\text{Ca}/\text{Si}$  and  $\text{Cl}/\text{Si}$ , derived from XPS spectra, show which ions stick to the surface at various  $\text{Ca}$  concentrations (Figure 1). The SS2 sandstone adsorbed more chloride than calcium, no matter what solution concentrations were used, whereas the opposite was observed for SS1. SS2 also had a higher affinity for adsorption in general than SS1. XRPD patterns confirmed a difference in mineral composition.

We are using the information about responses from natural sandstone and natural clay minerals to design model systems for determining the mechanism behind the oil release that is observed on the reservoir scale in response to low salinity water injection.



**Figure 1:** The ratio of  $\text{Ca}/\text{Si}$  and  $\text{Cl}/\text{Si}$  for the two bulk sandstones presented as a function of the calcium concentration of the solution.

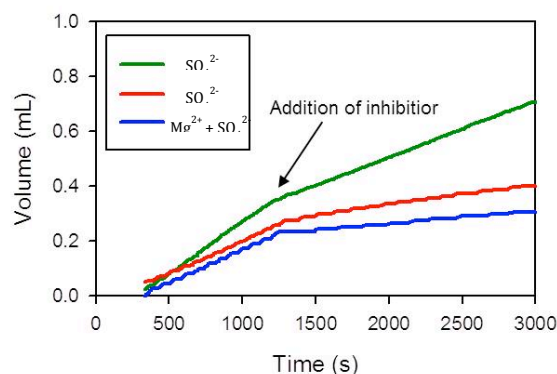
## Calcite scaling: Growth inhibition by $\text{Mg}^{2+}$ , $\text{SO}_4^{2-}$ and $\text{Mg}^{2+} + \text{SO}_4^{2-}$

M. R. NIELSEN\*, K. K. SAND AND S. L. S. STIPP

Nano-Science Center, Department of Chemistry, University of Copenhagen, Denmark (\*mia.rohde.nielsen@nano.ku.dk)

Calcite precipitation in wells, pipes, boilers and the like causes problems for industry. Effective inhibition would save huge amounts of energy and money. Magnesium ( $\text{Mg}^{2+}$ ) is known to poison calcite growth [1-3], so better understanding of how it works could lead to improved scale inhibitors. It has recently been shown that adsorption of both  $\text{Mg}^{2+}$  and sulfate ( $\text{SO}_4^{2-}$ ) changes calcite surface tension [4-5].

We investigated the effect of each ion singly and in combination by precipitating calcite at room temperature in a constant composition reactor [6]. Calcite precipitated at constant rate, then ions were added and the change in growth rate was monitored with time.



**Figure 1.** Typical plots for reagent addition versus time. Concentration of the inhibitors was 7.4 mM in all cases

Growth rate for pure calcite ranged from  $1.8 \cdot 10^6$  to  $6.0 \cdot 10^6$   $\text{mol s}^{-1} \text{m}^{-2}$ , consistent with previous data. Increased  $\text{Mg}^{2+}$  concentration correlated directly with increased inhibition. Dissolved  $\text{Mg}^{2+}$  decreased with growth, suggesting incorporation into the newly formed calcite. Although there is less inhibition by  $\text{SO}_4^{2-}$  alone than  $\text{Mg}^{2+}$  alone, when the two are present together, inhibition is strongest (Figure 1).

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## Toxic effects of butyl elastomers on aerobic methane oxidation

HELGE NIEMANN<sup>1</sup>, LEA I. STEINLE<sup>1,2</sup>, JAN H. BLEES<sup>1</sup>,  
STEFAN KRAUSE<sup>2</sup>, INGEBORG BUSSMANN<sup>3</sup>, TINA  
TREUDE<sup>2</sup> AND MORITZ F. LEHMANN<sup>1</sup>

<sup>1</sup>University of Basel, Dept. of Env. Geosciences, CH  
(helge.niemann@unibas.ch)

<sup>2</sup>Helmholtz Centre for Ocean Research (GEOMAR), DE

<sup>3</sup>Alfred Wegener Institute, Messtation Helgoland, DE

Large quantities of the potent greenhouse gas methane are liberated into the water column of marine and lacustrine environments where it may be consumed by aerobic methane oxidising bacteria before reaching the atmosphere. The reliable quantification of aerobic methane oxidation (MOx) rates is consequently of paramount importance for estimating methane budgets. A widely used set of methods for measuring MOx rates is based on the incubation of water samples during which the consumption of methane is monitored. Typically, incubation vessels are sealed with butyl rubber stoppers because these elastomers are essentially impermeable for gases at the relevant time scales. We tested the effect of different stopper materials (unmodified- and halogenated butyl rubber) on MOx activity. MOx rates in samples sealed with unmodified butyl rubber were > 75% lower compared to parallel incubations with halogenated butyl rubber seals, suggesting inhibiting/toxic effects associated with the use of unmodified butyl elastomers. In aqueous extracts of unmodified butyl stoppers, we detected various organic compounds including potential bactericides such as benzyltoluenes, phenylalkanes and benzothiazoles. The inhibition of MOx is most probably caused by organic contaminants that bleed off from the unmodified butyl elastomer into the incubation water.

## Multidisciplinary geophysical-geochemical analysis for qualitative renovation by artificial recharge of aquifers (WARBO LIFE)

NASSER ABU ZEID<sup>1</sup>, DANIEL NIETO<sup>2\*</sup>, ALESSANDRO AFFATATO<sup>2</sup>, LUCA BARADELLO<sup>2</sup>, FLAVIO ACCAINO<sup>2</sup>  
SALVATORE PEPI<sup>1</sup>, SABRINA RUSSO<sup>1</sup> AND CARMELA VACCARO<sup>1</sup>

<sup>1</sup>Dip. Fisica e Scienze della Terra, Università di Ferrara, Italy

<sup>1</sup>OGS (Istituto Nazionale di Oceanografia e di Geofisica Sperimentale) Borgo Grotta Gigante 42/C - 34010 - Sgonico (TS) - Italy \* (dniето@ogs.trieste.it)

Large areas of the Po Valley proximal to the delta show serious problems related to salinization of the superficial aquifers which are vital for the sustainability of the agricultural activities in the area. Since 2012 the EU life WARBO project activities regards the application of integrated direct and indirect technologies aiming at the monitoring of the possibility to enhance ground water quality in two test sites. One test site is located few km's to the south of the Po River and about 40 km on-shore the western margin of the Adriatic Sea, Northern Italy. In this area, the artificial recharge shall be initiated by flooding an existing lake formed after the termination of pre-existing quarry.

Subsurface geological and hydrogeological model of this test site have been constructed based on through analysis of existing information about surface and subsurface lithology. These were integrated by the acquisition of new geophysical data employing surface and borehole geoelectromagnetic and seismic techniques. The geophysical results helped in the definition of the geohydrogeological conceptual model. This model, together with the geochemical data, aided in the definition of the possible interactions between surface and ground water bodies. Moreover, the outcomes of the integrated analyses helped in the optimization of the monitoring network.

One of the expected results of this project is to succeed in diluting the high salinity of fossil ground water whose presence, surely, contrasts the natural recharge from the Po River. This may be possible by accumulating fresh water in the existing lake. Monitoring activities shall aid in defining the rate of salinisation attenuation in aquifers characterised by modest to low average permeability. Understanding the advantages and drawbacks of artificial recharge activities shall help in defining its usefulness or its applicability in other sites having similar characteristics.

## Carbon isotope fractionation of injected CO<sub>2</sub> in carbonate reservoirs: Comparison of results from the laboratory and enhanced oil recovery field sites in Alberta, Canada

M. NIGHTINGALE<sup>1\*</sup>, B. MAYER<sup>1</sup>, M. SHEVALIER<sup>1</sup>  
C. DALKHAA<sup>1</sup> AND V. BECKER<sup>1</sup>

<sup>1</sup>University of Calgary, Calgary, Canada, T2N 1N4.

(\*correspondance: night@earth.geo.ucalgary.ca)

Much of what can be surmised about the geochemical reaction of injected CO<sub>2</sub> when sequestered in geological formations has been gleaned from the chemical and isotopic analysis of produced fluids during CO<sub>2</sub> enhanced oil recovery (CO<sub>2</sub>-EOR). Carbon isotopes of produced CO<sub>2</sub> have been shown to be a valuable tool for tracing the fate of injected CO<sub>2</sub> [1]. When CO<sub>2</sub> is injected into water bearing carbonate rock, carbon from four distinct sources: 1) injected CO<sub>2</sub>, 2) in-situ CO<sub>2</sub>, 3) dissolved inorganic carbon (largely bicarbonate) and 4) dissolution of carbonate minerals in carbonic acid, can be expected to contribute to the overall “carbon pool” and may have an impact on the equilibrium carbon isotope ratios of both the produced CO<sub>2</sub> and dissolved inorganic carbon (DIC). We present the results of chemical and isotopic analyses of produced CO<sub>2</sub> and DIC before and after the initiation of CO<sub>2</sub> injection at two carbonate hosted CO<sub>2</sub> enhanced oil recovery projects in Alberta, Canada. Results suggest carbon isotope equilibrium is established in a fashion similar to open system carbonate dissolution in shallow environments [2]. In spite of large increases in dissolved bicarbonate attributed to carbonate mineral dissolution, the equilibrium carbon isotope values of the bicarbonate appear to be controlled largely by the injected CO<sub>2</sub> and system temperature. Field observations were verified via a series of laboratory experiments using artificial brines and isotopically distinct CO<sub>2</sub> ( $\delta^{13}\text{C} = -37.5\text{‰}$ ) and carbonate rock ( $\delta^{13}\text{C} = +1.2\text{‰}$ ). Observed increases in dissolved calcium up to 575 mg/l, and dissolved bicarbonate up to 1500 mg/l, can be attributed to the dissolution of added calcite. The  $\delta^{13}\text{C}_{\text{HCO}_3}$  of -28.1‰ at the end of the experiment demonstrates the dominance of the CO<sub>2</sub> and system temperature (20°C) in determining the  $\delta^{13}\text{C}$  values of DIC under equilibrium conditions and the “overprinting” of the isotopic signature of the carbon contributed through calcite dissolution.

[1] Johnson *et al.* (2011), IJGGC 5, 933-941. [2] Clark, I.D. & Fritz, P. (1997) *Environmental Isotopes in Hydrogeology*. Lewis Publishers, Boca Raton, FL.

## Magma sources within the Armenian territory since the Jurassic

I. NIKOGOSIAN<sup>1</sup>, KH. MELIKSETIAN<sup>2</sup>, M.J VAN BERGEN<sup>1</sup>,  
P.R.D. MASON<sup>1</sup> AND G. NAVASARDYAN<sup>2</sup>

<sup>1</sup>Department of Earth Sciences, Utrecht University,  
Budapestlaan 4, the Netherlands, (iniki@geo.uu.nl)

<sup>2</sup>Institute of Geological Sciences, ANA of Sciences, Yerevan,  
Armenia, (km@geology.am)

The Armenian Highland forms part of the intensely deformed central segment of the Alpine-Himalayan belt, where fragments of continental blocks of Gondwanaland origin, Mesozoic Tethian island arcs and Late Cretaceous ophiolite sequences constitute a complex geological mosaic. Extensive magmatic activity between the Early Jurassic and Holocene developed under a diversity of geological regimes, ranging between rift and post-collisional settings.

