

## Arsenate precipitation: An alternative fate of As in soils contaminated with mine-related wastes

K. VACA-ESCOBAR<sup>1</sup> AND M. VILLALOBOS<sup>1,2\*</sup>

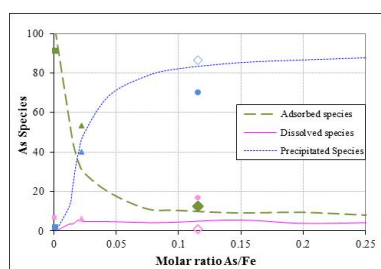
<sup>1</sup>Environmental Bio-Geochemistry Group, Chemistry School

<sup>2</sup>Earth Sciences Graduate Program, Geology Institute, UNAM,  
Coyoacan, CU, Mexico 04510, D.F

(\*correspondence: mariov@geologia.unam.mx)

### Introduction

Arsenic and heavy metals are highly abundant elements in soils contaminated with mining and metallurgical wastes [1]. The final fate of arsenic in aerated environments is usually reported as As(V) bound to iron oxide surfaces [2]. However, we have found evidence of an alternative mechanism as insoluble heavy metal arsenates [3]. In this work we investigate the conditions that favor one mechanism over the other by both modeling and experimental methods. We applied a triple layer surface complexation modeling scheme [4] simultaneously with arsenate precipitation equilibria to predict the speciation expected as a function of total As/Fe ratios, and pH in a simple goethite /Pb(II)/ carbonate system, and compared the results with experimental data under selected conditions.



**Figure 1:** As(V) species distribution in goethite/Pb(II)/ carbonate systems. Model and experimental results at pH 7.

### Discussion of Results

Adsorption processes only prevail at very low As/Fe ratios, and precipitation as Pb(II) arsenate quickly becomes predominant (Fig. 1). Modeling results as a function of pH will also be presented.

[1] Vaughan (2006) *Elements* **2**, 71–75. [2] Foster *et al.* (1998) *Am. Mineral* **83**, 553–568. [3] Villalobos *et al.* (2010) *Aquat. Geochem.* **16**, 225–250. [4] Salazar-Camacho & Villalobos (2010) *Geochim. Cosmochim. Acta* **74**, 2257–2280.

## Microbial and photochemical mineralization of dissolved organic carbon from big rivers

A.V. VÄHÄTALO<sup>1,2</sup> AND H. AARNOS<sup>2</sup>

<sup>1</sup>Coastal Zone Research Tem, Aronia Research and  
Development Institute, Novia University of Applied  
Sciences and Åbo Akademi University  
(anssi.vahatalo@helsinki.fi)

<sup>2</sup>Department of Environmental Sciences, University of  
Helsinki (hanna.aarnos@helsinki.fi)

We addressed the potential for microbial and photochemical mineralization of dissolved organic carbon (DOC) from ten big rivers. In order to quantify the direct photochemical mineralization of DOC to CO<sub>2</sub>, the sterile-filtered river waters were irradiated with an artificial solar radiation until photochemical reactions photobleached chromophoric dissolved organic matter (CDOM) completely. For the assessment of biological mineralization of DOC, irradiated waters and their dark controls received nutrients and indigenous microbes from rivers. The concentration of DOC was followed over one year to quantify the amount of DOC consumed by microbes. Photochemical reactions mineralized DOC directly to CO<sub>2</sub> and also produced biologically available photoproducts. The magnitude of photoreactive DOC depended on the magnitude of CDOM. A part of DOC was resistant to photoreactions but was decomposed with low rate by microbes.

## The first data about the concentrations REEs in waters from weathering zone of Berezitovoe gold deposit (Priamurye, Russia)

ELENA A. VAKH, ALEKSANDR S. VAKH  
AND NATALIA A. KHARITONOVA

Far East Geological Institute FEB RAS, Russia,  
Adasea@mail.ru

The Berezitovoy gold deposit located in the northeastern Amur gold province in the downstream basin of the Khaikta River. In 2007, two mining companies: Berezitovoy Mine Ltd. and High River Gold Mines Ltd., started to mine this deposit. Geologically, the deposit is localized in a southeast part of the North Asian craton, in a zone of its joint with formations of northern frame Tukuringra-Dzhagdinsky terrain Mongolo-Ohotsky zone. Two formations of sediments (granites and ore-metasomatic rocks) occur in the deposit. Main minerals bearing REEs are allanit, monatsit - (Ce), chervandonit - (Ce).

In this study we present the preliminary results of investigation the content and distribution of REEs in the bedrock and water from weathering zone of deposit. Our data indicate that the content of REEs in bedrock of Berezitovoe deposit can reach up to 230 ppm and the content of LREEs is at about 90% of total REEs. All types of bedrock display of strong negative Eu anomalies.

The surface water of area is enriched in total REEs (1, 4 ppm), although the content of LREEs is higher in 8-10 times than HREEs. Drainage water is yellow, dark -yellow color with TDS up to 10 g/l and pH varies from 3, 0 to 4, 5. This water belongs to Mg-K-SO<sub>4</sub> type and content a huge amount of REEs (up to 16, 1 ppm). The concentration LREEs is higher than HREEs as well. It is established that drainage water is a selective accumulation of middle REEs.

Comparison of REEs content in bedrocks, ore and surface water is appeared the similarity of their profiles.

## Speleothem record of permafrost in Siberia and aridity in Mongolia during the last 450 kyr

A. VAKS<sup>1\*</sup>, O.S. GUTAREVA<sup>2</sup>, S.F.M. BREITENBACH<sup>3</sup>,  
E. AVIRMED<sup>4</sup>, A.M. KONONOV<sup>2</sup>, A.V. OSINZEV,<sup>5</sup>  
AND G.M. HENDERSON<sup>1</sup>

<sup>1</sup>Department of Earth Sciences, University of Oxford, Oxford,  
United Kingdom

(\*correspondence: Anton.Vaks@earth.ox.ac.uk)

<sup>2</sup>Institute of Earth's Crust, Russian Academy of Science,  
Siberian Branch, Irkutsk, Russia

<sup>3</sup>Swiss Federal Institute of Technology Zurich, Geological  
Institute, Zurich, Switzerland

<sup>4</sup>Institute of Geography, Mongolian Academy of Sciences,  
Ulaanbaatar, Mongolia

<sup>5</sup>Arabica Speleological Club, Irkutsk, Russia

We have used speleothems from six caves along a north-south transect in Eastern Siberia and the Mongolian Gobi Desert (60°22'N - 42°50'N) to track the evolution of permafrost and desert aridity. The studied caves are located in various climate zones: from the southern boundary of continuous permafrost, through the discontinuous/island permafrost, to the dry Gobi Desert.

More than 90 horizons of 22 speleothems were dated by U-Th method. The youngest speleothem age in the northernmost cave was 404 ± 32 kyr, corresponding to interglacial Marine Isotopic Stage (MIS) 11, while eleven other horizons in six speleothems from this cave were older than the ~500 kyr U-Th dating limit. These results suggest that MIS-11 in Eastern Siberia was warmer than today, causing brief permafrost degradation at 60°N, followed by re-establishment and continuous permafrost since then. Between 56°N and 52°N speleothem ages clustered into the warmest intervals of interglacial MIS-11, 9, 7, 5 and 1, showing intermittent melting of the permafrost. This data provides constraints on glacial-interglacial migrations of the southern boundary of continuous permafrost in Eastern Siberia during the last 450 kyr. No speleothem deposition younger than 500 kyr was found in the Gobi Desert, showing that arid conditions prevailed during this entire period.

The year-round monitoring of δ<sup>18</sup>O and δD values of cave water and atmospheric precipitation in the city of Irkutsk and nearby cave shows that δ<sup>18</sup>O and δD values of rain and snow are in direct relationship with temperature throughout the year, and δ<sup>18</sup>O and δD values of the cave water reflect the weighted annual average of precipitation. Ongoing work is making use of these observations to create stable isotope records of the Siberian speleothems.

## Mantle source components of the Early Cretaceous to Paleogene mafic tholeiitic and alkaline magmatism in Rio and related mantle metassomatism processes

S.C. VALENTE

Geosciences Dept., UFRuralRJ, Seropédica, RJ, 23890-00, Brazil (sergio@ufrj.br)

The Early Cretaceous (*c.* 132 Ma) to Paleogene (*c.* 55 Ma) mafic magmatism in Rio is mostly represented by tholeiitic dolerites and ultramafic and alkaline lamprophyres, respectively [1]. The tholeiites are often regular, long, tens of metres-thick, vertical, ENE-trending intrusions with remarkably uniform textures and structures. In contrast, the ultramafic and alkaline lamprophyre dykes are generally less than one metre thick and display variable textures, structures and morphologies. Litogeochemical and Sr-Nd-O isotopic data show that the least evolved tholeiitic dolerites seem not to represent contaminated melts and are likely to be related to a predominantly asthenospheric, plume source similar in composition to Tristan da Cunha lavas. Small contributions (~10%) from the overlying subcontinental lithospheric mantle may have imprinted lithospheric signatures in the least evolved dolerites such as negative Nb anomalies. The Paleogene alkaline dykes comprise a strongly undersaturated suite including ultramafic and alkaline lamprophyres and sodic aegaitic phonolites. Sr-Nd isotope data point to a contribution of asthenospheric mantle sources for the generation of the alkaline dykes likely to be related to the Trindade plume. Heat conduction and advection from the plume triggered the melting of the readily fusible, volatile-rich, mafic potassic parts of the overlying subcontinental lithospheric mantle beneath Rio, leading to the generation of the most primitive ultramafic ultrapotassic lamprophyres. Major and trace element characteristics of the ultrapotassic ultramafic lamprophyres (*e.g.* CaO/Al<sub>2</sub>O<sub>3</sub> <1; (La/Nb)<sub>N</sub>~0.9) and their Sm-Nd model DM ages (496-660 Ma) indicate that the Late Proterozoic enrichment process of the subcontinental lithospheric mantle seems to have been unrelated to subduction processes but largely controlled by the migration of high H<sub>2</sub>O/CO<sub>2</sub> silicate melts from the underlying asthenosphere.

[1] Valente (1997) *PhD* thesis, QUB, UK. 400pp.

## Lunar zircon: Primitive $\delta^{18}\text{O}$ of dry evolved and mafic magmas

J.W. VALLEY\*, M.J. SPICUZZA AND T. USHIKUBO

WiscSIMS, Dept. of Geoscience, Univ. Wisconsin, Madison, WI, 53706, USA

(\*correspondence: valley@geology.wisc.edu)

Oxygen isotope ratios of zircons from the Moon have been measured *in situ* by SIMS [1], including grains from: quartz monzodiorite (*n*=4; 4, 294 Ma [2]), impact melt (*n*=1), breccia and shocked norite (*n*=2), and Apollo 12 (*n*=6) and 14 (*n*=3) regolith. Zircons from regolith may represent lithologies not found at Apollo landing sites. Some zircons have K-feldspar  $\pm$  silica as inclusions or infilling cracks, suggesting they represent extreme differentiates of mafic magmas, similar to zircons in lunar granophyre [2]. The average  $\delta^{18}\text{O}$  for lunar zircons ranges from 5.19 to 5.82 ‰ (ave. = 5.59  $\pm$ 0.33‰, 2SD). Trace element concentrations of these zircons, also measured by SIMS, are: Ti 37-170 ppm; P 425-1120 ppm; Y 780-2850 ppm; total REE 485-1780; Hf 10, 500-12, 750 ppm; Th 4-38 ppm; and U 12-108 ppm [1].

The  $\delta^{18}\text{O}$  (whole rock) values of mare basalts range from 5.33 to 5.81: 5.69  $\pm$ 0.17 (2SD, *n*=23) for low-Ti and 5.54  $\pm$  0.26‰ (*n*=15) for high-Ti basalts [3, 4]. The low variability allows comparison with zircons from other samples. The average basalt has the same  $\delta^{18}\text{O}$  as igneous zircons:  $\Delta^{18}\text{O}$  (WR-Zrc)  $\sim$  0. This WR-Zrc fractionation contrasts with samples from Earth, where  $\Delta^{18}\text{O}$  (WR-Zrc)  $\sim$  0.0612 (wt.% SiO<sub>2</sub>) -2.50‰ [5]. For instance, unaltered MORB  $\delta^{18}\text{O}$  (WR) values average  $\sim$  5.6-5.7, while  $\delta^{18}\text{O}$  (Zrc) values average 5.2  $\pm$ 0.5 (*n*=197) for gabbro and plagiogranite from ocean crust:  $\Delta^{18}\text{O}$  (WR-Zrc)  $\sim$ 0.5 [6]. Thus  $\Delta^{18}\text{O}$  (WR-Zrc) values on the Moon deviate significantly from relations on Earth.

In general, values of  $\delta^{18}\text{O}$  (Zrc) vary negligibly during closed system magmatic differentiation because  $\Delta^{18}\text{O}$  (WR-Zrc) correlates to  $\delta^{18}\text{O}$  (WR); both increase for siliceous rocks with high  $\delta^{18}\text{O}$  minerals (Qt, Flds). However, in detail, variable T will change this relation and the best explanation of the lunar results is that magmatic T's were significantly higher due to low water content. High crystallization T for lunar zircons is supported by values of [Ti] in lunar zircons (37-170 ppm) that are significantly higher than in terrestrial igneous zircons (0.2-30 ppm) [7]. We thus infer a low water content of these highly evolved lunar melts and that mafic parent magmas on the Moon were significantly drier.

[1] Spicuzza *et al.* (2011) *LPSC*, abst 2455. [2] Meyer *et al.* (1996) *Met. Plan. Sci.* **31**, 370-387. [3] Spicuzza *et al.* (2007) *EPSL* **253**, 254-265. [4] Liu *et al.* (2010) *GCA* **74**, 6249-6262. [5] Lackey *et al.* (2008) *J Pet* **49**, 1397-1426. [6] Grimes *et al.* (2011) *CMP* **161**, 13-33. [7] Fu *et al.* (2008) *CMP* **156**, 197-215.

## The role and effect of boron during the crystallization of CaCO<sub>3</sub>

B. VALLINA-ANTUÑA<sup>1,2</sup>, J.D. RODRIGUEZ-BLANCO<sup>1</sup>,  
J.A. BLANCO<sup>2</sup> AND L.G. BENNING<sup>1</sup>

<sup>1</sup>School of Earth and Environment, University of Leeds, LS2  
9JT, United Kingdom (beatrizvallina@gmail.com)

<sup>2</sup>Departamento de Física, Universidad de Oviedo, E-33007  
Oviedo, Spain

Boron (B) is a crucial element in carbonate biominerals and its isotopic signature is used as a paleo-acidity proxy and to reconstruct atmospheric CO<sub>2</sub> levels through time [1, 2]. Most studies however, focused on compositional or isotopic analyses of natural marine carbonates, but the mechanisms of boron incorporation or the role and effect that [B]<sub>aq</sub> plays during the nucleation and growth of the various calcium carbonate polymorphs is still unknown. Therefore the aim of this research was to quantitatively assess the crystallization pathways of CaCO<sub>3</sub> polymorph in the presence of [B]<sub>aq</sub> and to mimic B/Ca ratios in modern seawater.

The experiments were performed at 10-30°C in stirred reactors by mixing equimolar solutions of CaCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> doped with 0-25mM of [B]<sub>aq</sub>. Reactions were followed for between ten minutes and eight hours, while simultaneously recording changes in pH as a direct proxy for the crystallization reactions. At regular time intervals solid and solution aliquots were collected and characterized by XRD, SEM, FTIR or wet-chemical analysis.

The results show that in the presence of [B]<sub>aq</sub> the initial amorphous calcium carbonate (ACC) remained stable for up to 5 minutes, while at equivalent conditions with no [B]<sub>aq</sub> the transformation to vaterite begins after ~1 minute [4]. However, after the full ACC breakdown, the crystallization pathways vary dramatically as a function of temperature and [B]<sub>aq</sub> concentration compared to the pure system [2]. For example, at 30°C and 10mM [B]<sub>aq</sub>, the ACC to calcite transformation via vaterite was ~ 25% faster compared to the pure system. Furthermore, when 25mM of [B]<sub>aq</sub> were added, the initial ACC transformed directly to calcite in less than 10 minutes with no vaterite intermediate. Overall our experiments revealed that the effect of temperature was inverse to that of the B/Ca ratio in solution. The effects were also reflected in the variations in polymorph distribution as a function of time and in the changes in morphologies of the various CaCO<sub>3</sub> polymorphs at the conditions tested.

- [1] Hemming *et al.* (1995) *Geochim Cosmochim Acta* **59**, 371–279. [2] Paris *et al.* (2010) *Geology* **38**, 1035-1038.  
[3] Rodriguez-Blanco *et al.* (2011) *Nanoscale* **3**, 265-271.  
[4] Bots *et al.* *Min Mag* (this volume)

## New characterization of uranium mineralogy in Ukrainian ores

A.A. VALTER<sup>1</sup> AND K.B. KNIGHT<sup>2</sup>

<sup>1</sup>Institute of Applied Physics, Nat. Acad. Sci. Ukraine, Sumy,  
40030, Ukraine (avalter@iop.kiev.ua)

<sup>2</sup>Lawrence Livermore National. Lab., (knight29@llnl.gov)

The economically significant uranium ores of Ukraine form one of the largest uranium ore reserves in Europe. Concentrated in the central Ukrainian shield, these ore bodies (~1, 8 Ga, inferred from U-Pb analyses [1]), are associated with albitites in granites. Carbonates, iron oxides and Ca-Fe garnets are found genetically associated with uranium minerals, while albite and other alkali silicates formed during earlier stage metasomatic processes. Albite has been altered at the margins adjacent to the uranium minerals from low to high albite. We present preliminary work characterizing primary uranium ores in Ukraine, as part of a larger effort to develop a database of nuclear materials for Ukraine.

We have studied uranium minerals from representative samples of the Severinskoje (I), Michurinskoje(II), and Vatutinskoje (III) deposits, as well as from the Adabash fracture zone mineralization (IV), using mineralogy and gamma spectrometry [2]. This study presents new X-ray diffraction (powder and single grains), SEM and TEM characterizations, and microprobe study of the principal U-minerals present:

*Uraninite (IV)*, a<sub>0</sub>=0, 542 nm, forming cubic crystals up to 0, 5 mm. Average composition is Na<sub>2</sub>O 5, 6%; SiO<sub>2</sub> 0, 8%; CaO 1, 74%; PbO 23%; U<sub>3</sub>O<sub>8</sub> 72, 4%. U, Ca, Pb appear to be associated with the host crystal matrix, while Na, Si and trace elements are concentrated in solid inclusions (up to 0, 5 mm). *Coffinite (I, II, III)* forms elongated crystals up to 0, 1 mm. Average composition is Al<sub>2</sub>O<sub>3</sub> 0, 9%; SiO<sub>2</sub> 15%; CaO 2, 5%; Fe<sub>2</sub>O<sub>3</sub> 1, 4%; U<sub>2</sub>O<sub>3</sub> 65%. *Brannerite (II, III)* forms elongated, needle-like crystals up to 0, 1 mm. Average composition is PbO 6, 17%; UO<sub>2</sub> 39, 18%; CaO 3, 15%; SiO<sub>2</sub> 2, 31%; TiO<sub>2</sub> 24, 49%; FeO 2, 08%. This mineral occurs intergrown with an unknown silicate mineral (mixture) with composition ~ (Ca, Pb, U)(Ti, Fe)<sub>2</sub>Si<sub>3</sub>O<sub>11</sub>. *Ca-Uraninite (I)* ~CaU<sub>2</sub>O<sub>6</sub>, is cubic, a<sub>0</sub> = 5, 37 nm. This is possibly a new mineral variety. It forms in thin veins (~20 μm thick) and globules (~1 μm). *Ca-boltwoodite (I)* occurs as thin veins of plate-like crystals up to 20 μm in diameter. The boltwoodite powder XRD pattern suggests a disordered layered structure, possibly representing a new mineral variety. The relative composition is U:Si:(Na+K+Ca<sub>0,5</sub>) ≈ 1:1:1.