We undertook a detailed geochemical and petrological study of representative, MgO-rich igneous products to explore relationships between magmatism and geodynamics in key areas of the Lesser Caucasus. Samples cover the entire Jurassic-Quaternary time interval, and include picrites, ophiolites, subalkaline and alkaline basalts, dolerites, and shoshonitic-high-K calcalkaline basalts.

Early liquidus assemblages in most of the samples virtually always include high-Fo (>88) olivine that presumably crystallized from (near-)primary mantle-derived melts. Exceptions are low-Fo olivines from the Quaternary Aragats, Gegam and partially Syunik volcanoes that probably crystallized from crust-contaminated AFC melts and/or mixtures of mantle and crust-derived (adakite-type) melts. Spinel inclusions trapped in high-Fo olivines contain variable amounts of Ti, Al, and Cr, that enable us to distinguish the nature of mantle sources involved (MORB-type, OIB-type, subduction-type).

Geochemical signatures of the parental melts were obtained for all studied samples using LA-ICP-MS analysis of melt inclusions trapped in the high-Fo olivines. A wide diversity of (near-) primary melts was found within and between distinct magmatic systems. Where partial melting and secondary effects can be ruled out, much of this variation reflects the amalgam of different mantle-lithosphere domains, which were mobilized in response to the changing geodynamic conditions that have affected the region since Jurassic times.

## Multiple origins of carbon in Italian kamafugite melt

I. NIKOGOSIAN, M.J. VAN BERGEN AND S. CHANEVA

<sup>1</sup> Department of Earth Sciences, Utrecht University, The Netherlands (m.j.vanbergen@uu.nl)

Despite ongoing discussion on magmagenesis and geodynamic controls, there are compelling indications that small volumes of kamafugitic magma in the Intra-Appennine Volcanic Province of peninsular Italy were derived from sources that had been affected by (past) subduction of the Adriatic lithosphere. A close association with carbonatitic rocks has posed the question concerning the origin of carbon, which may have been derived from the mantle sources or from interaction with Mesozoic carbonates residing in the crust. We explored the crystallization history of olivines and their melt inclusions, separated from a representative specimen from San Venanzo, which enables us to (1) determine the primary composition(s) of mantle-derived kamafugite melt and (2) to trace the effects of crustal interaction on melt composition and magma evolution. Complex textures of olivine phenocrysts and their trace element compositions provide a framework for the sequence in which melt evolved within a single plumbing system.

Pristine core parts, characterized by high  $Fo_{93-90}$ , low CaO, (0.2-0.3 wt.%) and Cr-spinel inclusions ( $Cr\# \sim 0.7$ ) are considered to have crystallized from primary mantle-derived melt. Compositions of melt inclusions in these cores are consistent with mantle derivation (8-12 wt.% MgO), but span a continuous range between 3 and 9 wt.%  $K_2O$ . The K-richest MI have compositions are relatively enriched in  $Na_2O$ ,  $P_2O_5$  and  $TiO_2$ , while the K-poor endmember is characterized by very high CaO contents (up to 21 wt.%). Rim parts show a strong compositional gradient of decreasing forsterite (down to  $Fo_{70}$ ) and increasing CaO (up to 1.8 wt.%). Profiles of phosphorous contents in the olivines point to steep increases in the rim parts, indicating that they originated as rapid overgrowths onto phenocryst cores. The combined signatures suggest that the rim parts crystallized from an evolved melt that was contaminated through interaction with carbonate-rich lithologies. Fluid inclusions indicate that this interaction occurred at relatively shallow crustal levels (2 – 10km).

From major and elements contents of core-hosted MI we infer that the kamafugite represents an assembly of primary melts with differentiated compositions, controlled by low-degree melt extraction from a mantle source with mineralogical variations. Our observations are consistent with a mantle source affected by siliceous K-rich and carbonate/apatite-rich metasomatic agents derived from subducted carbonate-bearing metapelites.

## Modeling soil structure and nutrient dynamics using the 1D-Integrated Critical Zone Model

N. P. NIKOLAIDIS<sup>1\*</sup>, J. VALSTAR<sup>2</sup>, E. ROWE<sup>3</sup>,  
K. MOIROGIORGOU<sup>1</sup> AND F.E. STAMATI<sup>1</sup>

<sup>1</sup>Department of Environmental Engineering, Technical University of Crete, Chania 73100, GREECE

(\*correspondence: nikolaos.nikolaidis@enveng.tuc.gr)

<sup>2</sup>Deltares Soil and Groundwater Systems, Utrecht, The Netherlands

<sup>3</sup>NERC Center for Ecology and Hydrology, Bangor, UK.

### Model Development

Soil structure has a strong influence on the physical, chemical and biological processes that take place within the soil, and these processes can in turn influence soil structure. The aim of this work was to develop a tractable and defensible mathematical model, the 1D Integrated Critical Zone (1D-ICZ) Model, that links soil aggregate formation and soil structure to nutrient dynamics and biodiversity. Models of flow and transport (Hydrus 1D); bioturbation; Chemical equilibrium, weathering (SAFE); C/N/P dynamics and soil structure, CAST; and vegetation dynamics, PROSUM, were integrated to formulate the 1D-ICZ Model. This model can simulate and quantify the dynamics of C, N and P sequestration in soils in relation to soil structure and organic matter protection, the effects of exudates and mycorrhizae on nutrient mobilisation and acquisition, above and below ground C stocks including microorganisms, fungi and consumers, and water transformation and filtration in soils.

### Model Application Results

Theoretical model simulations will be presented to illustrate the sensitivity of nutrient dynamics to dynamic changes of soil structure due to carbon amendments in the system. The inter-relationships between nutrient dynamics and soil structure dynamics will be elucidated. Soil structure and nutrient content data from cropland to set-aside land conversions will be used to validate the 1D-ICZ model. It will be shown that the 1D-ICZ model can quantify four of the most important soil functions: biomass production, C sequestration, water filtration, and biodiversity and thus be an integral component of soil Life Cycle Assessments and Ecosystem Valuation Analyses by linking inventory data to midpoint indicators for soil functions and services.



## Fe<sup>3+</sup> partitioning systematics between orthopyroxene and garnet in well-equilibrated mantle xenoliths

P. NIMIS<sup>1\*</sup>, A. GONCHAROV<sup>2</sup> AND D. IONOV<sup>3</sup>

<sup>1</sup> Dipartimento di Geoscienze, Università di Padova, Italy  
(\*correspondence: paolo.nimis@unipd.it)

<sup>2</sup> Faculty of Geology, Saint-Petersburg State University, Russia (aleksey.g.goncharov@gmail.com)

<sup>3</sup> Université J. Monnet and UMR6524-CNRS, Saint Etienne, France (dmitri.ionov@univ-st-etienne.fr)

Ferric iron to total iron ratios in coexisting orthopyroxene and garnet from eighteen mantle xenoliths from Siberia (Udachnaya, Obnazhennaya) and Mongolia (Dariganga) were measured by <sup>57</sup>Fe Mössbauer spectroscopy at room temperature. The xenoliths include both coarse and sheared types and were checked for equilibrium based on textural and compositional criteria. A further check was made through cross-evaluation of thermometric estimates using internally consistent thermometers (cf. [1]). Thermobarometric estimates encompass a large P–T field (1.9–6.4 GPa; 740–1295 °C) relevant to Earth's upper mantle in both on-craton and off-craton settings. The Mössbauer data show that the partitioning of Fe<sup>3+</sup> between orthopyroxene and garnet is essentially independent of the temperature of equilibration, but varies significantly with pressure. The  $(\text{Fe}^{3+}/\text{Fe}_{\text{tot}})_{\text{Grt}}/(\text{Fe}^{3+}/\text{Fe}_{\text{tot}})_{\text{Opx}}$  ratio increases with pressure and is lower than unity at P < ca. 3.5 GPa and higher than unity at higher pressure. These partitioning systematics imply that thermometers based on Fe–Mg exchange equilibrium between orthopyroxene and garnet will fail at very low and very high pressure if redox conditions in the natural rocks are different from those in the experiments that were used to calibrate the thermometer. In particular, increased bulk Fe<sup>3+</sup> contents due to more oxidized conditions will lead to over-estimated Opx–Grt temperatures at low P and under-estimated temperatures at high P. Conversely, decreased bulk Fe<sup>3+</sup> contents due to more reduced conditions will lead to under-estimated Opx–Grt temperatures at low P and over-estimated temperatures at high P. The observed Fe<sup>3+</sup> systematics may in part explain recognized inconsistencies between two-pyroxene and Opx–Grt thermometry of mantle xenoliths (cf. [1]).

[1] Nimis & Grütter (2010), *Contrib. Mineral. Petrol.* **159**, 411–427.

## Dynamical and isotopic perspectives on accretion and core formation

FRANCIS NIMMO<sup>1</sup>

<sup>1</sup>Dept. Earth & Planetary Sciences, University of California Santa Cruz, CA 95064, USA (fnimmo@es.ucsc.edu)

Numerical modelling of accretion suggests the following characteristics: Mars-sized bodies can form fast (~1 Myr) but completing an Earth takes longer (10–100 Myr); late-stage impacts can remove (or add) material in a stochastic fashion; the “feeding zone” of a growing planet expands with time. All these characteristics can potentially be quantified using cosmochemical measurements.

Isotopic systems such as Hf–W [1], Pd–Ag [2] and Fe–Ni [3] provide constraints on the timing of core formation. The biggest challenge is to better understand the degree of mantle re-equilibration during large impacts [4]. Re-equilibration occurs at cm-scales during impacts involving Mm-scale objects; it is thus hard to model numerically, but can perhaps be better quantified via laboratory experiments [5]. The effective conditions under which core formation occurred can also be probed with stable Fe or Si isotopes, though the presence of S complicates matters [6].

The bulk compositions of planets may have been affected by late-stage removal of material [7], and spall fragments such as the Moon produced [8]. Models show that smaller surviving bodies show more variability in bulk chemistry and isotopic signatures [9]; larger bodies experience more averaging and are harder to fragment. Stochastic late impacts may be responsible for the variable amount of “late veneer” apparently added to the terrestrial planets [10].

Feeding zone expansion and the Pd–Ag [2] and I–Xe systems [11] both suggest late impactors are more volatile-rich. Later impactors may also have been more oxidized [12], but recent high-P partitioning experiments suggest this is not required [13].

Late-stage impacts probably caused several episodes of regional if not global melting. For both Earth and Mars, mantle convection subsequent to these magma ocean episodes has not been able to erase initial heterogeneities [11,14].

[1] Kleine *et al.* *GCA* 73, 2009 [2] Schonbachler *et al.*, *Science* 328, 2010 [3] Dauphas *et al.*, *LPSC* 44, 2013 [4] Daphuas & Pourmand, *Nature* 473, 2011. [5] Deguen *et al.* *EPSL* 310, 2011 [6] Shahar *et al.*, *LPSC* 44, 2013 [7] O'Neill & Palme, *PTRSL-A* 366, 2008. [8] Cuk & Stewart, *Science* 338, 2012 [9] Dwyer *et al.*, this meeting [10] Bottke *et al.*, *Science* 330, 2010 [11] Mukhopadhyay, *Nature* 486, 2012 [12] Rubie *et al.* *EPSL* 301, 2011 [13] Siebert *et al.* *Science* 339, 2013. [14] Halliday *et al.* *Space Sci. Rev.* 96, 2001.