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- [1] Belevtsev *et al.* (1995) *Naukova Dumka*, 396p (in Russian). [2] Valter *et al.* (2007) *Prob. Atom. Sci. Tech.* **5**, 69–75.

## Re-Os in pyrite as a constraint on the timing of HP metamorphism during the Tianshan orogeny (NW China)

D. VAN ACKEN<sup>1</sup>, R.A. CREASER<sup>1</sup>, W. SU<sup>2</sup> AND J. GAO<sup>2</sup>

<sup>1</sup>University of Alberta (vanacken@ualberta.ca, rcreaser@ualberta.ca)

<sup>2</sup>Chinese Academy of Sciences (suwen@mail.igcas.ac.cn, gaojun@mail.igcas.ac.cn)

The Tianshan mountain belt in Central Asia is situated between the Junggar and Tarim basins. Because of its large extension of over 2500 km of length and complex geological history, it is a key piece to understand the tectonic evolution of Eurasia. Paleozoic collision resulted in the closure of the Paleo-Asia ocean and amalgamation of small continental fragments. Dating of metamorphic units within the Tianshan is important to understand the timing of its tectonic evolution throughout the Phanerozoic.

Collision between the Yili-Central Tianshan and Tarim-Karakum plates in the southwestern Tianshan is recorded by eclogites embedded in greenschist and blueschist-facies metapelites, in the high-pressure, low-temperature belt in the Southern Tianshan, NW China. The majority of ages obtained with Sm-Nd, Ar-Ar, and U-Pb time the peak of metamorphism in the Late Carboniferous around 345 Ma, while younger Ar-Ar and Rb-Sr ages around 310 Ma are interpreted as mica cooling ages or recrystallization due to fluid flow. Younger U-Pb ages of about 225 – 230 Ma suggest later peak metamorphism, and thus a later continental collision, or resetting of the U-Pb system during the Triassic.

New Re-Os data, obtained on pyrite mineral separates from eclogites from the western Tianshan HP-LT belt, confirm the older Carboniferous ages. Sulfides from three eclogite samples yield ages between 310 and 380 Ma, with large uncertainties up to 100 Ma resulting from the few data points per sample available. These ages likely represent sulfide formation or recrystallization during eclogite-facies metamorphism, and provide independent evidence for Carboniferous ages of eclogite formation.

The similar ages yielded by isotope systems hosted in silicates and sulfides from Tianshan eclogite confirm a) Carboniferous ages for the eclogite-facies metamorphism during the Tianshan orogeny and b) the potential of the Re-Os system to date sulfide formation in metamorphic rocks. However, ages obtained in this manner may represent ages of sulfide formation by fluid flow or remobilization during later stages of metamorphism, and thus needs to be compared with independent, silicate mineral-hosted isotope chronometers.

## Metal pollution assessment in sediment of the Talar River, N. Iran

M. VANAEI, A. MAGHSOUDI, A.S. SAEEDI AND M. NAJJARAN

In the Ghaemshahr Area the Length of the Talar River Separated to 8 sample site and 112 Samples Collected from Sediment and For the Distinguition of Geogenic Pollution for each sample, 1 gr of sample was digested with the solution of HF+HClO<sub>4</sub>+HNO<sub>3</sub> but in the Antropogenic Pollution the sample was digested with the solution Acetic Acid, hydroxileamine, Hydrochloride and hydrogenproxide and then Analyzed with Atomic Absorbtion Method

The Enrichment Ratio and Geo-accumulation Index has been Calculated and Evaluated the Degree of Contamination Metals (Zn, V, Sn, Pb, Ni, Cu, Cr, Co, Cd, Ag, Fe) In the Sediment of the Talar River.

According to the contamination categories, the Ag has been Enriched and show very high absorption and Cd in the 1, 2, 4, 5, 7 Site and Sn in the 2, 4, 6, 7 Site Shows Intense to Very High Absorption.

Degree of Geo-accumulation Index Show that the Ag in the 1, 2, 3, 4, 5, 7, 6 Sites has been Enriched and Show Heavily Contaminated and Cd in the 1 Site and Sn in the 2, 5 Site Shows Heavily Contaminated.

In the Dogol Railway Station to Orim Village the Cd, Ag and Sn Contain of High Level of Antropogenic Contamination and Fe Contain of Low Level of Antropogenic Contamination and in the Babolsar-Bahmanir site Cd, Ag and V Contain of High Level of Antropogenic Contamination and Fe Contain of Low Level of Antropogenic Contamination

Activity Mining (Coal and Fluorite) and Depo of Coal in the Upper part of River Very Affected the Absorption and Contamination but in the Downstream, Realize of Industry and Urban Sewage very Affected the Absorption and Contamination

## Causes and consequences of isotopically heavy dissolved molybdenum in rivers

DEREK VANCE<sup>1\*</sup>, ANDREW R. KEECH<sup>1</sup>,  
ALAN MATTHEWS<sup>2</sup> AND COREY ARCHER<sup>1</sup>

<sup>1</sup>Bristol Isotope Group, School of Earth Sciences, University of Bristol, Wills Memorial Building, Bristol, BS8 1RJ, UK (\*correspondence: d.vance@bristol.ac.uk)

<sup>2</sup>Institute of Earth Sciences, Hebrew University of Jerusalem, 91904 Israel

The molybdenum (Mo) isotopic composition of the dissolved load of rivers is isotopically heavy relative to likely average continental crust. Two key aspects of this finding are not understood. The first is the origin of this isotopic fractionation. The second is the degree to which the riverine dissolved load reflects the delivery of Mo isotopes from the continents to the oceans. Both of these issues are crucial to the interpretation of oceanic Mo isotope records, and to their use as redox indicators. Here we address both these issues, the first using new data from soil profiles that constrain processes by which Mo and its isotopes are released during weathering, and the second through data and models that have implications for the release of Mo from riverine particulate material in estuaries and shallow seas.

We have studied Mo isotope systematics in a range of soil chronosequences, and the data suggest that the behaviour of Mo and its isotopes in the weathering environment is dependent on an array of controls. In one key chronosequence from Scotland, however, there is a previously un-heralded role implied for biological processes. In these soils, there is pronounced retention of Mo in organic material at the top of the profile, that becomes more pronounced as the soil ages. In these soils Mo isotope retention/release in/from soils is controlled by both Fe-Mn oxides and organic material. These data are consistent with recent findings that Mo is limiting in many terrestrial ecosystems and that soil bacteria take up the light isotope.

A key issue for oceanic Mo isotope records is the isotopic composition of the input from the continents. The heavy dissolved load of rivers presents some severe problems for models of the Mo isotope mass balance in the modern oceans. Recent data from continental margin settings, however, particularly those that are marginally sub-oxic, suggests that diagenetic reactions could release the light particulate Mo washed into the oceans as the counterpart of the heavy dissolved load. The implications of this suggestion for the oceanic Mo isotope budget will be explored.

## GEOTRACES intercalibration results for Nd isotopes and REE on seawater and particulate samples

TINA VAN DE FLIERDT<sup>1</sup>, KATHARINA PAHNKE<sup>2</sup>  
AND GEOTRACES INTERCALIBRATION PARTICIPANTS

<sup>1</sup>Department of Earth Science and Engineering, Imperial College London, South Kensington Campus, London, SW7 2AZ, UK

<sup>2</sup>Department of Geology and Geophysics, University of Hawaii, Honolulu, HI 96822, USA

One of the key activities during the initial phase of the international GEOTRACES program was an extensive international intercalibration effort for all trace elements and isotopes (TEIs) targeted by the program, to ensure that results from different cruises and from different labs can be compared in a meaningful way. Two intercalibration cruises sailed in 2008 and 2009 to enable systematic testing of sampling equipment and methods, and to collect large amounts of homogenous seawater samples to check whether results for dissolved and particulate TEIs obtained by different laboratories are accurate and reproducible.

Here we present the results from the intercalibration efforts on neodymium isotopes and rare earth elements in seawater and marine particulates. For seawater, we obtained Nd isotope results from 11 different laboratories on duplicate seawater samples from two different water depths (2000m and 15m) at the Bermuda Atlantic time series study site (BATS). Average  $\epsilon_{Nd}$  values are  $-13.1 \pm 0.6$  and  $-9.1 \pm 0.6$ . This is a very satisfactory result for the community, as individual labs typically achieve external reproducibilities of  $^{143}Nd/^{144}Nd$  measurements between 0.2 and 0.4  $\epsilon$  units (2  $\sigma$  standard deviation). In an attempt to test whether the spread in reported isotope ratios is due to different protocols used for pre-concentration and ion chromatography, or rather due to different methods applied on the mass spectrometry end, we distributed an isotopic standard of unknown composition to all labs. Averaged results from all laboratories reveal a very similar external reproducibility of 60 ppm (2 $\sigma$  SD) on  $^{143}Nd/^{144}Nd$ , indicating that mass spectrometry is the main variable in achieving accurate and precise Nd isotope ratios.

We will furthermore present Nd isotope results on systematic shipboard filtration tests, a comparison of different sampling systems, as well as intercalibration results for Nd isotopes in marine particulates and REE patterns in seawater and particulates. While the community is definitely ready for Nd isotope measurements in seawater, the analyses of marine particulates seems to require a common methodology to provide comparable results.

## Crystallization of low-K calc-alkaline igneous rocks at lower crustal pressures

G. VAN DEN BLEEKEN<sup>1\*</sup>, O. MÜNTENER<sup>1</sup>  
AND P. ÜLMER<sup>2</sup>

<sup>1</sup>Institute of Mineralogy and Geochemistry, University of Lausanne, Switzerland (\*correspondence: g.vandenbleeken@opgc.univ-bpclermont.fr, othmar.muntener@unil.ch)

<sup>2</sup>Institute for Mineralogy and Petrology, ETH Zürich, Switzerland (peter.ulmer@erdw.ethz.ch)

We will present phase relations and compositions from high-pressure equilibrium crystallization experiments on low-K calc-alkaline rocks saturated in H<sub>2</sub>O. The wider rationale of this study is to advocate the role of crystal fractionation in the lower crust of subduction-related magmatic arcs, as an alternative to the more conventional partial melting of amphibolites [1]. Furthermore, we aim to clarify the role of epidote (+Na-mica) during igneous crystallization near the solidus, and its potential effect on derivative granitic rock compositions by comparing our results with studies on natural sodium-rich granitoids [2].