## Influence of gelatin hydrogel porosity on the formation of calcite mesocrystals

F. NINDIYASARI<sup>1</sup>, L. FERNÁNDEZ-DÍAZ<sup>2,3\*</sup>, E. GRIESSHABER<sup>1</sup>, J. M. ASTILLEROS<sup>2,3</sup>, N. SÁNCHEZ-PASTOR<sup>2</sup> AND W. W. SCHMAHL<sup>1</sup>

<sup>1</sup> Department für Geo- und Umweltwissenschaften, Ludwig-Maximilians-Universität München, München, Germany

<sup>2</sup> Department of Crystallography and Mineralogy, Complutense University, Madrid, Spain. (correspondence: \*Ifdiaz@geo.ucm.es)

<sup>3</sup> Institute of Geoscience (CSIC, UCM), Madrid, Spain

The formation of biological hard tissues occurs in confined environments within organic matrices and involves the oriented attachment of nanoparticles. Similarities between hydrogels and organic matrices make hydrogels an adequate support for studying biomineralization. In this work the crystallization of CaCO<sub>3</sub> in gelatin hydrogels with solid contents ranging between 2.5 and 10 wt% was investigated at 15°C. Changes in the gelatin concentration correlated with changes in the characteristics of the CaCO<sub>3</sub> precipitates, with heavier hydrogels leading to smaller nucleation densities, diminishing proportions of vaterite with respect to calcite and calcite crystals showing smaller sizes, progressively rougher surfaces and more complex morphologies. Moreover, the calcite crystals grown in heavier hydrogels were identified as mesocrystals consisting in assembled nanometric basically equally-oriented rhombohedral subunits separated by small amounts of gelatine (Fig. 1a). Hydrogels with higher gelatin contents were characterized by more complex porosities, which correlated with lower ion diffusivities through the hydrogel and higher supersaturations at nucleation (Fig. 1b). These results highlight the connection between medium porosity, supersaturation and mesocrystals formation.

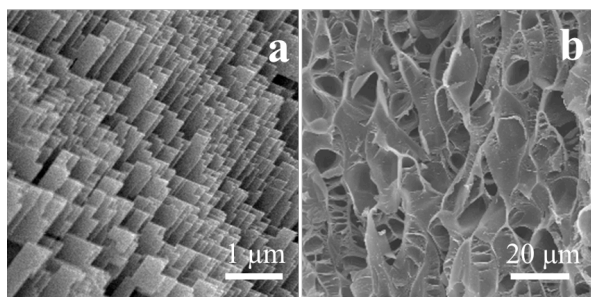


Fig 1. (a) Surface of calcite mesocrystal (10 wt% gelatine hydrogel)  
(b) Porous structure of a 10 wt% gelatine hydrogel

## A Modeling Framework to Predict Changes in Soil Chemistry and Agricultural Return Flow in Seawater Farming of Halophytes

\*QINGQIAN NING<sup>1</sup>, WAN ABDUL-MATIIN<sup>1</sup> AND FARRUKH AHMAD<sup>1</sup>

<sup>1</sup>Bio-Energy and Environmental Laboratory (BEEL), Water and Environmental Engineering, Masdar Institute of Science and Technology, PO Box 54225, Abu Dhabi, United Arab Emirates. (qing@masdar.ac.ae)

Growing halophyte plants using Integrated Seawater Energy and Agriculture Systems (ISEAS) offers a sustainable solution for the generation of biomass feedstock for carbon neutral biofuels; halophytes neither enter the foodchain, nor do they compete with food-crops for natural resources. One such field demonstration of ISEAS for biomass production to generate aviation biofuels, is planned for the coastal regions of Abu Dhabi, UAE, where it will likely face a number of region-specific soil chemistry and hydrogeology challenges not encountered in past demonstrations in Mexico and Eritrea. The unique soil chemistry (evaporite deposits, especially gypsum), and hypersaline coastal hydrogeology of Abu Dhabi will affect long-term halophyte agricultural productivity when Arabian Gulf seawater is applied to coastal soils as part of ISEAS. As an initial phase of the demonstration project, a salt deposition numerical modeling framework was developed to test different seawater loadings onto coastal soils. The aim of this exercise was to predict changes in irrigation return flow and soil chemistry over time in order to establish salt and water balances for sustained operation of the site. These modeling results will be further validated with laboratory lysimeter studies and with field monitoring data collected during one year of ISEAS operation. The results from this study could be used to (i) determine the optimal saline water loading correlating with peak soil salinities that selected halophytes can tolerate, (ii) potential for sodicity of the soil with saline water application, (iii) impacts of land application of saline water on underlying coastal groundwater, and (iv) develop strategies to control soil water activities in favor of halophyte agricultural productivity at ISEAS sites.

## Can modern methane events and $\delta^{13}\text{CH}_4$ measurements say anything about glacial/interglacial transitions?

EUAN G NISBET<sup>1</sup>, DAVID LOWRY<sup>1</sup>, REBECCA E. FISHER<sup>1</sup>,  
JAMES L. FRANCE<sup>1</sup> AND REBECCA BROWNLOW<sup>1</sup>

<sup>1</sup>Dept. Earth Sciences, Royal Holloway, Univ. of London,  
Egham TW20 0EX, UK. ( n.name@rhul.ac.uk)

Over the past decade several major excursions, in the southern tropics, mid-latitudes and Arctic, have occurred in the atmospheric methane record. These recent growth rates, though short-lived, are comparable to those seen in the glacial-interglacial transitions. In the tropics recently, transient growth rates in excess of 10 ppb/yr have been observed, with sustained though lower growth rates through 2007-late 2012. This southern tropical event was apparently driven by increased rainfall, not directly by anthropogenic emissions as in the high  $\text{CH}_4$ -growth events in the 1980s. A brief strong growth event occurred in the Arctic in 2007/8, while high growth in the northern mid-latitudes occurred in 2003 and again in 2009. These latter events may have been partly driven by anthropogenic inputs.

$\delta^{13}\text{CH}_4$  studies of sources and polar flights suggest that Arctic and boreal wetlands, not hydrates, have been the dominant regional summer  $\text{CH}_4$  source in recent years. Hydrate-fed submarine plumes occur but their main near-future impact may be local ocean acidification and deoxygenation. In winter, Arctic anthropogenic emissions likely dominate. These modern changes, and their rapid fluctuations, suggest boreal and tropical wetland emissions, responding very quickly to warming or cooling, could have dominated the increase in  $\text{CH}_4$  at glacial terminations. Modern Atlantic transects and observations also show the importance of distinct air masses in shaping the annual average record.

## Temperature effects on cathodoluminescence of calcite

H. NISHIDO<sup>1</sup>, S. NISHIZAWA<sup>1</sup> AND N. KUSANO<sup>1</sup>

<sup>1</sup>Department of Biosphere-Geosphere Science, Okayama  
University of Science, 1-1 Ridai-cho, Okayama 700-0005,  
Japan (correspondence: nishido@rins.ous.ac.jp)

Cathodoluminescence (CL) of calcite has been extensively investigated by many researchers, and used for a wide range of geoscientific applications. The CL features are affected by many factors such as activator, sensitizer and quencher of transition metal elements. However, the temperature effects on calcite CL have not been precisely clarified so far. In this study we have quantitatively evaluate temperature quenching effects on calcite CL with various activator concentrations.

Six calcite samples with Mn concentrations of 13, 129, 1259, 3520, 9170, 66500 ppm were selected for CL spectral measurements at various temperatures from  $-190\sim 25^\circ\text{C}$ .

CL intensity of low-Mn calcite increases with an increase in sample temperature, but the intensity of medium-Mn calcite shows almost unchangeable at a wide range of temperature. In contrast CL intensity of high-Mn calcite decreases with increasing temperature. These facts imply that temperature effects on calcite CL depend on activator concentrations in calcite, whereas luminescence efficiency generally decreases with rising temperature due to an increase in non-radiative transitions, which has been known as temperature quenching.

A least-square fitting of the Arrhenius plot by assuming a Mott-Seitz model provides an activation energy of 0.04~0.07 eV for high-Mn calcite in a temperature quenching process. These values correspond to lattice vibration energy, suggesting that the energy of non-radiative transition might be transferred to lattice as phonon. The result leads that activator (Mn ion) concentration considerably affects temperature quenching effect on CL of calcite.

## ***In situ* observation of dehydration and incongruent dissolution of Serpentine (Antigorite) into aqueous fluids**

RYO NISHIZAKI AND TATSUHIKO KAWAMOTO <sup>1</sup>

<sup>1</sup> Inst. Geothermal Sci., Graduate School of Science, Kyoto Univ. Kyoto 606-8502, Japan (ryo.nishizaki@gmail.com)

Serpentine plays important roles as triggering earthquakes through its dehydration and controlling the rheological coupling between slab/mantle. We heated a natural polycrystalline antigorite ( $\text{Mg}_{51}\text{Si}_{36}\text{O}_{90}(\text{OH})_{66}$ ) in  $\text{H}_2\text{O}$  in the Basset-type externally heated diamond anvil cell [1]. During 600-620°C, we observed that antigorite slightly dissolved into aqueous fluids and then forsterite started crystallizing under a pressure range from 0.27 to 0.64 GPa. The forsterite grew up to about 30  $\mu\text{m}$  across in an hour. According to the previous studies, a dehydration reaction of antigorite = forsterite + talc +  $\text{H}_2\text{O}$  [2] can occur under the present experimental conditions. Nevertheless, talc was not found in our experiments during 1-4 hours. The experimental duration may be too short for antigorite to dehydrate and nucleate talc. Alternatively our observation indicates that antigorite dissolves incongruently into aqueous fluids at the dehydration reaction in the presence of aqueous fluids.

Takahashi *et al.* [3] conducted shear-sliding tests on antigorite gauge at temperature higher than the stability of antigorite under constant pore water pressure of 30MPa at confined pressure of 0.1GPa. They observe forsterite using SEM and trace amounts of talc using XRD in shear-localized zones. The incongruent dissolution of antigorite in our experiments can explain that the dehydration of antigorite forms forsterite, which can cause strengthening and embrittlement of the gouge even at constant pore water pressure. The talc-dissolved aqueous fluids can be silica-rich, and such fluids can migrate upwards to precipitate talc in the plate boundary [4].