As starting materials, we use a powdered natural paragonite+epidote+garnet-bearing mafic rock derived from the lower crust of the Kohistan paleo-island arc, and a trace-element-doped gel of similar composition. Experimental pressure and temperature were varied in the near-solidus domain (1.0-1.6 GPa; 650-800 °C), representing conditions relevant for deep arc crust formation. All experimental runs were buffered at NNO.

First results show that amphibole occurs in all runs, garnet is present at pressures above 1.0 GPa, and plagioclase is present in all runs except where epidote is present. As minor phases, rutile or ilmenite, and quartz are observed. In accordance with the addition of ~15 wt% water, coexisting liquids were saturated in H<sub>2</sub>O, as indicated by the occurrence of 'bubbles'. Close to the solidus at 1.2 GPa, plagioclase disappears and an amphibole+garnet+rutile+epidote+quartz assemblage coexists with vapour and hydrous melt. On a water-free basis (EMP analyses recalculated to 100 wt%), the glasses have high silica contents (~70-76 wt%) and low amounts of total alkali (~1.1-1.5 wt%), placing them into the dacite and rhyolite fields on the TAS diagram.

More experimental and analytical work is underway, and we will present a comprehensive set of data on phase relations, major-element compositions and element partitioning at the Conference.

[1] Brown & Rushmer (2006.) *Cambridge University Press*.

[2] Petford & Atherton (1996) *J. Pet.* **37**, 1491–1521.

## How deep is deep? Plant biogeochemistry for detecting deep mineralisation

B.G. VAN DER HOEK\*, S.M. HILL AND ROBERT C. DART

Deep Exploration Technologies Cooperative Research Centre, School of Earth & Environmental Sciences, University of Adelaide, Australia, 5005 (\*correspondence: benjamin.vanderhoek@adelaide.edu.au)

Transported and potentially deep regolith extends across much of Australia, presenting a challenge for mineral explorers using traditional surface geochemical exploration techniques. Plant biogeochemistry is emerging as a valuable supplementary tool in exploration programs within these environments.

The application of plant biogeochemistry involves the chemical analysis of plant material (subaerial), where the elements are sourced from the regolith via the roots. Accumulation of elements in plant material is dependant on the element and its bioavailability. Element concentrations in plants are typically orders of magnitude lower than in geochemical material and exhibit different element associations.

Plant material has been analysed from the Tunkillia Au-prospect in the Gawler Craton, South Australia. Extensive exploration drilling has defined a bimodal distribution of Au – low concentrations at near-surface, a depletion zone, and primary mineralisation at depths exceeding 40 m. Gold concentrations in a variety of plant species have been up to 20 times background levels of plants in the region.

At Tunkillia, a large plant biogeochemistry and down-hole geochemistry dataset is integrated with isotope and soil biota analysis. This assists modelling of the vertical transportation of elements and limitations of plant root systems that access deep into the regolith profile.

## Carbonation of steel slag II

SIEGER R. VAN DER LAAN<sup>1\*</sup>, CHRISTIAN LIEBSKE<sup>1</sup>,  
HANS KOBESSEN<sup>2</sup>, ELEANOR J. BERRYMAN<sup>3</sup>,  
ANTHONY E. WILLIAMS-JONES<sup>3</sup>  
AND ARTACHES A. MIGDISOV<sup>3</sup>

<sup>1</sup>TATA Steel RD&T, Ceramics Research Centre, TATA Steel  
Europe OSF2, IJmuiden, The Netherlands  
(\*correspondence: sieger.van-der-laan@tatasteel.com)

<sup>3</sup>Department of Earth and Planetary Sciences, McGill  
University, Montreal, Quebec, Canada

One of the options that the steel industry has to mitigate some of its CO<sub>2</sub> emissions is mineral carbonation of steel slag, a by-product of the steel refining process. Our study investigates reactions taking place during dissolution and carbonation of steel slag, with the aim of determining optimal conditions for conversion. A H<sub>2</sub>O-CO<sub>2</sub> fluid is pumped through slag grains (2 – 3 mm) in a flow-through reactor at elevated pressure, and temperatures of 125 to 200°C, as described in a companion abstract [1]

The starting steel slag contains ~50 wt% CaO in larnite (Ca<sub>2</sub>SiO<sub>4</sub>), srebrodolskite (Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>) and free lime. In addition, there is an inert phase, Mg-wuestite ((Fe, Mg)O). After an experiment, entire cross sections of slag grains were analysed by SEM-EDS spectral imaging. Based on the information in the images, the volume proportions and distribution of reactant and product minerals were quantified using in-house developed PARC (PhAse Recognition & Characterization) software. This method reliably reproduces bulk compositions of solids as confirmed with XRF analysis [2]. The PARC results were used to calculate the mass balance between starting material, reacted slag and fluid and, in conjunction with the fluid chemistry, helped reconstruct the reaction path.

[1] Berryman *et al.* (2011) Goldschmidt Conference, this issue. [2] van Hoek & van der Laan (2011) Goldschmidt Conference, this issue

## δD of alkenones as proxy for paleo sea surface salinity

M.T.J. VAN DER MEER<sup>1\*</sup>, S. KASPER<sup>1</sup>, A. BENTHIE<sup>2</sup>,  
J. BIJMA<sup>2</sup>, R. ZAHN<sup>3</sup>, J.S. SINNINGHAM DAMSTÉ<sup>1</sup>  
AND S. SCHOUTEN<sup>1</sup>

<sup>1</sup>NIOZ, BGC, PO Box 59, 1790 AB Den Burg, The  
Netherlands

(\*correspondence: Marcel.van.der.Meer@nioz.nl)

<sup>2</sup>AWI, PO Box 12 01 61, D-27515 Bremerhaven, Germany

<sup>3</sup>ICREA and UAB, E-08193 Bellaterra (Cerdanyola), Spain

Culture studies of haptophyte algae showed that there is a strong correlation between the fractionation factor  $\alpha_{\text{alkenones-growth}}$  water and salinity [1], with less fractionation at higher salinities. Based on these results, paleosalinities of the Black Sea and the Eastern Mediterranean have been reconstructed using the δD of alkenones [2, 3].

However, there has been some debate about whether analyzing the C<sub>37</sub> alkenones together is appropriate for reconstructing paleosalinity since there is a relatively large difference in the δD of the C<sub>37:2</sub> and C<sub>37:3</sub> alkenones, respectively [4-6]. To examine this potential problem we analyzed the C<sub>37:2</sub> and C<sub>37:3</sub> alkenones of the original Schouten *et al.* [1] *E. huxleyi* samples separately and found an increasing difference in δD between the C<sub>37:2</sub> and C<sub>37:3</sub> alkenone with decreasing temperature and, therefore, decreasing relative abundance of the C<sub>37:2</sub> alkenone. These results suggested that for the purpose of reconstructing paleo SSS it might be better to analyze the C<sub>37</sub> alkenones together rather than the separate isomers.

To test this δD paleo sea surface salinity proxy in open marine settings it was applied to assess Agulhas current variability during the transition from Marine Isotope Stage (MIS) 6 to 5 and MIS 2 to 1. The reconstructed paleo SSS show a substantial shift to lower salinities during both deglaciations in agreement with reconstructions based on oxygen isotopes and Mg/Ca of planktonic foraminifera. These results indicate the potential of this proxy in open marine settings where salinity shifts are relatively small.

[1] Schouten *et al.* (2006) *Biogeosciences* **3**, 113–119. [2] van der Meer *et al.* (2007) *EPSL* **262**, 594–600. [3] van der Meer *et al.* (2008) *EPSL* **267**, 426–434. [4] D'Andrea *et al.* (2007) *Anal. Chem.* **79**, 3430–3435. Schwab & Sachs (2009) *Org. Geochem.* **40**, 111–118. [6] Wolhowe *et al.* (2009) *Biogeosciences* **6**, 1681–1694.



## The age and origin of the Limpopo sub-continental lithospheric mantle

Q.H.A. VAN DER MEER<sup>1</sup>, M. KLAVER<sup>1</sup>, L. REISBERG<sup>2</sup>,  
B. DAVIDHEISER<sup>1</sup> AND G.R. DAVIES<sup>1\*</sup>

<sup>1</sup>VU Amsterdam, De Boelelaan 1085, 1081HV Amsterdam,  
The Netherlands

(\*correspondence: gareth.davies@falw.vu.nl)

<sup>2</sup>CRPG, 15 rue Notre-Dame de Pauvres, B.P. 20, 54501  
Vandoeuvre-lès-Nancy, France

The Limpopo Mobile Belt (LMB) represents the suture zone between the Kaapvaal and Zimbabwe cratons, but the timing of the collision is still highly debated. Mantle tomography indicates a clear continuation of subcratonic mantle beneath LMB and the adjacent cratons. The origin of both the crust and lithospheric mantle of the LMB is also the subject of controversy and a Zimbabwean, Kaapvaal and allochthonous origin have all been proposed.

The Venetia kimberlite cluster is located within the central zone of the mobile belt and mantle xenoliths from the diamond mine provide an excellent opportunity to address the origin of LMB. We present an extensive petrology-geochemical dataset on a selection of Venetia peridotitic xenoliths, including 24 Re-Os isotope analyses.

Whole rock and mineral major element analyses of garnet-harzburgites and lherzolites indicate that the Venetian lithospheric mantle underwent up to 50% melt depletion, at least partially in the absence of garnet and by implication <70km. The depleted residue was subsequently re-enriched in silica and incompatible elements by subduction-related and asthenospheric melts. The mode of whole rock rhenium depletion ages is 2.6 Ga, which is significantly younger than both the Zimbabwe and Kaapvaal cratons.