[1] Bassett *et al.* (1993) *Rev. Sci. Instrum.* [2] Evans *et al.* (1976) *Schweiz. Mineral. Petrogr. Mitt.* [3] Takahashi *et al.* (2011) *J. Geophys. Res.* [4] Hirauchi *et al.* (2013) *Geology*

## **Physiological and isotopic characteristics of nitrogen fixation by hyperthermophilic methanogens: Implication for nitrogen anabolism of the seafloor microbial communities on the early Earth**

MANABU NISHIZAWA<sup>1</sup>, JUNICHI MIYAZAKI<sup>1,2</sup>, AKIKO MAKABE<sup>3</sup>, KEISUKE KOBAYASHI<sup>3</sup>, AND KEN TAKAI<sup>1,2</sup>

<sup>1</sup> Precambrian Ecosystem Laboratory, JAMSTEC (e-mail: m\_nishizawa@jamstec.go.jp)

<sup>2</sup> SUGAR Program, JAMSTEC

<sup>3</sup> Tokyo University of Agriculture and Technology

Hyperthermophilic hydrogenotrophic methanogens are considered to represent one of the most important classes of primary producers in hydrogen ( $\text{H}_2$ )-abundant hydrothermal environments throughout the history of Earth. Despite extensive studies of methanogenesis, comprehensive research on nutrient anabolism in hyperthermophilic methanogens is limited. This study first investigated the physiological properties and isotopic characteristics of experimental cultures of hyperthermophilic methanogens during the fixation of dinitrogen ( $\text{N}_2$ ), an abundant but less-bioavailable compound in hydrothermal fluids. We found that these hyperthermophilic methanogens actively assimilated  $\text{N}_2$  via molybdenum (Mo)-iron (Fe) nitrogenase under broad ranges of Mo and Fe concentrations relevant to present and past oceanic and hydrothermal environments. Furthermore, the methanogens produced more  $^{15}\text{N}$ -depleted biomass than that previously reported for diazotrophic photosynthetic prokaryotes. These results indicate that diazotrophic methanogens can be broadly distributed in seafloor and subseafloor hydrothermal environments, where the availability of the transition metals is variable and organic carbon and nitrogen compounds and ammonium are extremely scarce. This perspective may provide key clues to understanding the geological and evolutionary history of the global nitrogen cycle if the nitrogen isotopic ratios of organic matter in the geological records associated with seafloor and subseafloor hydrothermal activities are linked to the potential functions of diazotrophic hyperthermophilic methanogens. The possible emergence and function of diazotrophy coupled with methanogenesis 3.5 billion years before the present may be inferred from the nitrogen and carbon isotopic records of kerogen and fluid inclusions from hydrothermal deposits.

## Acid water problem: Mining districts from Tuscany (central Italy)

B. NISI<sup>1\*</sup>, B. RACO<sup>1</sup>, O. VASELLI<sup>2</sup>, T. ABEBE<sup>3</sup>,  
R. BATTAGLINI<sup>3</sup>, G. MASETTI<sup>1</sup>, F. TASSI<sup>2</sup>, M. LELLI<sup>1</sup>  
AND M. DOVERI<sup>1</sup>

<sup>1</sup>CNR-IGG Institute of Geosciences and Earth Resources, Via Moruzzi 1, 56124, Pisa, Italy; (\*correspondence: b.nisi@igg.cnr.it; b.raco@igg.cnr.it; masetti@igg.cnr.it; m.elli@igg.cnr.it; m.doveri@igg.cnr.it)

<sup>2</sup>Department of Earth Sciences; Via G. La Pira 4, 50121 Florence, Italy; (oraldo.vaselli@unifi.it; franco.tassi@unifi.it)

<sup>3</sup>MASSA spin-off, largo G. Novello 1c, 50126, Florence; Italy; (t.abebe@massaspinoff.com; r.battaglini@massaspinoff.com)

Acid mine drainage (AMD) is a major source of water contamination in metal- and coal-mining districts worldwide. AMD is a natural consequence of mining activity where the excavation of mineral deposits (metal bearing or coal), below the natural groundwater level, exposes sulphur-bearing compounds to atmospheric O<sub>2</sub> and water. The most common reactions that lead to the production of AMD involve the chemical and biological oxidation of metal sulfides contained in mine waste heaps, active or abandoned mine workings, or in tailings piles left over from the processing of sulfide ores. Chemicals used for treating AMD after formation are hydrated lime, pebble quicklime, caustic soda, soda ash briquettes, and ammonia. Each chemical reacts differently with a specific AMD. Therefore, it is essential that each AMD source has been treated and evaluated chemically/physically to determine which is most environmentally sound, efficient and cost effective. In this study a geochemical survey of mine waters discharging in the main mining districts of Tuscany (central Italy) was carried out to establish their geochemical features to provide information on AMD processes at mining-impacted sites in order to supply a background information necessary to the scientists responsible for assessing remediation technologies.

## The composition of Mercury's crust from MESSENGER observations

LARRY R. NITTLER<sup>1\*</sup>, SHOSHANA Z. WEIDER<sup>1</sup>  
AND SEAN C. SOLOMON<sup>2</sup>

<sup>1</sup>Carnegie Institution of Washington, Washington DC 20015 USA (\*lnittler@ciw.edu)

<sup>2</sup>Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY 10964, USA

The MERCURY Surface, Space ENVIRONMENT, GEOchemistry, and Ranging (MESSENGER) spacecraft has returned a wealth of data since it began orbiting the innermost planet more than two years ago. Imaging observations reveal a surface shaped by widespread volcanism that produced both flood lavas and pyroclastic deposits [1]. Geochemical measurements from X-ray and gamma-ray spectroscopy show Mercury's crust to be chemically distinct from those of the other terrestrial planets and rich in volatile elements [2-4]. Mg/Si ratios are generally higher, and Al/Si and Ca/Si ratios lower than typical crustal materials on other planets; there is no evidence for a lunar-like, feldspar-rich crust. The abundance of sulfur is surprisingly high (~1-4 wt %), which most likely indicates that Mercury formed under highly reducing conditions, and is consistent with the low total surface Fe abundance (1-2 wt %) [4,5]. Correlations between Mg/Si, Ca/Si, and S/Si suggest that MgS and CaS are important crustal minerals. The average K/Th ratio and Na abundance are similar to those of other terrestrial planets, ruling out some high-temperature models of Mercury's formation. The high abundance of volatiles likely plays a key role in the formation of "hollows", enigmatic shallow depressions observed only on Mercury [6]. Substantial chemical heterogeneity is also observed [7,8]: high-reflectance smooth volcanic plains are, on average, enriched in Al, Na, and K and depleted in Mg, Ca, and S, relative to older, darker terrains. The observed compositional variations most likely reflect intrinsic differences in the magmas that produced the surface materials, as well as possible thermal redistribution of K and Na from hot surficial regions to colder ones. The Fe abundance also appears to be heterogeneous on 1000-km scales and is uncorrelated with other elements [5].

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## Arsenic mobility in limestone and fertiliser-amended tailings

TARYN L. NOBLE<sup>1,3</sup> AND BERND G. LOTTERMOSER<sup>2,3</sup>

<sup>1</sup>School of Earth Sciences, University of Tasmania, Private Bag 79, Hobart, 7007, TAS (Taryn.Noble@utas.edu.au)

<sup>2</sup>Environment and Sustainability Institute, University of Exeter, Cornwall Campus, Penryn, Cornwall, TR10 9EZ, UK (B.Lottermoser@exeter.ac.uk)

<sup>3</sup>Cooperative Research Centre for Optimising Resource Extraction (CRC ORE), Australia

Remediation of acid rock drainage (ARD) through the addition of limestone results in the removal of deleterious metals (e.g. Cd, Cu, Pb) from solution, by mineral precipitation and adsorption reactions as the pH increases. However, arsenic (As) can be mobilised under neutral to alkaline pH conditions due to desorption reactions from different mineral surfaces. Also, the mobility of As is complicated by fluctuations in redox chemistry as well as As desorption in the presence of competitive anions. We investigated the mobility of As at a historic cassiterite tailings deposit (Royal George, Tasmania), where recent remediation efforts by statutory authorities included the application of crushed limestone and phosphate fertiliser pellets to the tailings surface.

Scorodite and iron oxide phases were identified to be the main As-host phases in non-amended tailings. Leaching experiments using different extraction solutions were conducted on amended and non-amended tailings. Results show that As mobility was considerably reduced in near neutral pH, low sulphate extraction solutions for both amended and non-amended tailings. However, a significant proportion of As was mobilised in the amended tailings relative to non-amended tailings, when extraction solutions with high sulphate concentrations were used. Since high dissolved sulphate (>1000 mg/L) waters are present in ARD environments, the application of phosphate fertiliser, in addition to limestone as an amendment strategy, may mobilise As from waste rocks and tailings in the long term. Rehabilitation efforts of As-rich wastes need to consider both the mineralogical siting of As and porewater chemistry.

## Trace Element and Isotope Geochemistry of Cretaceous Basalts from Axel Heiberg Island, Arctic Canada

INÊS G. NOBRE SILVA<sup>1\*</sup>, VICTORIA PEASE<sup>1</sup>  
AND GEORGE MORRIS<sup>2</sup>

<sup>1</sup>Dept. of Geological Sciences, Stockholm University, SE-106 91, Stockholm, Sweden (\*inobre@geo.su.se)

<sup>2</sup>Geological Survey of Sweden, Box 670 SE-751 28 Uppsala

Cretaceous volcanic rocks related to the High Arctic Large Igneous Province (HALIP) in the Canadian Arctic Islands comprise dykes, sills and lava flows emplaced within the Sverdrup Basin. During an expedition to northwestern Axel Heiberg Island in the summer of 2007, a suite of 114 - 130 Ma basaltic rocks was recovered from the Bukken Fiord region. We present the first geochemical study on 11 of these basalts, including isotopic compositions by MC-ICP-MS (Pb) and TIMS (Sr and Nd).

All samples are tholeiitic. They cover a narrow range of MgO (3.2 to 7 wt%) and SiO<sub>2</sub> (45 to 54 wt%) contents and have high TiO<sub>2</sub> contents that range from 2 to 4 wt%. Trace element ratios of immobile, alteration resistant elements (e.g., Th/Nb, Th/Ta, La/Yb, Zr/Y, Nb/Y) suggest interaction and incorporation of crustal material by an enriched mantle source. The preliminary isotopic compositions of these basalts also support contamination by a crustal component. This is evidenced by their high <sup>87</sup>Sr/<sup>86</sup>Sr (0.7036 to 0.7084), <sup>206</sup>Pb/<sup>204</sup>Pb (18.5 to 19.1) and <sup>208</sup>Pb/<sup>204</sup>Pb (38.2 to 38.9) values despite the acid leaching treatment prior to isotopic analyses to remove the disturbance effects of post-magmatic alteration.

Additional isotopic analysis will further constrain the mantle-crustal components involved in the formation of these basalts and the extent of contamination or assimilation. Integration of these new data with prior HALIP studies will contribute to a better understanding of Cretaceous magmatism during the opening of the Canada Basin.

## XAS crystal-chemistry of Fe in mangrove sediments from New Caledonia. Implication for iron biogeochemical cycling

V. NOËL<sup>1,3\*</sup>, C. MARCHAND<sup>2</sup>, F. JUILLOT<sup>1,2</sup>, G. ONA-NGUEMA<sup>1</sup>, G. MARAKOVIC<sup>3</sup> AND G. MORIN<sup>1</sup>

<sup>1</sup>IMPMC, Université Pierre et Marie Curie, 75005 Paris, France (\*correspondence: Vincent.Noel@impmc.upmc.fr, Farid.Juillot@ird.fr, Georges.Ona-Nguema@impmc.upmc.fr, Guillaume.Morin@impmc.upmc.fr)

<sup>2</sup>IRD, 98848 Noumea, New Caledonia (Cyril.marchand@ird.fr)

<sup>3</sup>KNS, 98860 Kone, New Caledonia (GMarakovic@koniambonickel.nc)

Mangrove forests are the dominant intertidal ecosystem of tropical coastlines and play a fundamental role in the ecological balance of these areas. They strongly influence the transfer of trace metals between land and sea. In New Caledonia, mangroves act as a buffer zone between massive Fe lateritic deposits and a lagoon registered as an UNESCO World Heritage site. Mangroves are composed of different stands, each dominated by a botanical species. Mangrove zonation mainly results from difference in soil elevation, and length of tidal immersion, and induces different ecosystem productivity, and redox conditions {1}. As a consequence, it may be responsible for differences in sediment geochemistry, and thus differences in metal speciation and bioavailability {2}.