Based on combined Os-Nd-Hf isotope systematics of the xenoliths we argue that the majority of the SCLM beneath LMB stabilised at ~2.6 Ga in a separate terrain, which is coeval with major crust forming recorded by zircon Hf and U-Pb model ages

## Patterns of cosmogenic age distributions for Late Quaternary moraines in Tibet

J. VAN DER WOERD<sup>1</sup>, E. KALI<sup>2</sup>, M.-L. CHEVALIER<sup>3</sup>,  
J. LIU-ZENG<sup>4</sup>, A.-S. MÉRIAUX<sup>5</sup>, P. TAPPONNIER<sup>6</sup>,  
G. HILLEY<sup>7</sup>, H. LI<sup>3</sup>, R.C. FINKEL<sup>8</sup> AND F.J. RYERSON<sup>9</sup>

<sup>1</sup>IPGS-EOST, UMR 7516, CNRS/Université de Strasbourg, 5,  
Rue Descartes 67000 Strasbourg, France  
(jeromev@unistra.fr)

<sup>2</sup>Université de Lyon 1, Lyon, France

<sup>3</sup>CAGS, Beijing, China

<sup>4</sup>ITPR-CAS, Beijing, China

<sup>5</sup>U. of Newcastle, UK

<sup>6</sup>EOS, Singapore

<sup>7</sup>Stanford University, Stanford, CA, USA

<sup>8</sup>U. of California, Berkeley, CA, USA

<sup>9</sup>LLNL, CA, USA

Uncertainties in moraine exposure ages have been recognized as a difficulty when trying to reconstruct past climate changes or comparing moraine exposure ages with known paleo-climate proxies such as  $\delta^{18}\text{O}$  variations. Many moraines have been dated although the number of samples on each moraine vary widely and may often be too small to assess the true geological scatter of the dated landform. Here we present cosmogenic age distributions for moraines of Tibet and present various explanations to explain the shape of the distributions for moraines dated with large numbers of samples. While it is true that the more samples are dated the more complexity may arise just by adding more information to the data set, it is also true that by targeting to few samples complex depositional or post-depositional processes may be completely overlooked. We focus on moraines deposited in comparable glacial setting from the last glacial maximum and before, and will show that similar geomorphologies are not necessarily correlated with age but most probably to similar glacier ice dynamics. Distributions of ages need to be explained by some independent assessment of depositional or post-depositional model, that can be further tested by the addition of observations, such as, for instance, the relative ages of inset moraines, or the amount of cumulated tectonic offset when available. True and independent moraine age assessments are preferable whenever possible, but it is noticeable that some patterns of ages can be recognized over large sets of data covering large areas of Tibet that argue for at least some synchronous glacial advances and moraine retreats, that with no surprise do correlate with global climate variations.

## Satellite-based estimates of fine particulate matter during the Moscow wildfires of 2010

AARON VAN DONKELAAR<sup>1\*</sup>, RANDALL V. MARTIN<sup>1,2</sup>,  
ROB LEVY<sup>3</sup>, ARLINDO DA SILVA<sup>4</sup>,  
MICHAL KRZYŻANOWSKI<sup>5</sup>, NATALIA CHUBAROVA<sup>6</sup>,  
EUGENIA SEMUTNIKOVA<sup>7</sup> AND AARON COHEN<sup>8</sup>

<sup>1</sup>Dept. of Physics and Atmospheric Science, Dalhousie University, Halifax, Nova Scotia, Canada  
(\*correspondence: aaron.van.donkelaar@dal.ca, randall.martin@dal.ca)

<sup>2</sup>Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts, USA

<sup>3</sup>NASA Goddard Space Flight Center, Greenbelt, Maryland, USA (robert.c.levy@nasa.gov)

<sup>4</sup>Global Modeling and Assimilation Office, NASA Goddard Space Flight Center, Greenbelt, Maryland, USA (arlindo.m.dasilva@nasa.gov)

<sup>5</sup>WHO European Centre for Environment and Health, Bonn, Germany (mkr@ecchbonn.euro.who.int)

<sup>6</sup>Geography Dept., Moscow State University, Moscow, Russia (chubarova@imp.kiae.ru)

<sup>7</sup>State Environmental Organization, Mosecomonitoring, Moscow, Russia (info@mosecom.ru)

<sup>8</sup>Health Effects Institute, Boston, MA, USA (acohen@healtheffects.org)

Acute exposure to high levels of fine particulate matter (PM<sub>2.5</sub>), such as emitted by the Moscow wildfires in summer 2010, are associated with serious adverse health effects, yet the location and scale of such events often make *in situ* monitoring difficult. Recent satellite retrieval developments have the potential to monitor surface pollution during these events. We estimate daily PM<sub>2.5</sub> concentrations using satellite observations during the Moscow fires. We increase the coverage of aerosol optical depth (AOD) retrieved from the Moderate Resolution Imaging Spectroradiometer (MODIS) by relaxing the operational cloud screening criteria which can mistake extreme aerosol events for cloud. This relaxed product shows excellent agreement with coincident operational retrievals ( $r^2=0.994$ ; slope = 1.010) and increases coverage during the fires by 21.3%. We relate MODIS AOD to PM<sub>2.5</sub> using a chemical transport model (GEOS-Chem) and find good agreement with PM<sub>2.5</sub> values estimated from *in situ* PM<sub>10</sub>. We find that the relationship between AOD and PM<sub>2.5</sub> is insensitive to uncertainties in biomass burning emissions. Satellite-derived and *in situ* values both indicate peak daily mean PM<sub>2.5</sub> of ~600 µg/m<sup>3</sup> on August 7, 2010 around Moscow, with a potential ~400 excess deaths during the fires.

## Growth rate of giant gypsum crystals

A.E.S. VAN DRIESSCHE<sup>1</sup>, J.M. GARCÍA-RUÍZ<sup>1</sup>,  
K. TSUKAMOTO<sup>2</sup>, L.D. PATIÑO<sup>1</sup> AND H. SATOH<sup>2</sup>

<sup>1</sup>LEC, IACT, CSIC - U.Granada, 18100 Granada, Spain

<sup>2</sup>Department of Mineralogy, Petrology and Economic Geology, Tohoku University, Sendai 980-8578, Japan

Mineralogical processes taking place close to equilibrium, or with very slow kinetics, are difficult to quantify precisely. The determination of ultra slow precipitation rates should reveal characteristic timing associated to processes that are important at geological scale. We designed a high-resolution phase-shift interferometer to measure growth rates of crystals at very low supersaturation values. To test this technique, we selected the giant crystals of gypsum of Naica ore mines



(Mexico), a challenging subject in mineral formation. They are formed by a self-feeding mechanism driven by solution-mediated anhydrite-gypsum phase transition, and are the result of an extremely slow crystallization process close to equilibrium [1]. To calculate the formation time of these crystals we measured the growth rates of the {010} face of gypsum growing from current waters from Naica at different temperatures. The slowest measurable growth rate was found at 55 °C, being  $1.4 \pm 0.2 \times 10^{-5}$  nm/s, the slowest value measured for a crystal growth process. At higher temperatures growth rates increase exponentially due to decreasing gypsum solubility and higher kinetic coefficient [2]. At 50 °C neither growth nor dissolution was observed indicating that growth of giant crystals of gypsum occurred at Naica between 58 °C and current temperature of Naica waters, confirming formation temperatures determined from fluid inclusion studies. Our results demonstrate the usefulness of applying advanced optical techniques in laboratory experiments to gain a better understanding of crystal growth processes occurring at a geological time scale.

[1] García-Ruiz *et al.* (2007) *Geology* **35**, 327–330. [2] Van Driessche *et al.* (2010) *Cryst. Growth Des.* **10**, 3909–3916.

## Effect of low-molecular-weight organic acids on thallium mobility in soil – A model rhizosphere solution approach

A. VANĚK\*, I. GALUŠKOVÁ AND M. KOMÁREK

Czech University of Life Sciences Prague, 16521 Prague, Czech Republic (\*correspondence: vaneka@af.czu.cz)

The kinetic batch leaching of Tl-bearing mineral soil in 500  $\mu\text{M}$  solutions of citric, oxalic and acetic acid was performed to simulate the release of Tl in the rhizosphere-like environment. The obtained data demonstrate that low-molecular-weight organic acids significantly contribute to soil alteration accompanied by the release of lithogenic Tl (if present). The highest mobilization rates for Tl were observed after 0.5 h of leaching (with maximal values obtained for oxalate) followed by a substantial decrease. Thallium extractability in the organic acid solutions was up to 2.8-fold higher compared to water. Based on the experimental and speciation modeling data, Tl release is mainly pH-driven and can be attributed to acid ion exchange and/or acid leaching, as the formation of Tl-LMWOA complexes is negligible. The main Tl solubility-controlling phases predicted include illite and the identified Mn (III, IV) oxide due to their ability to efficiently sorb  $\text{Tl}^+$  on the mineral surfaces from which Tl can be potentially mobilized. The role of primary silicates (i.e. orthoclase and muscovite) in the total process of Tl mobilization seems to be of lesser importance because the supposed alteration/dissolution of these phases during LWMOA leaching was limited.

## A geochemical reference (baseline) for the natural geogenic variation in Pb isotope ratios in sedimentary soils

P.F.M. VAN GAANS<sup>1\*</sup>, N. WALRAVEN<sup>2</sup>,  
G. VAN DER VEER<sup>3</sup>, S.P. VRIEND<sup>3</sup>, B.J.H. VAN OS<sup>4</sup>  
AND G.TH. KLAVER<sup>1</sup>

<sup>1</sup>Deltares, Utrecht, the Netherlands

(\*correspondence: pauline.vangaans@deltares.nl,  
gerard.klaver@deltares.nl)

<sup>2</sup>GeoConnect, Castricum, the Netherlands  
(n.walraven@geoconnect.nl)

<sup>3</sup>Universiteit Utrecht, Utrecht, the Netherlands

<sup>4</sup>Rijksdienst voor het Cultureel Erfgoed, Amersfoort, the Netherlands (b.van.os@cultureelerfgoed.nl)

Given the wide historic to recent use of lead, enhanced Pb concentrations in soils may pose serious problems. The Pb isotopic composition (Pb-ic) can be used to distinguish natural from anthropogenic Pb and to appoint anthropogenic Pb sources. Often, a local reference is used to establish the natural geogenic Pb-ic, with which to compare the observed ratios in contaminated soils. However, Pb-ic is known to depend on soil type and show high spatial variability. Here we go for a regional approach, using as reference a set of 342 samples of sand and clay subsoils in the Netherlands. The combined geogenic Pb isotope ratios ( $^{206}\text{Pb}/^{207}\text{Pb}$ ,  $^{208}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{208}\text{Pb}$ ) are empirically modelled, through regression with geochemical proxies as predictors.

Total concentrations of Al and Zr, as measured by XRF, were found to be suitable, mutually independent predictors of the geogenic Pb isotope variability. To eliminate the effects of outliers and high variability, we used a robust trimmed least squares regression, based on a core dataset containing the 70% of the data having the smallest absolute regression residuals. For this core dataset, the percentage of variance explained is about 70%. The model grasps the main trends displayed in the measured data: a) an apparent age range within both sands and clays, tending towards higher  $^{208}\text{Pb}$  with increasing apparent age, and b) a clear shift towards lower  $^{207}\text{Pb}$  from sands to clays. The Zr content is hypothesized to represent the proportion of U-Th containing 'parent' minerals to Pb containing 'daughter' minerals; the Al content represents the proportion of secondary minerals.

The regional reference allows prediction of the baseline Pb-ic where no local reference is available, e.g. in topsoils that differ in lithology from their subsoil or where subsoil Pb contamination is suspected. Otherwise the regional reference is as suitable as a local subsoil reference.

## Characterization of Fe(0) electro-coagulation reaction products using synchrotron-based techniques

C.M. VAN GENUCHTEN<sup>1\*</sup>, J. PEÑA<sup>2</sup>, S.E.A. ADDY<sup>1</sup>,  
G. SPOSITO<sup>1,2</sup> AND A.J. GADGIL<sup>1,2</sup>

<sup>1</sup>University of California, Berkeley, Berkeley, CA

(\*correspondence: cmvangenuchten@berkeley.edu)

<sup>2</sup>Lawrence Berkeley National Laboratory, Berkeley, CA

Electrocoagulation (EC) using Fe (0) electrodes is a promising technology capable of cheaply and efficiently removing arsenic from drinking water. In EC, an electric current is applied to Fe (0) electrodes inserted into pumped groundwater contaminated with arsenic. Electrolysis of the Fe (0) anode leads to the *in situ* formation of iron (oxyhydr)oxides, which form surface complexes with arsenic. Of concern in such systems are common groundwater constituents ( $\text{PO}_4^{3-}$ ,  $\text{SiO}_2$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ), which can influence the structure of the generated precipitates in both subtle and complex ways. To assess the influence of these ions, synchrotron-based techniques were used to characterize EC precipitates generated in chemically varying electrolytes. Electrolytes were chosen to clarify the individual effect of strongly-adsorbed ions (0.5mM  $\text{Na}_2\text{HPO}_4$ , 0.75mM  $\text{SiO}_2$ ) and weakly-adsorbed ions (1mM  $\text{CaCl}_2$ , 1mM  $\text{MgCl}_2$ , 2mM  $\text{NaCl}$ ) on the removal of  $1\mu\text{M}$  As(V) at pH 7.5. The As K-edge XANES and EXAFS spectra of precipitates generated in the  $\text{Na}_2\text{HPO}_4$  electrolyte differed in both phase and line shape from those of precipitates generated in the  $\text{NaCl}$  and  $\text{CaCl}_2$  electrolytes. These differences likely reflect a change in the adsorbent structure due to sorption of the surface-poisoning  $\text{PO}_4^{3-}$  oxyanion. The Fe K-edge EXAFS spectra and PDFs of similar samples will be presented to provide complementary views of the adsorbent structure (phase, crystallite size, and degree of  $\text{FeO}_6$  octahedral polymerization) in instances where variations in the As K-edge spectra were observed. These results provide an important molecular-scale understanding of arsenic removal during EC.

## On the way to medical diagnosis based on the isotopic analysis of metabolically relevant transition metals

L. VAN HEGHE<sup>1\*</sup>, E. ENGSTRÖM<sup>2</sup>, I. RODUSHKIN<sup>2</sup>,  
A. VERSTRAETE<sup>3</sup>, H. VAN VLIERBERGHE<sup>4</sup>, C. CLOQUET<sup>5</sup>  
AND F. VANHAECKE<sup>1</sup>

<sup>1</sup>Department of Analytical Chemistry, Ghent University,  
Krijkslaan 281-S12, Ghent, Belgium

(\*correspondence: lana.vanheghe@ugent.be)

<sup>2</sup>ALS Scandinavia, Aurorum 10, 977 75 Luleå, Sweden

<sup>3</sup>Department of Clinical Chemistry, Ghent University, De  
Pintelaan 185, Ghent, Belgium

<sup>4</sup>Department of Gastroenterology and Hepatology, Ghent  
University, De Pintelaan 185, Ghent, Belgium

<sup>5</sup>CRPG/CNRS, BP 20, 54501, Vandoeuvre-Nancy, France

Although modern medicine already has many sophisticated tools for the diagnosis of a large variety of diseases, there are still diseases for which diagnosis is difficult or can only be accomplished at a later stage of progression. New diagnostic tools are therefore highly needed for drawing unequivocal conclusions or start medicating people at an earlier stage.

A promising approach for diagnosis is the isotopic analysis of elements the metabolism of which is affected by the disease (e.g. Fe)[1]. Next to Fe, also Zn and Cu are important transition metals because of their great catalytic, structural and regulating importance in the human body [2].

These non-radiogenic elements show natural variations in isotopic composition due to isotope fractionation. As a result, we aim at developing a minimally invasive method, based on isotopic analysis using MC-ICPMS. In the method developed for this purpose Cu, Fe and Zn were isolated from blood within the same chromatographic separation with quantitative recovery, thus avoiding the effect of on-column isotope fractionation. External precisions for this method are 0.02; 0.05 and 0.03 ‰ (2s) for  $\delta^{56}\text{Fe}$ ,  $\delta^{66}\text{Zn}$  and  $\delta^{65}\text{Cu}$ , respectively. A first sample set comes from supposedly healthy human volunteers (reference population, including vegetarians and omnivorous) to investigate the dependence of isotope composition and nutrition. Whole blood from patient populations will be investigated at a later phase.

[1] Krayenbuehl (2005) *Blood* **105**, 3812–3816. [2] Walravens (1979) *Western J of Medicine* **130**, 133–142.

## Towards a quantitative record of Archaean ocean water chemistry: An element partitioning approach

VINCENT J. VAN HINSBERG<sup>1\*</sup>, KRISTOFFER SZILAS<sup>2</sup>  
AND BERNARD J. WOOD<sup>1</sup>

<sup>1</sup>Department of Earth Sciences, University of Oxford, United Kingdom (\*correspondence: V.J.vanHinsberg@gmx.net)

<sup>2</sup>Geological Survey of Denmark and Greenland - GEUS, Copenhagen, Denmark

The composition of the Archaean ocean is of interest for two reasons in particular: 1. Ocean water is the reaction product of processes operating on the surface of the early Earth and in its interior, and its composition thus allows for insights into, and constraints on these processes, including the nature of Archaean plate tectonics; and 2. Ocean water is the likely medium in which life originated and developed, and knowledge of its composition, and changes therein over time provides insights into the inorganic forcing on life's evolution.

Qualitative information on the composition of the early Earth ocean has been obtained from the mineralogy and compositions of marine sediments preserved in the geological rock record. Banded Iron Formations, in particular, appear a viable source of information on changes in (trace) element abundance [1]. At present, it is not possible to translate this qualitative record into actual concentrations, and information is furthermore restricted to a small suite of elements, which severely limits the information that can be gained.

In this contribution, we present an approach that uses the lattice-strain theory systematics in element partitioning to reconstruct *quantitative* information on water chemistry from the composition of minerals. Although this approach can be applied to marine sediments, we use it here on samples of altered ridge basalts (greenstones), which are an indirect source of information on ocean water chemistry, because the interaction between ocean water and fresh oceanic crust at the ridges has a dominant control on the composition of the ocean. Combining experimentally determined mineral - fluid partition coefficients for chlorite and plagioclase at appropriate conditions, with the compositions of these minerals in well-preserved Archaean greenstones, we are able to track the evolving composition of the early Earth ocean.

[1] Konhauser, Pecoits, Lalonde, Papineau, Nisbet, Barley, Arndt, Zahnle & Kamber (2009) *Nature* **458**, 750-754.

## Innovative low kV X-ray microanalysis of submicron particles using PARC algorithms

CORRIE J.G. VAN HOEK\*  
AND SIEGER R. VAN DER LAAN

TATA Steel RD&T, Ceramics Research Centre, IJmuiden, The Netherlands

(\*correspondence: corrie.van-hoek@tatasteel.com)

One of the challenges in microanalysis is to get accurate qualitative and quantitative analysis on the smallest phases present in a sample. Using PARC (**Ph**ase **R**ecognition and **C**haracterization) algorithms as developed at CRC, we can arrive at the theoretical resolution using a FEG-SEM equipped with X-ray microanalysis equipment as will be shown in this paper.

The analytical spatial resolution for microanalysis is dictated by the SEM acceleration voltage, and the average atomic number of the phases present in the specimen. The challenge is finding the proper spot in a sample where the best analysis (without contaminated signal from the surrounding), can be obtained of the smallest phase for a given analytical condition.

The PARC approach simply circumvents manual selection of spots by including ALL pixels of an image field in the spectral image (SI) dataset. PARC software sorts all pixels of the SI dataset according to the phases they represent. The pixel populations can then be automatically cleaned from contaminant signals, leaving pure spectra for ZAF corrected quantification. The quality of analysis subsequently can be assessed from the resulting phase stoichiometry. In addition, phase area proportions and phase chemistry can be combined to reproduce the bulk composition of the sample material. We will show that using PARC in combination with FEG-SEM-EDS good stoichiometric analysis can be obtained on samples with crystals of less than 500 nm, even for trace phases.

Several PARC applications will be presented during this conference.