In the present study, we have determined the distribution and speciation of iron in mangrove sediments in relation with organic content, redox, salinity and botanical gradients. Chemical and mineralogical analyses of mangrove sediment core samples were complemented by direct speciation of Fe using EXAFS spectroscopy. The results obtained show that crystal-chemistry of Fe strongly follows the marked change in sediment redox conditions that range from oxic in surface horizons to anoxic in deep horizons. The Fe-bearing minerals (mainly goethite, with minor amounts of Fe-phyllsilicates) are major phases in the upwards horizons and are inherited from lateritic, then progressively disappear from the surface horizons towards deepest horizons where pyrite forms.

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## Back to basics: Boron isotopic fractionation in synthetic calcite and aragonite

J. NOIREAUX<sup>1\*</sup>, V. MAVROMATIS<sup>2</sup>, J. SCHOTT<sup>2</sup>, J. GAILLARDET<sup>1</sup>, V. MONTOUILLOUT<sup>3</sup>, P. LOUVAT<sup>1</sup> AND D. R. NEUVILLE<sup>1</sup>

<sup>1</sup>IPGP, Univ Paris Diderot, Paris, France, (\*correspondence: noireaux@ipgp.fr)

<sup>2</sup>GET, Univ Paul Sabatier, Toulouse, France

<sup>3</sup>CNRS-CEMHTI UPR3079, 45071 Orléans France

Boron isotopic fractionation in marine carbonates, such as foraminifera and corals, is dependent on the pH of the seawater in which they form, allowing boron isotopes to be used as a proxy of the ocean-pH. The pH-dependency of the boron isotopic composition in organic calcium carbonates has been confirmed in laboratory environment. This behavior of boron isotopes is classically explained by the incorporation of the borate ion from seawater, whose isotopic composition is a function of its abundance and hence of pH. Modern biologically-precipitated calcium carbonates however display widely spread boron isotopic compositions which can be partially explained by vital effects but do not fit the simple model of preferential incorporation of the borate ion.

In order to better understand the mechanisms responsible for boron isotopic fractionation in calcium carbonates, we precipitated, in laboratory, inorganic calcite, Mg-calcite and aragonite over a wide pH range and performed both isotopic and <sup>11</sup>B MAS NMR (Magic Angle Spinning Nuclear Magnetic Resonance) analyses on the solids. Results show that, although  $\delta^{11}\text{B}$  rises with pH for all crystal types, calcite and Mg-calcite display a smaller fractionation (more marked for calcite) with respect to the precipitation solution and a much lesser sensitivity to solution pH than expected. NMR spectra show almost exclusively tetrahedral boron in aragonite but highly variable proportions of trigonal and tetrahedral boron in calcite. We therefore suggest that both borate ion and boric acid are incorporated in calcite and Mg-calcite and that boron is present in both crystalline and non-crystalline sites whereas in aragonite the borate ion is the dominant species, representing over 90% of the total boron. These results overall suggest that aragonite-based calibrations should be favoured in future paleo-pH reconstructions. Calcite-based calibrations require a rigorous characterization via NMR spectroscopy of boron speciation and site occupancy in the crystals.

## Impact of calcite precipitation on flow alteration in porous media

CATHERINE NOIRIEL<sup>1</sup>, CARL I. STEEFEL<sup>2</sup>, LI YANG<sup>2</sup> AND DOMINIQUE BERNARD<sup>3</sup>

<sup>1</sup>Géosciences Environnement Toulouse, Université Paul Sabatier, CNRS, IRD, 14 av. Edouard Belin, F-31400 Toulouse, (catherine.noiriel@get.obs-mip.fr)

<sup>2</sup>Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, (CISteeffel@lbl.gov, lyang@lbl.gov)

<sup>3</sup>Insitut de Chimie de la Matière Condensée de Bordeaux, CNRS, 87, av. du Dr Schweitzer F-33608 Pessac, (bernard@icmcb-bordeaux.cnrs.fr)

One of the major challenges associated with sequestration of carbon dioxide, given the complexity and range of coupled thermal, hydrological, mechanical, and chemical processes involved, is the understanding of geochemical reactivity in the case of long-term sequestration. Mineral trapping involves precipitation of minerals like calcite, which can cause a significant reduction in permeability of reservoirs by altering the shape, size and connectivity of the pores, the roughness of their surface, or by plugging the pore throats.

The effects of calcite precipitation in porous media are evaluated through an experimental and modeling study. Two experiments using cylindrical core packed with glass beads and calcite (Iceland spar) or aragonite (Bahamas ooids) were injected with a supersaturated mixture of  $\text{CaCl}_2$  and  $\text{NaHCO}_3$  to induce calcite growth. Bulk rates of precipitation based on the change in aqueous chemistry over the length of the columns are compared with spatially resolved determinations of carbonate precipitation using X-ray synchrotron microtomography with a resolution of  $4.46 \mu\text{m}$ . The new crystals are shown to be very different according to the initial mineral surface on which they grow. Results are compared in terms of growth rate, crystal shape, surface area and pore roughness. The impact of crystal distribution on roughness increase and on pore scale flow and permeability is evaluated through numerical modeling. The results are compared with results for several model porous media for which different crystal growth rates were implemented. The effect of differing calcite growth rate laws and surface roughness are compared for cases in which the total porosity change is comparable.

## Ten years of ground deformations monitored by the ground-based SAR system on Stromboli volcano and its use in forecasting intense volcanic activity

TERESA NOLESINI<sup>1</sup>, FEDERICO DI TRAGLIA<sup>1,2</sup>, EMANUELE INTRIERI<sup>1</sup>, FEDERICA BARDI<sup>1</sup>, FEDERICA FERRIGNO<sup>1</sup>, SARA FRANGIONI<sup>1</sup>, WILLIAM FRODELLA<sup>1</sup>, CARLO TACCONI STEFANELLI<sup>1</sup>, LUCA TANTERI<sup>1</sup>, CHIARA DEL VENTISETTE<sup>1</sup> AND NICOLA CASAGLI<sup>1</sup>

<sup>1</sup>Dip. Scienze della Terra, Università di Firenze, Via La Pira 4, Firenze

<sup>2</sup>Dip. Scienze della Terra, Università di Pisa, Via Santa Maria 53, Pisa

A Ground Based Interferometric Synthetic Aperture Radar (GBInSAR) system has been installed on Stromboli Volcano since 2003, when on the 30 December 2002, after a major eruption a subsequently large landslide occurred on the NW flank (Sciara del Fuoco, SdF) of the volcano. This GBInSAR is a remote sensing technique based on microwaves interferometry that permits the production of 2D displacement maps, called interferograms, with millimetre precision. The apparatus installed on Stromboli, exploits a metric spatial resolution and acquisition frequency of about 11 min. Only the component of the displacement vector to parallel to the line of sight can be assessed.

The investigation conducted by analysis of the GBInSAR data, has permit to divided the crater area and the SdF area in five different sectors, to better analyze and understand the behaviour of the volcano flank dynamics.

The GBInSAR installed at Stromboli volcano has been used as a remarkable early-advice tool for mass and gravitative movements on the Sciara del Fuoco. GBInSAR monitoring highlights different deformation patterns, related to the imminent new vent openings. The analysis of the displacement rates in the summit crater area has been used as early warning signal before the occurrence of major explosions and lava emission. Changing in displacement rate registered by the GBInSAR system in the upper part of the volcano, corresponding to the external flank of the summit craters and at the base of the summit area, has been used to forecast the change in the pressure conditions in the shallow plumbing system and the lateral propagation of the conduit-dike system of Stromboli volcano.



## Low core-mantle boundary temperature inferred from the solidus of pyrolite

R. NOMURA<sup>1\*</sup>, K. HIROSE<sup>1,2,3</sup>, K. UESUGI<sup>4</sup>, Y. OHISHI<sup>4</sup>  
AND A. TSUCHIYAMA<sup>5</sup>

<sup>1</sup>Tokyo Institute of Technology (Titech), Tokyo 152-8551, Japan (\*correspondence: nomura.r.ab@m.titech.ac.jp)

<sup>2</sup>Earth-Life Science Institute/Titech, Tokyo 152-8551, Japan

<sup>3</sup>IFREE/JAMSTEC, Kanagawa 237-0061, Japan

<sup>4</sup>JASRI/SPring-8, Hyogo 679-5198, Japan

<sup>5</sup>Kyoto University, Kyoto 606-8501, Japan

The solidus of a pyrolite-like composition plays a fundamental role for understanding structure and evolution of the deep Earth, such as temperature profile in the lowermost mantle and melting in the early Earth. Fiquet *et al.* [1] determined the solidus of a pyrolitic composition up to 120 GPa with X-ray diffraction (XRD) measurements using laser-heated diamond anvil cell techniques (LH-DAC). They identified melting by the disappearance of Debye rings of CaSiO<sub>3</sub>-rich perovskite and/or ferropericlaase, however, this melting criteria has a potential to overestimate the solidus temperature due to high temperature gradient along X-ray transmitted axis in LH-DAC.

Solidus temperatures of pyrolitic mantle material were determined by discerning a melting texture from synchrotron dual-energy three-dimensional micro-tomographic images measured at BL47XU of SPring8 [2]. The melting was identified by the existence of (a) round-shaped and (b) iron-enriched region at the hottest part of the sample. The measured solidus temperature of the pyrolitic material was 3700 K at 135 GPa, which is extensively lower than that of 4200 K at 135 GPa measured by XRD [1]. Since seismic observations suggest that melting of the current lowermost mantle is very localized [3], the solidus of pyrolite set an upper limit to the present temperature at core-mantle boundary below 3700 K.

The subsolidus phase assemblage and the phase transition boundary between MgSiO<sub>3</sub>-rich perovskite and post-perovskite were also determined near the solidus temperature on the basis of high *P-T* XRD measurements in LH-DAC.

These results have great significance for understanding temperature profile in the lowermost mantle and melting in the early Earth such as volume of basal magma [4] remnants, since these remnants should have lower solidus temperature than that of pyrolite.

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## A practical constraint on entrainment and condensate evaporation and from aircraft and satellite observations of isotope ratios of water

DAVID NOONE<sup>1</sup>

<sup>1</sup>Department of Atmospheric and Oceanic Sciences and Cooperative Institute for research in Environmental Sciences, University of Colorado, Boulder, CO, 80309-USA (\*correspondence: dcn@colorado.edu)

Convective clouds play a significant role in the moisture and heat balance of the tropics. The dynamics of organized and isolated convection are a function of the background thermodynamic profile and wind shear, buoyancy sources near the surface and the latent heating inside convective updrafts. The stable oxygen and hydrogen isotope ratios in water vapour and condensate can be used to identify dominant moisture exchanges and aspects of the cloud microphysics that are otherwise difficult to observe. Aircraft observations show that there is significant disequilibrium between the cloud core and the ambient environment, which allows an estimate of exchange at cloud boundaries that lead to condensate evaporation. Indeed, the mechanisms for condensate evaporation gives a basis for using satellite profiles of D/H isotope ratios to yield estimates of the rate of moistening of the troposphere above the boundary layer. In the western tropical Pacific and over tropical continents in excess of 60% of condensate evaporates into the environment, and is the principal moisture source for tropospheric water. The success of the calculation relies on both an adequate parameterization of the mechanisms driving the water budget, and the use of isotope ratio data to satisfactorily constrain the parameters. The unique information on moisture history provided by the isotope ratio measurements allows assessment of moisture transport that is not otherwise easily observed.

## Au mineralization and its relationship with shear zones in senjedeh gold deposit

ZAHRA NOORIAN RAMSHEH\* AND MOHAMMAD YAZDI

Department of Geology, Shahid Beheshti University, Tehran  
Iran\* (zn5562@yahoo.com)

Senjedeh gold deposit is located in middle part of the Sanandaj-Sirjan zone, central Iran. It consists of several gold deposits such as Chah-katoom, Dareh Ashky and Senjedeh. Lithological and stratigraphic investigations show that the geological units in this area include metamorphic rocks (different facies of greenschist to amphibolite schist), silicified and mineralized veins and granitic intrusions. These series have been deformed in effect of tectonic alternating phases and lost their primary sequence and order during late Cretaceous-Tertiary continental collision between the Afro-Arabian and the Iranian micro continent. As a result of these tectonic activities, different rock fabric has been formed. Based on structural studies, major tectonic structure in this area is shear zones. According to oriented sample studies, some of the fabric features related to shear zone. Ore-mineral assemblages mainly include pyrite and chalcopyrite. Gold mineralization in Senjedeh area occurred in relation to hydrothermal alterations in metamorphic units during to normal faulting. The pervasive alterations in this area are silicification and sulfidation which are responsible of gold mineralization. The field and petrographic studies show a direct relationship between structures and gold mineralization. The petro fabric studies and correlation mineralization direction show that Senjedeh Gold deposit can be an example of orogenic gold deposit in Iran.

**Key words:** Senjedeh gold deposit, shear zone, Sanandaj-Sirjan zone

## Structure-property relationship of Na/Ca silicate liquids under pressure by molecular dynamics simulation

FUMIYA NORITAKE<sup>1</sup>\* AND KATSUYUKI KAWAMURA<sup>1</sup>

<sup>1</sup> Okayama University, Okayama, 700-8530, Japan.

(\*Correspondence: f.noritake@s.okayama-u.ac.jp)

Peculiar behaviours of physical properties of silicate liquids under high pressure are long standing issue in high pressure earth science. For instance, it is well known that shear viscosities of acidic silicate liquids decreases with increasing pressure [1, 2]. In order to explain the softening of silicate liquids at high pressure, several mechanisms have been proposed by various researchers [1, 3]. To investigate the relationship between structure and properties of silicate liquids, we apply the molecular dynamics method to obtain precise information on structures of silicate liquids under high pressure.

Molecular dynamics simulations of  $\text{Na}_2\text{O}\cdot n\text{SiO}_2$  and  $\text{CaO}\cdot n\text{SiO}_2$  liquids were performed using the MXDORTO code. The simulated pressure range is from 0.1 MPa to 6 GPa with NPT ensembles and the potential model which well reproduces structures various silicate crystals [4].

In the compression, Si-O and M-O distance remains constant, however Si-Si distances shorten and coordination numbers of O atoms around M atom increase. Adding to those, 3 and 4 membered rings in -Si-O- network decrease with increasing pressure. Those suggest that densification of silicate liquids consist of increasing of flexibility of -Si-O- network, bending of Si-O-Si and increase of coordination number of M atoms. Up to 6 GPa, the decrease of Si-O-Si angle and distortion of  $\text{SiO}_4$  tetrahedra in acidic silicate liquids ( $n < 3$ ) are obviously confirmed. Decrease of Si-O-Si angle by densification causes distortion of  $\text{SiO}_4$  tetrahedra and weakening of Si-O bonding [5]. These structural change might cause the softening of silicate liquids under high pressure. Differences between Na and Ca was observed in structure, properties and behaviours of those at high pressure.

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## Montmorillonite colloid size heterogeneity – Fractionation and Characterization

K. K. NORRFORS<sup>1\*</sup>, M. BOUBY<sup>2</sup>, S. HECK<sup>2</sup>, N. FINCK<sup>2</sup>, R. MARSAC<sup>2</sup>, T. SCHÄFER<sup>2</sup> AND H. GECKEIS<sup>2</sup>, S. WOLD<sup>1</sup>

<sup>1</sup>Department of Chemistry/Applied Physical Chemistry, KTH Royal Institute of Technology, Teknikringen 30, SE-100 44 Stockholm, Sweden (\*correspondence: norrfors@kth.se, wold@kth.se)

<sup>2</sup>Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology (KIT), P.O. Box 3640, D-76021 Karlsruhe, Germany (muriel.bouby@kit.edu, stephanie.heck@kit.edu, nicolas.finck@kit.edu, remi.marsac@kit.edu, thorsten.schaefer@kit.edu, horst.geckeis@kit.edu)

Highly compacted bentonite is planned to be one component of the engineered barrier system in many spent nuclear fuel final repository designs. The potential release of montmorillonite colloids, acting as carriers, may enhance the transport of radionuclides in case of a leaching canister. During transport, size exclusion/filtration may occur, resulting in migration of specific size fractions only. Therefore, it is necessary to determine the size heterogeneity of the mobile bentonite clay colloid and its radionuclide association.

In this study, unpurified MX-80 bentonite consisting mainly of smectite with impurities of quartz, plagioclase, orthoclase, muscovite as well as calcite/dolomite, gypsum and pyrite, was sedimented in low ionic strength carbonated synthetic ground water (SGW) at 10g/L. Thereafter, seven colloidal suspensions of various size fractions were obtained by sequential and direct centrifugation. Their particle size distributions were measured by PCS and AsFIFFF/UV-Vis/LLS/ICP-MS. The concentrations of colloids and other elements present in the suspensions were measured by IC and ICP-OES. The mineralogical composition was analyzed by XRD.

The mean particle size is decreasing with the number of fractionation steps, from ~500 down to ~50 nm. The presence of predominantly montmorillonite colloids is confirmed by: i) XRD results, for all colloidal fractions and ii) the Si/Al and Al/Mg mole ratios. There is an instant release of Na and SO<sub>4</sub><sup>2-</sup> to the SGW while adding the bentonite indicating the dissolution of accessory minerals and cation exchange processes. An increasing release of natural <sup>238</sup>U with decreasing size fractions (i.e. larger exposed surface area) is evidenced. The results are discussed with respect to the implication on radionuclide speciation and transport.

## Activities and volatilities of trace components in CaO-MgO-FeO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> melts

C.ASHLEY NORRIS AND BERNARD J.WOOD

University of Oxford, U.K.,

(ashley.norris@earth.ox.ac.uk;berniew@earth.ox.ac.uk)

Knowledge of the activities of trace components in silicate melts is extremely important for addressing such problems as (a) degassing in volcanic systems (b) volatilities in protoplanetary systems and (c) the effect of melt composition on trace element partitioning. Nevertheless these activities are very difficult to measure by conventional phase equilibrium techniques except under circumstances where the metallic element is stable in a readily accessible  $f_{O_2}$  range<sup>1</sup>. We have modified the “metal-saturation” approach by measuring the partitioning of a large number of elements (V, Cr, Cu, Zn, Ga, Ge, Mo, Ag, Cd, In, Sn, Sb, W, Tl, Pb and Bi) between liquid Fe alloys and liquid silicate at 1.5 GPa and 1650°C. The data provide activity coefficients for oxide components relative to the activity of FeO, whose partitioning between metal and silicate is also measured. Use of graphite capsules means that the silicate melt composition can be varied over a wide range, but also means that the metal is carbon-saturated, a factor which has a profound effect on the activities of some components (e.g Pb, Ag, W) in the liquid metal.

We find that the activity coefficients of a number of the most important trace components, notably WO<sub>3</sub>, MoO<sub>2</sub>, GeO<sub>2</sub>, TiO<sub>0.5</sub>, GaO<sub>1.5</sub>, BiO<sub>1.5</sub> and SbO<sub>1.5</sub> are strongly dependent on melt composition each showing variations of 1-2 orders of magnitude over the accessible range of silicate melt compositions. Values for CuO<sub>0.5</sub> are in excellent agreement with previous experimental data<sup>2</sup> on Cu-saturated compositions which shows that the method is viable. When combined with thermodynamic data on the gas species we find that volatilities under solar nebula conditions are displaced relative to those of the “conventional” condensation sequence<sup>3</sup>.

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## Geochemical characterization of uranium mill tailings

J. NOS<sup>1\*</sup>, A. BOIZARD<sup>2</sup>, C. PEIFFERT<sup>2</sup>,  
V. PHROMMAVANH<sup>1</sup>, M. CATHELINÉAU<sup>2</sup> AND  
M. DESCOSTES<sup>1</sup>

<sup>1</sup>AREVA Mines – DR&D, 92084, Paris La Défense, France

(\*correspondence: jeremy.nos@areva.com)

<sup>2</sup>CREGU, 54500, Vandoeuvre-lès-Nancy, France

In France, uranium mines were exploited between 1945 and 2001, leading to the production of 76,000 t of U and 50 Mt of mill tailings stored on 16 storage sites. Studies are being performed to determine the long term behaviour of these storage sites, focusing on the mobility of U and <sup>226</sup>Ra.

Following previous work [1] on mill tailings issued from dynamic treatment, coring and sampling were performed in four storage sites, including heap leaching tailings. All the tailings studied come from sulphuric acid treatment of granitic ore. Radio-geochemical variations were assessed through analyses on 10 to 20 samples for each site. Focus was put on the mobility of U and <sup>226</sup>Ra by characterizing their granulometric distribution and performing sequential leachings. Concurrently, water-rock interactions were constrained by pore water sampling on one site.

Samples issued from each site feature strong similarities, typical of a mix of tailings and water treatment sludges. Three main mineralogical families are identified: “inherited minerals”, initially present in the granitic rock (quartz, micas, K-feldspars, ancillary minerals such as sulfides and oxides), “refractory” U-bearing minerals (uraninite, coffinite) and newly formed minerals. The latter are clay minerals and Fe<sup>III</sup> oxy-hydroxides (from the alteration of the granite host rock), gypsum (due to reagents input during the ore treatment) and U-phosphates (both inherited and newly formed). Geochemical modellings indicate the presence of soddyite controlling the [U] in the porewater.

The average U content is 100 ppm. The <sup>238</sup>U/<sup>226</sup>Ra disequilibrium is constant in dynamic treatment tailings, consistent with a homogeneous ore treatment and a limited migration of U and Ra. This ratio is more variable in heap leaching tailings, suggesting a heterogeneous ore treatment.

All these results are considered in the modelling of the long term evolution of mill tailings, taking into account the sorption properties of the newly-formed minerals.

[1] Somot *et al.* (2000) *Tailings and Mine Waste '00*, 343-352.