## H<sub>2</sub>O and CO<sub>2</sub> devolatilization in subduction zones: Implications for the global water and carbon cycles

PETER VAN KEKEN<sup>1\*</sup>, BRAD HACKER<sup>2</sup>,  
ELLEN SYRACUSE<sup>3</sup> AND GEOFF ABERS<sup>4</sup>

<sup>1</sup>University of Michigan, Ann Arbor, MI, USA

(\*correspondence: keken@umich.edu)

<sup>2</sup>University of California, Santa Barbara, CA, USA

<sup>3</sup>University of Wisconsin, Madison, WI, USA

<sup>4</sup>Columbia University, Palisades, NY, USA

Subduction of sediments and altered oceanic crust functions as a major water and carbon sink. Upon subduction the water and carbon may be released by progressive metamorphic reactions. Quantification of the volatile release from subducting slabs is important to determine the provenance of volatiles that is released by the volcanic arc and to constrain the flux of water and carbon to the deeper mantle. In recent work we used a global set of high resolution thermal models of subduction zones to predict the flux of H<sub>2</sub>O from the subducting slab [1] which provides a new estimate of the dehydration efficiency of the global subducting system. It is found that mineralogically bound water can pass efficiently through old and fast subduction zones (such as in the western Pacific) but that warm subduction zones (such as Cascadia) see nearly complete dehydration of the subducting slab. The top of the slab is sufficiently hot in all subduction zones that the upper crust dehydrates significantly. The degree and depth of dehydration is highly diverse and strongly depends on (p, T) and bulk rock composition. On average about one third of subducted H<sub>2</sub>O reaches 240 km depth, carried principally and roughly equally in the gabbro and peridotite sections. The present-day global flux of H<sub>2</sub>O to the deep mantle translates to an addition of about one ocean mass over the age of the Earth. We extend the slab devolatilization work to carbon by providing an update to Gorman *et al.* [2], who quantified the effects of free fluids on CO<sub>2</sub> release. We use the new high resolution and global set of models to provide higher resolution predictions for the provenance of CO<sub>2</sub> release to the mantle wedge.

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## Geology, age and origin of the oldest terrestrial rocks and minerals

MARTIN J. VAN KRANENDONK

Geological Survey of Western Australia, 100 Plain St., East  
Perth, WA 6004 Australia

(martin.vankranendonk@dmp.wa.gov.au)

School of Earth and Environment, The University of Western  
Australia, Crawley WA 6009 Australia

Earth's mineral and rock record extends back to an astonishing 4.4 Ga. The earliest history (4.4–4.03 Ga, 'The Hadean') is represented by zircon crystals and isotopic evidence from younger rocks of buried and/or vanished sources of this age [1, 2]. In the Archean, increasing amounts of crust are preserved from 4.03–3.5 Ga, but only as high-grade gneiss terrains with little primary sedimentary or volcanic material. Strangely, these rocks contain little or no evidence for meteorite bombardment at this time. Nevertheless, these remnants contain important clues to crust-forming processes and tantalising hints of the earliest biosphere. After 3.5 Ga, better-preserved crustal remnants yield more robust clues to early Earth processes and biosphere components.

Debate continues on the nature of early crust formation processes, specifically whether plate tectonics (of any kind) operated in early (or even middle) Earth history. Hadean crust may have been thick and basaltic, crystallised from a magma ocean and locally internally differentiated to form tonalite [3]. The early Archean was characterised by two types of crustal growth mechanisms, as on modern Earth [4]: 1) plateau formation over zones of upwelling mantle, forming thick welts of autochthonous crust affected by internal differentiation (e.g. East Pilbara Terrane, Pilbara Craton); 2) subduction-accretion in zones with voluminous arc-like magmatism and crustal imbrication (e.g. Western Greenland). By 3.1 Ga, modern-style (i.e. steep) subduction had commenced locally [5], and a significant proportion of the continental crust may have formed by 3.0 Ga, starting the supercontinent cycle.

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## Freeze-fry cycles in the Paleoproterozoic Turee Creek Group, Western Australia

MARTIN J. VAN KRANENDONK<sup>1\*</sup>, AIVO LEPLAND<sup>2</sup>  
AND KOSEI E. YAMAGUCHI<sup>3,4</sup>

<sup>1</sup>Geological Survey of Western Australia, 100 Plain St., East Perth WA, 6004 Australia (\*correspondence: martin.vankranendonk@dmp.wa.gov.au)

<sup>2</sup>Geological Survey of Norway, 7491 Trondheim, Norway

<sup>3</sup>Dept. Chemistry, Toho University, 2-2-1 Miyama, Funabashi, Chiba 274-8510, Japan

<sup>4</sup>NASA Astrobiology Institute

Previous research has suggested a Paleoproterozoic Snowball Earth consisted of up to three glaciations from 2.42–2.22 Ga, coincident with the timing of the inferred rise in atmospheric oxygen [1, 2]. Supporting geological and isotopic data from North America, Fennoscandia, and South Africa are supported by the occurrence of glacial rocks in the Turee Creek Group (TCG), Australia, and their geochemical characteristics [3, 4].

New  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  isotope data on bedded and stromatolitic dolomites, combined with previously available results [5] - recast in the light of corrected stratigraphic assignment - suggest that three freeze-fry cycles are recorded in the TCG. The first cycle is preserved in the lowest Kungarra Formation, reflected by a decrease and subsequent increase in  $\delta^{13}\text{C}$  upsection, from 0–2‰→–6‰→0‰, associated with a decrease in  $\delta^{18}\text{O}$  from 0→–4‰. Part of a second cycle is recorded in rocks of the glaciomarine Meteorite Bore Member and immediately overlying rocks of the upper Kungarra Formation ( $\delta^{13}\text{C}$  from –2.5 to –6‰→–1‰, and  $\delta^{18}\text{O}$  from 0 to –3→–12‰), whereas a third cycle is recorded in rocks of the overlying Kazput Formation ( $\delta^{13}\text{C}$  from –3→1‰, and  $\delta^{18}\text{O}$  from 0→–16→5‰).

The low-grade TCG carbonates are considered to have escaped significant post-depositional resetting.  $\delta^{18}\text{O}$  variability and trends are interpreted to reflect changes in the temperature of basinal diagenetic fluids across cooling and warming periods, while mantle-like  $\delta^{13}\text{C}$  values support periodic global collapse of the biosphere.

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[4] Williford *et al.* (2011) *Geochim. Cosmochim. Acta* (in press). [5] Lindsay & Brasier (2002) *Precamb. Res.* **114**, 1–34.

## Ion diffusion in argillaceous materials

L.R. VAN LOON

Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

Molecular diffusion is the dominant transport process of radionuclides which needs to be considered when evaluating the safety of radioactive waste repositories in argillaceous host rocks. The diffusive behaviour of radionuclides depends both on the properties of the porous medium and on the diffusing species.

Clay minerals (notably montmorillonite and illite) have a permanent negative surface charge which attracts cations and repulses anions leading to the formation of a diffuse double layer (DDL). The net positive charge of the DDL compensates the negative charge of the clay surface [1]. In the case of the diffusion of neutral species, no interaction between the electrostatic field and the species occurs and diffusion can be described by Fick's law [2]. The concentration gradient in the pore water is the driving force for diffusion of neutral species. In this case, only geometrical factors such as constrictivity and tortuosity are important. In the case of charged species, the situation is different. Because cations are attracted by the negative surface charge, the concentration gradients in the DDL and in the interlayers of the clay grains are larger than in the free pore water and consequently the diffusive flux is also larger. The electrostatic field thus enhances cation diffusion. Unlike cations, anions are repelled from the surface leading to anion exclusion from the interlayers and the DDL. Anion exclusion leads to a lower accessible porosity for the anions, resulting in lower diffusive fluxes. All factors directly influencing the DDL thus also affect the diffusive behaviour of cations and anions.

This study gives an overview of the state-of-the art of knowledge on diffusion processes in dense argillaceous materials. Focus will be on tracer diffusion of ion exchanging cations, anions and neutral species in a constant electrolyte background and in different argillaceous materials [3]. The diffusive behaviour of cations which sorb via surface complexation is expected to be different and a brief outlook on current activities will be discussed.

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## A predictive model for cation diffusion in periclase

JAMES A. VAN ORMAN AND KATHERINE L. CRISPIN

<sup>1</sup>Department of Geological Sciences, Case Western Reserve University (james.vanorman@case.edu, klc24@case.edu)

Understanding rates of diffusion in periclase is essential for understanding chemical transport in Earth's lower mantle. Cation diffusion through periclase is faster than through any other major crystalline phase in the lower mantle, and thus provides an upper limit on the bulk diffusive transport that is possible in the absence of fluids.

The variation in diffusivity among different cations is controlled by their ionic properties, including size, charge, polarizability and electron configurations. No clear relationships among ionic properties and diffusivity have previously been recognized in periclase, despite the existence of a large diffusion database. The trends are obscured by variations in diffusivity that are likely due to the variable chemical purity of the MgO crystals used in the experiments. Here we take advantage of constraints provided by diffusion and ionic conductivity studies on doped MgO crystals to compare the cation diffusion data at a common vacancy concentration. Clear trends emerge between diffusivity and ionic size, charge, polarizability and crystal field stabilization energy. These trends are parameterized to provide a predictive expression for cation diffusion rates in periclase over a broad range of conditions relevant to Earth's lower mantle.

## <sup>40</sup>Ar-<sup>39</sup>Ar geochronology and PT estimations on garnet-hornblende-muscovite-plagioclase schists from the Kheis Belt, South Africa

V. VAN SCHIJNDEL\* AND D.H. CORNELL

Department of Earth Sciences, The University of Gothenburg, SE-40530, Sweden

(\*correspondence: valby.van.schijndel@gvc.gu.se)

The Kheis Belt on the western margin of the Kaapvaal Craton, South Africa, is often referred to as a thin-skinned fold and thrust belt. However, Humphreys *et al.* [1] indicated that the schists of the Palaeoproterozoic Groblershoop Formation within the Kheis Belt reached equilibrium conditions between 600-700°C and 8-11 kBar. The schists of this study contain a main mineral assemblage of grt+hbl+plag+musc+epi+qtz with accessory chlorite, biotite, ilmenite and rutile. The peak metamorphic mineral assemblage is represented by grt+hbl+musc and the plagioclase has an Ab content of 0.83. The garnet and hornblende have inclusions of quartz, epidote and ilmenite, indicating a greenschist facies mineralogy assemblage. This is oldest assemblage preserved in the sample. Preliminary modeled results, obtained by equilibrium phase diagrams based on bulk composition were calculated for the NaCaKFMASH system with the program Theriak/Domino [2, 3]. These diagrams indicate that the garnet and hornblende growth started at 520°C and 9.5-10 kBar. An increase in Mg in the rims of the garnets points to a prograde reaction. PT conditions went up during garnet growth and reached a possible maximum at 660°C and 12.5 kBar. At higher temperatures kyanite becomes stable and this is not present in the samples. It is unlikely that the temperature reached above 660°C. Retrograde chlorite postdates all other minerals. <sup>40</sup>Ar-<sup>39</sup>Ar dating on both muscovite and hornblende gave 1147±4 Ma and 1141±3 Ma. These ages are related to the Namaqua Orogeny and the agreement between the cooling ages of muscovite and hornblende arguments for a rapid uplift. Therefore are these ages thought to represent cooling ages that can be directly correlated with the peak metamorphic conditions.