## The importance of dry deposition in estimating nitrogen input in peat bogs

M. NOVAK<sup>1\*</sup>, L. BOHDALKOVA<sup>1</sup>, D. FOTTOVA<sup>1</sup>,  
J. CURIK<sup>1</sup>, M. STEPANOVA<sup>1</sup>, M. DARMOVZALOVA<sup>1</sup>  
AND F. VESELOVSKY<sup>1</sup>

<sup>1</sup>Czech Geological Survey, Geologicka 6, 15200 Prague 5,

Czech Republic (\*correspondence:

martin.novak@geology.cz)

It has been recently reported that rain-fed peat bogs in pristine areas store more nitrogen (N) than the amount of N that could have been supplied by atmospheric deposition. In such calculations, cumulative input of nitrate and ammonium are compared with the total N content in <sup>210</sup>Pb-dated peat cores. We have performed a similar comparison in N-polluted Central Europe. Four sites exhibited 2 – 3 times higher N pool size in *Sphagnum* peat since 1880 than cumulative atmospheric input. This discrepancy might be explained by a large contribution of dry deposition. Dry deposition depends on the surface roughness (leaf area index) and is extremely difficult to measure directly in peatlands. In a first approximation, we have used data on spruce canopy throughfall as a proxy for *Sphagnum* interception of airborne N. At 6 sites of the monitoring network GEOMON, N input via spruce throughfall was smaller than via open area deposition. At another 7 sites, N input via spruce throughfall was slightly higher than via open area deposition (59 vs. 26 kg N ha<sup>-1</sup> yr<sup>-1</sup> in Orlicke Mts. was an extreme). It appears that dry deposition may not fully explain excess N in wetland ecosystems.

## Comparison of $\delta^{53}\text{Cr}$ ratios between geogenic and anthropogenic chromium in Central European waters

M. NOVAK<sup>1\*</sup>, V. CHRASTNY<sup>1</sup>, J. FARKAS<sup>1</sup>,  
T.D. BULLEN<sup>2</sup>, E. CADKOVA<sup>1</sup>, Z. SZURMANOVA<sup>3</sup>,  
J. TYLCER<sup>3</sup>, L. ERBANOVA<sup>1</sup>, E. PRECHOVA<sup>1</sup>  
AND J. PASAVA<sup>1</sup>

<sup>1</sup>Czech Geological Survey, Prague, Czech Republic  
(\*correspondence: martin.novak@geology.cz)

<sup>2</sup>U.S.Geological Survey, Menlo Park, Ca., U.S.A.

<sup>3</sup>AQD-envitest, Ostrava, Czech Republic

$^{53}\text{Cr}/^{52}\text{Cr}$  isotope ratios can be used to distinguish between geogenic and anthropogenic sources of chromium in surface waters and groundwaters. Often, a multiple-tracer approach is needed. Since 2011, we have monitored Cr concentrations and  $\delta^{53}\text{Cr}$  values in seven different areas of the Czech Republic, Central Europe. At two sites, we sampled first-order streams on ultrabasic (serpentinite) bedrock. At five sites, we sampled shallow groundwater in the vicinity of Cr-processing industrial operations. Water samples were complemented with globally distributed minerals and whole-rock samples. So far, we have isotopically analyzed 110 samples. Mean Cr concentrations were 6500 ppb in industrial waters, and 20 ppb in geogenic waters. The range of  $\delta^{53}\text{Cr}$  values increased from minerals/rocks to geogenic and industrial waters. The  $\delta^{53}\text{Cr}$  of solid samples was close to 0 per mil, with isotopically slightly heavier Cr in some serpentinites (+1.1 per mil). The range of  $\delta^{53}\text{Cr}$  of geogenic waters was 4.0 per mil (from -0.1 to +3.9 per mil). The range of  $\delta^{53}\text{Cr}$  of anthropogenic waters was 4.6 per mil (from +1.2 to + 5.8 per mil). In general, Cr in anthropogenic waters was isotopically heavier than Cr in geogenic waters. None of the industrial waters had a  $\delta^{53}\text{Cr}$  close to 0 per mil. So far, we have not observed C-isotope indices of natural attenuation of the anthropogenically polluted groundwaters.

## Fluvial sediments: Assessment of contamination by trace metals respecting natural variability

TEREZA NOVAKOVA<sup>1,2</sup>, TOMAS MATYS GRYGAR<sup>2</sup>,  
MARTIN MIHALJEVIC<sup>1</sup> AND LADISLAV STRNAD<sup>1</sup>

<sup>1</sup>Charles University, Faculty of Science, Albertov 6, 128 43 Prague (\*correspondence: Tereza.Novakova@natur.cuni.cz, Mihal@natur.cuni.cz, Lada@natur.cuni.cz)

<sup>2</sup>Institute of Inorganic Chemistry AS CR, 250 68, Rez (Grygar@iic.cas.cz)

According to the latest studies, proper assessment of trace metal contamination levels in fluvial sediments of different rivers necessarily requires individual approaches for each river, according to the local geological proveniences and individual river sedimentation dynamic characteristic.

Such special approach includes sampling respecting floodplain architecture, use of different normalisation elements for each trace metal (e.g., Al, Ti, Rb, Fe) to eliminate highly possible dependence of natural lithogenic background values on lithofacies and finally also use of sufficient method for contamination level assessment.

In this study, comparison of trace elements contamination level (Pb, Zn, Cu, Cr and Ni) of floodplain sediments of five different rivers in Czech Republic (the Berounka, the Jizera, the Morava, the Ohře and the Ploučnice) was done. Floodplain sedimentary profiles were obtained from hand drilled cores, elementary analysis was done by energy dispersive X-ray fluorescence (ED XRF) and by inductively coupled plasma mass spectrometer (ICP MS); cation exchange capacity measurement (CEC) was used for determination of expandable clay mineral content.

Regional lithogenic background values were obtained from "safe" parts of profiles (uniform facies, i.e. no sandy strata, unaffected by reductimorphic processes, unpolluted) and were further used for revelation of potential post-depositional trace elements migrations within profiles and also for determination of anthropogenically contaminated layers.

Elimination of potential influences of lithofacies and also elimination of different provenience influences was allowed by using of carefully chosen normalisation elements for trace elements in the rivers (e.g., Rb normalisation was used for all trace metals in the Morava River sediments or in the case of the Jizera River, Ti normalisation was used for Pb, Zn, Cr and Ni and Rb normalisation for Cu).

The only exception was the upper part of the Ohře River, where no normalisation element was yet established, due to the different proveniences influence and hence simple normalisation could not be used.

## The formation of low degree hydrous melts in the Earth's upper mantle

D. NOVELLA<sup>1\*</sup>, D.J. FROST<sup>1</sup> AND E.H. HAURI<sup>2</sup>

<sup>1</sup>Bayerisches Geoinstitut, Universitaet Bayreuth, Germany

(\*correspondence: davide.novella@uni-bayreuth.de)

<sup>2</sup>Carnegie Institution of Washington, DC, USA

Melting processes in the Earth's interior play a crucial role in the chemical evolution of our planet. The presence of low degree, volatile-bearing melts in the deep mantle is supported by the occurrence of volatile-bearing minerals in xenoliths and by geophysical observations. In order to quantify the proportion of melts formed as a function of mantle water content, we have performed a series of crystallization experiments, following a similar methodology to the sandwich technique, where large pools of hydrous melt composition were equilibrated with a complete mantle peridotite phase assemblage. In particular, we determined the chemical composition of these incipient hydrous melts forming at pressures above 3 GPa. Following this approach, we assessed the water content of the low degree melts by mass balance calculation, based on accurate chemical analyses performed on the large portions of melt. The H<sub>2</sub>O concentration of the peridotite mineral phases was determined by NanoSIMS analyses in order to obtain information on the partitioning of water between mantle minerals and low degree hydrous melts.

Based on some estimates of the water content of the mantle, a deep onset for the inception of adiabatic melting can also be implied. However, accurate information regarding the chemistry of low degree H<sub>2</sub>O-bearing melts is limited to pressures below 3 GPa. This is a consequence of a number of experimental challenges encountered in performing experiments at high pressure within complex systems, such as quench crystallisation and loss of H<sub>2</sub>O and FeO from charges. In addition, the small volume of hydrous melts created by plausible mantle H<sub>2</sub>O contents at depth creates challenges even for the analysis of major elements. Sandwich experiments are very useful because they permit large proportions of low degree composition melts to be equilibrated with mantle residual assemblages. Large amounts of melt promote crystal growth and facilitate melt analyses.

Using these results the H<sub>2</sub>O contents of mineral and melt phases can be addressed as a function of mantle H<sub>2</sub>O content. Our results indicate H<sub>2</sub>O concentrations in mineral phases that are significantly greater than previous studies performed at similar pressure, temperature and low degree of melting conditions.

## Origin of two different zircon types in metabasite veins from the Izera metagranites, West Sudetes, Poland

I. NOWAK<sup>1\*</sup> AND M.J. WHITEHOUSE<sup>2</sup>

<sup>1</sup>Institute of Geological Sciences, Polish Academy of Sciences  
INGPAN, Podwale 75, 50-449 Wrocław, Poland

(\*correspondence: izanowak@twarda.pan.pl)

<sup>2</sup>Swedish Museum of Natural History, Stockholm, Sweden

In the northern part of the Izera-Karkonosze Massif, which represents the passive margin of the Saxothuringian terrane, c. 500 Ma granites were intruded by a swarm of the WNW-trending subvertical basic veins and then deformed and metamorphosed. Two types of zircon, types I and II, that differ in colour, size, habit and internal structure were identified in six metabasite veins. Colourless, transparent and euhedral, 300  $\mu\text{m}$  sized, CL-bright zircon of type I display inherited old cores as well as c. 500 Ma oscillatory zoned rims. Their U-Pb ages are almost identical with the previously determined intrusion age of a protolith for the Izera metagranites (U-Pb, zircon, 515-480 Ma). Grains of type I show  $\delta^{18}\text{O}$  (6.2-9.1‰) values and Ti-zircon temperatures (600-780°C) similar to the data from the Izera gneiss zircons. Their REE patterns exhibit a narrow range. Such coincidence indicates that the zircons of type I are probably inherited xenocrysts incorporated into the basic magma via assimilation of material of local granitic crust. Type II zircons, which yield ages of c. 370 Ma, are brown, turbid, subhedral crystals up to 600  $\mu\text{m}$  size, and dark in CL. Their large (c. 2/3 of the grain size), almost homogeneous and microinclusion-rich inner parts are surrounded by thinner oscillatory zoned rims. They display a wide range of Ti-zircon temperatures (630-800°C), variable REE contents and  $\delta^{18}\text{O}$  (4.5-8.9‰) values. The origin of these brown zircons is ambiguous. Their homogeneous interiors and oscillatory zoned rims indicate growth in a magmatic melt. Grains showing  $\delta^{18}\text{O}$  from 5.1-5.5‰ present coherent magmatic-style REE patterns with positive Ce and negative Eu anomalies, also indicative of their magmatic origin. However, dark and inclusion-rich centres of type II grains suggest precipitation from hydrothermal fluids, while low  $\delta^{18}\text{O}$  (4.5-5.0‰) values, incoherent REE patterns, LREE enrichment and a lack of Ce anomaly in many grains suggest interaction of the metabasites with hydrothermal fluids during crystallization of the brown zircons. The results are consistent with type II zircon of crystallizing from a fluid-saturated residual melt or more likely representing magmatic crystals hydrothermally altered by fluids coming from the surrounding metagranites.

## Delaminated Lithospheric Mantle and exotic metasomatism beneath East Russia

NTAFLOS TH<sup>1</sup>, ASCHCHEPKOV I.<sup>2</sup>, KOUTSOVITIS P.<sup>1</sup>, HAUZENBERGER A.<sup>3</sup>, PRIKHODKO V.<sup>4</sup> AND ASSEVA A.<sup>5</sup>

<sup>1</sup>Dept. of Lithospheric Research, University of Vienna, Austria (theodoros.ntaflos@univie.ac.at)

<sup>2</sup>RAS, Institute of Geology and Mineralogy, Novosibirsk, Russia

<sup>3</sup>Institute für Erdwissenschaften, University of Graz, Austria

<sup>4</sup>RAS, Far-Eastern Branch, Institute of Tectonics and Geophysics, Khabarovsk, Russia

<sup>5</sup>RAS, Far-Eastern Branch, Geological Institute, Vladivostok, Russia

In the back-arc environment of Far East Russia, mantle xenoliths from Sikhote-Alin(KO) and Primorie (SV), Far East Russia are fertile spinel lherzolites with amphibole, phlogopite armalcolite, fassaite and röhnite in some of the studied samples. Though samples from both localities are fertile there is a systematic difference in their fertility. The KO samples have mg# varying from 0.891 to 0.899 and are slightly more fertile than the SV samples that have mg# ranging from 0.898 to 0.904. The cpx REE confirm this trend as the  $(La/Yb)_N$  in KO samples range from 0.10 to 1.00 and in SV samples from 0.15 to 1.73.

The clinopyroxene Sr and Nd isotopic ratios range from 0.702599 to 0.703567 and 0.512915 to 513153, respectively, resembling Pacific MORB isotopic ratios.

En route breakdown of disseminated amphibole produces second generation of cpx and olivine and traces of glass as well fassaite and röhnite indicating crystallization at very shallow depths. Melt pockets consisting of Ca-rich glass plagioclase rutile, ilmenite and armalcolite suggest introduction of small amount of an unusual Ti-Ca-rich anhydrous silicate melt at mantle depths.

The lithospheric mantle beneath the studied area represents the residue after partial melting of up to 5% of a primitive mantle. Despite the fact that the studied area experienced several subducting episodes, the lithospheric mantle appears to be unaffected from the upwelling fluids/melts of the subducted slab(s). Since there is no indication for plume activity, and/or evidence for refertilization, it is likely that the lithospheric mantle has been delaminated as the result of tectonic events (lithospheric attenuation, inverse tectonic) associated with the subduction processes and that the studied spinel lherzolites represent upwelling asthenosphere.

## Resilience Biomimcry model for natural disturbance scenarios

NUNES L<sup>1</sup> AND NAROG M<sup>2</sup>

<sup>1</sup>Luisa Nunes, ESACB/CEABN, Qta Sra Mercules, 6000 Castelo Branco Portugal, (lfnunes@ipcb.pt)

<sup>2</sup>Marcia Narog, USDA Forest Service, Pacific Southwest Research Station, Riverside, CA, mnarog@fs.fed.us

Mobile links are 'keystone' organisms that move among habitats and provide essential ecosystem functions such as pollination, seed dispersal, or nutrient translocation. After disturbance, some ecosystem functions may become disrupted or may disappear altogether. Much like similar habitats joined by corridors, the mobile links connect areas that may be widely separated spatially or temporally. Species strategies and interactions must be reconfigured after disturbance based on residual organisms and any altered environmental constraints. Reassembly of organisms might be based on an ecological memory that contributes and leads to the recovery of the affected area. This ecological memory is the complex network of species and their relations with each other and the environment.

Based on the renewal cycle of Holling, we developed a biomimcry resilience model that identifies recovery strategies inspired by opportunistic species colonization, their accumulation and storage of resources and the reorganization phases to a new stability.

We studied and characterized which interactions take place within and between disturbed and undisturbed areas that facilitate proliferation, regeneration and nutrient translocation. The resilience model also considered limitations such as distance from source areas, availability of dispersal agents and suitability of the disturbed environment.

This resilience model was created to help understand natural recovery processes that can be emulated after disturbances and applied to human community disaster planning.

## Probing paleoearthquakes with *in situ* U-Pb SHRIMP-RG analyses of fault-related opals

PERACH NURIEL<sup>1\*</sup>, KATE MAHER<sup>1J</sup>  
AND DAVID M. MILLER<sup>2</sup>

<sup>1</sup> Department of Geological and Environmental Sciences,  
Stanford University, CA 94305, US (\*correspondence:  
perach@stanford.edu, kmaher@stanford.edu)

<sup>2</sup> U. S. Geological Survey, 345 Middlefield Road, MS-973,  
Menlo Park, CA 94025, USA (dmiller@usgu.gov)

In the past decade U-Pb and U-series dating techniques have been successfully applied to opals from arid regions, providing important temporal constraints on paleohydrology, paleoclimate, and depositional environments. In particular, the use of *in situ* SHRIMP-RG (Sensitive High Resolution Ion Microprobe – Reverse Geometry) dating techniques has been demonstrated to resolve mixed multiage problems that arise from slow-growth or multi-stage growth at the sub-millimeter scale. Building upon these advances, we apply *in situ* SHRIMP-RG dating methods to fault-related opal precipitates taken from seismically active fault zones with the aim of dating brittle deformation events. The Mojave Desert fault segments within the Eastern California Shear Zone (ECSZ) are ideal faults to investigate the long-term history because of the need for improved constraints on the timing of fault initiation and the observed discrepancy between long-term and short-term estimates for strain accumulation rates.

We analyzed fault-related opal samples from five different fault exposures within the Camp Rock and the Cave Mountain fault systems. Millimeter size fragments of fault-related opal, occurring as fault coating, filling or fault-breccia cement, were imaged using cathodoluminescence and backscattering electron microscopy in order to identify distinct phases of opal associated with specific syntectonic microstructures. Sub-samples within each phase are then targeted with multiple SHRIMP-RG analyses (<50 µm in diameter) to allow the construction of <sup>238</sup>U/<sup>208</sup>Pb-<sup>206</sup>Pb/<sup>208</sup>Pb and/or Tera-Wasserburg U-Pb isochrons. Of the 30 distinct phases that were identified, 10 were successfully dated, providing U-Pb ages with 2σ ≤ 10% and MSWD between 0.42 and 1.8. The most important factors for successful age determinations were low amounts of common Pb, high U concentrations (between 50 and 1300 ppm) and heterogeneities within each phase. Ages range from 1.45 to 0.58 Ma and coeval ages are clustered into several periods during this time interval, suggesting periods of enhanced fault activity. Additional analyses of syntectonic opals, taken from several sites and from additional faults segments can constrain the long-term deformational history and contribute to our understanding of how strain is distributed both locally (within a specific structure) and regionally (within different fault systems) over a geological time scale.

## U-series isotopes as tracers of particles fluxes and deposition rates of Heinrich layers H2 and H1 from a core raised off Hudson Strait

L. NUTTIN\* AND C. HILLAIRE-MARCEL

GEOTOP research centre, Université du Québec à Montréal,  
Montreal, Canada (correspondence: lanuttin@gmail.com)

A ~9 m-long core was retrieved from the lower Labrador Sea slope (2674 m water-depth), approximately 180 km off the Hudson Strait shelf edge. It yielded a high resolution record of recent detrital carbonate (DC) sedimentary pulses from the Hudson Strait outlet of the Laurentide ice sheet, assigned to "Heinrich events" H2 and H1. These fine carbonate-rich layers (calcite/dolomite ~ 2.5) originated from glacial erosion of Paleozoic rocks in Hudson Strait and Ungava Bay. The coarse sediment fraction content of the layers suggest intense iceberg calving at the ice-stream edge, while sub-glacial meltwater flushing over the Hudson Strait sill carried fine silt-sized, carbonate-rich glacial flour to the shelf edge. Such suspended sediment pulses led to the spreading of turbidites into the deep Labrador Sea. These layers are characterized by a <sup>234</sup>U deficit (vs <sup>238</sup>U) and by very low <sup>230</sup>Th excesses corrected from decay to the time of deposition (<sup>230</sup>Th<sub>xs</sub>)<sub>0</sub>. These low values indicate extremely fast deposition. Inventories of (<sup>230</sup>Th<sub>xs</sub>)<sub>0</sub> were used to estimate durations of ~1.28 and ~1.99 ka respectively for H2 and H1, relative to estimates of ~1.15 and ~2.12 ka from calibrated <sup>14</sup>C ages on planktic foraminifers. Another DC-layer was deposited at ~8.3 cal ka BP, during the final drainage of Lake Agassiz. Above, high (<sup>230</sup>Th<sub>xs</sub>)<sub>0</sub> activities but low <sup>230</sup>Th<sub>xs</sub>-fluxes point to some <sup>230</sup>Th-focussing with enhanced biogenic carbonate fluxes, under a stronger Western Boundary Undercurrent influence leading to the winnowing of slope sediments, thus reduced sedimentation rates at the site. <sup>231</sup>Pa/<sup>230</sup>Th ratios are used to further document sedimentary regimes at the site.



## Carbonate mineralization in shallow Lake Balaton

I. NYIRÓ-KÓSA<sup>1</sup>, É. TOMPA<sup>1</sup>, Á. ROSTÁSI<sup>1</sup>, T. CSERNY<sup>2</sup>  
AND M. PÓSFAI<sup>1\*</sup>

<sup>1</sup>Dept. of Earth & Env. Sci., Univ. Pannonia, Veszprém, 8200  
Hungary, (\*correspondence: mihaly.posfai@gmail.com)

<sup>2</sup>Geol. Geophys. Inst. Hungary, Stefánia 14, H1143 Budapest

Calcite precipitates in hardwater lakes as a result of CO<sub>2</sub> consumption by algae through photosynthesis. Lake Balaton has a large surface area (~600 km<sup>2</sup>) but an average depth of only ~3.5 m. Its sediment is dominated by carbonate minerals, including Mg-calcite that precipitates from lakewater, aragonite from shells, diagenetic 'protodolomite' and allochthonous calcite and dolomite [1]. We studied various aspects of carbonate formation relevant for the biogeochemical cycles in the lake: the relationships between Mg-content, crystal structure, particle size and morphology, the potential autochthonous formation of dolomite, the roles of organisms in nucleating and reprocessing mineral matter, and the association of P with the carbonate minerals.

Both sediment cores and freshly precipitated material were collected, either by placing sediment traps under the ice (in order to avoid the resuspension of sediments by wind-driven turbulence) or by filtering lakewater. Mg incorporation into calcite was studied by X-ray powder diffraction analysis of d(104) spacings. Particle morphologies, microstructures and compositions were observed using scanning and transmission electron microscopies. The Mg content of calcite increases from west to east in the lake, reflecting a gradient in water composition. Mg-calcite particles are elongated, few µm-large aggregates in which the crystallites occur in a consensus crystallographic orientation. Smaller, euhedral dolomite crystals also occur in the sediment traps; in places their cell parameters slightly differ from those of stoichiometric dolomite. Concerning the roles of organisms in mineral precipitation, no evidence has been found for the microorganism-assisted nucleation of Mg-calcite; however, the reprocessing of mineral matter by filtering organisms (zooplankton and mussels) typically produces pellets of several hundred µm in size that are major constituents of the sediment. Studies are in progress to map the distribution of P in the various carbonate minerals, and to explore the origin of the dolomite that has anomalous lattice parameters [2].

[1] Müller & Wagner (1978) *Spec. Publ. Intl. Assoc. Sed.* **2**, 57-81. [2] This study was supported by a joint EU-European Social Fund grant (TÁMOP-4.2.2.A-11/1/KONV-2012-0064).

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