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## Monitoring nutrients cycles at catchment scale

T.P. VAN TOL<sup>1</sup> AND B. VAN DER GRIFT<sup>2\*</sup>

<sup>1</sup>Alterra, Wageningen University and Research Centre, P.O. Box 47, NL-6700 AA Wageningen, The Netherlands (dorothee.vantol-leenders@wur.nl)

<sup>2</sup>Deltares, P.O. Box 85467, NL-3508 TA Utrecht, The Netherlands  
(\*correspondence: bas.vandergrift@deltares.nl)

In The Netherlands, the high concentration of nitrogen and phosphorus has an adverse affect on the quality of our surface water. The abundant growth of algae, water plants and reed is a recurring problem in Summer. Furthermore, the discharge of nutrient-rich water into the sea is a real threat to the marine ecosystem. Unfortunately, the origin and fate of all these nutrients often remains unclear.

The total nutrient concentration in surface water is determined by a range of sources, transport routes and chemical or biological processes. Nutrient cycles at a watershed scale are therefore very complex. To come up with solutions to improve the water quality it is very important to gain insight into the origin of the sources, their transportation time and what happens en route. In four typical watersheds in the Nederland's we studied the biogeochemical cycling of nitrogen en phosphorus at regional scale. The main goal of the project is to understand the relationship between long term changes in nutrient surplus and the quality of the surface water. The four watersheds are: a sandy with high loads of nutrients due to intensive cattle breeding, a more natural sandy area, a clay polder and a polder with peat soil. Each area has its own characteristics regarding the sources and transport route for nutrients. For this study we analysed soil, groundwater, sediment and surface water quality on several locations. The surface water quality and quantities were monitored continuously in the period 2004-2010. Combined with data collected on nutrient loads this resulted in an extensive dataset to study biogeochemical cycling of nitrogen and phosphorus in the soil-groundwater-surface water system at regional scale. A combined soil-groundwater-surface water model is used to predict the effectiveness of different source or transport route oriented measures to improve the quality of the surface water.

One of the major findings is the importance of sediments in the binding and release of phosphorus when transported from groundwater to surface water and the role of sulfate in this process.

## Uranyl coordination chemistry on magnesite and brucite surfaces: Polarisation dependent EXAFS

A. VAN VEELLEN<sup>1\*</sup>, G.T.W. LAW<sup>1</sup>, A.J. SMITH<sup>1</sup>, J.R. BARGAR<sup>2</sup>, J. ROGERS<sup>2</sup> AND R.A. WOGELIUS<sup>1</sup>

<sup>1</sup>University of Manchester, School of Earth, Atmospheric and Environmental Sciences, Oxford Road, Manchester, M13 9PL, United Kingdom (\*correspondence: arjen.vanveelen@postgrad.manchester.ac.uk)

<sup>2</sup>Stanford Synchrotron Radiation Laboratory, PO Box 4349, Stanford, CA 94309, USA

Previous studies have examined uranium uptake by calcium carbonate minerals (calcite and aragonite) under conditions pertinent to both natural and anthropogenically perturbed systems. However, research on uranyl uptake by magnesium-rich minerals such as magnesite [MgCO<sub>3</sub>], brucite [Mg(OH)<sub>2</sub>], nesquehonite [MgCO<sub>3</sub>·3H<sub>2</sub>O] and hydromagnesite [Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O] has not, to the best of our knowledge, been previously conducted. Such experiments will improve our understanding of the mobility of uranium and other actinides in natural lithologies such as dolomitic limestones or mafic igneous emplacements, as well as provide key information applicable to nuclear waste repository strategies involving Mg-rich phases. Thus, experiments with mineral powders were used to determine the partition coefficients and coordination of UO<sub>2</sub><sup>2+</sup> during adsorption and coprecipitation with magnesite, brucite nesquehonite and hydromagnesite. A second set of experiments used single crystal magnesite (10.4) cleavage surfaces and MgO(111) surfaces engineered and hydroxylated to be equivalent to the Mg(OH)<sub>2</sub>(00.1). Here EXAFS measurements were made at  $\chi = 0^\circ$  and  $\chi = 90^\circ$  in order to use the polarisation of the incident beam to unequivocally determine adsorbate and coprecipitate structures. The selected minerals were reacted with uranyl chloride at three different concentrations (500, 50 and 5 ppm) above and below solubility boundaries of schoepite (UO<sub>2</sub>(OH)<sub>2</sub>·H<sub>2</sub>O) at pH 8 and PCO<sub>2</sub> = 10<sup>-3.5</sup> atm. K<sub>d</sub> values for Mg carbonate phases were comparable to or exceeded those published for calcium carbonates. EXAFS results showed clear polarisation dependence of surface uranyl. The spectra demonstrated consistently that the uranyl molecule is preferentially oriented with the axial oxygens perpendicular to the mineral surface. This implies the creation of local rutherfordine-like regions which may polymerise at high uranyl activities into a thin film.

## Nanoscale structural variation in pyrobitumen of the 2.0 Ga Zaonega Formation, Karelia, Russia

M.A. VAN ZUILEN<sup>1\*</sup>, D. FLIEGEL<sup>2</sup>, R. WIRTH<sup>3</sup>,  
A. LEPLAND<sup>4</sup>, Y. QU<sup>5</sup>, A. SCHREIBER<sup>3</sup>,  
A.E. ROMASHKIN<sup>6</sup> AND P. PHILIPPOT<sup>1</sup>

<sup>1</sup>Institut de Physique du Globe, 75005 Paris, France  
(\*correspondence: vanzuielen@ipgp.fr)

<sup>2</sup>National Institute of Nutrition and Seafood Research,  
<sup>5</sup>004 Bergen, Norway

<sup>3</sup>GeoForschungsZentrum Potsdam, Telegrafenberg  
<sup>1</sup>4473 Potsdam, Germany

<sup>4</sup>Geological Survey of Norway, 7491 Trondheim, Norway

<sup>5</sup>Centre for Geobiology, University of Bergen, 5007,  
Bergen, Norway

<sup>6</sup>Institute of Geology, Karelian Science Centre  
<sup>1</sup>85610 Petrozavodsk, Russia

Alteration and especially remobilization of organic material and carbonic fluids in Archean rocks has led to many controversies regarding early life. It is therefore important to establish the detailed changes that occur when carbonaceous materials are affected by metamorphism. A case study is presented here of carbonaceous matter that occurs in sediments of the 2.0 Ga old Zaonega Formation, Karelia, Russia. Petroleum generation and contact-metamorphism caused by intersecting magmatic bodies, regional greenschist-facies metamorphism, and circulation of silicate-saturated fluids, led to complex mixtures of silicious and bituminous materials. Raman spectroscopy and transmission electron microscopy on pyrobitumen-rich samples revealed two significantly distinct carbon allotropes; 1) graphitic films representing highly ordered carbon, and 2) variously oriented nm-scale crystallites representing strongly disordered carbon that comprises the bulk pyrobitumen matrix. This clear bimodal distribution in structural order cannot be related to a simple temperature- or pressure-induced graphitization process, and requires additional effects that caused annealing of sp<sup>2</sup>-bound carbon crystallites. Potential effects include variations in graphitizing precursor materials, local stress and strain caused by mineral authigenesis or gas bubble growth, and reorganization of graphitic clusters by hydrothermal fluid circulation. The details of these effects and their implications for the general alteration and remobilization process of organic structures in the Archean rock record will be discussed.

## Evaluation of chromium reductive immobilization and oxidative re-mobilization in flow-through aquifer sediment columns

CHARULEKA VARADHARAJAN\*, PETER S. NICO,  
LI YANG, MATTHEW A. MARCUS, RUYANG HAN,  
MARKUS BILL, JOERN LARSEN, APRIL VAN HISE,  
SERGI MOLINS, CARL STEEFEL, MARK CONRAD,  
EOIN L. BRODIE AND HARRY R. BELLER

Earth Sciences Division, Lawrence Berkeley National  
Laboratory, 1 Cyclotron Road, Berkeley, CA  
(\*correspondence: cvaradharajan@lbl.gov)

Remediation of chromium contamination typically involves reducing the toxic and soluble hexavalent form, Cr(VI), to the relatively harmless and mostly immobile trivalent state, Cr(III). The objective of the overall project is to identify the biogeochemical mechanisms that control *in situ* chromium reduction and oxidation.

In the initial phase of the experiment, reduction under anaerobic conditions was observed for over 12 months by subjecting flow-through columns containing homogenized sediments from the Hanford 100H site to different dominant electron acceptors, i.e. NO<sub>3</sub><sup>-</sup>, Fe(III), and SO<sub>4</sub><sup>2-</sup>, in the presence of Cr(VI) and lactate. Cr(VI) was depleted in the effluent solutions of the nitrate-treated columns, all of which exhibited denitrifying conditions, as well as in some of the sulfate-amended columns where fermentative conditions were dominant. However, only a small amount of Cr(VI) was removed under other electron-accepting conditions. Spectroscopic analysis of the column sediments showed that most of the chromium was precipitated as mixed phase Cr-Fe hydroxides.

In the second phase of the study, the denitrifying and fermentative columns were subjected to oxidizing conditions that are expected to be prevalent once the bioremediation is completed (with nitrate and O<sub>2</sub> present). Preliminary results show that the chromium precipitated in the denitrifying columns was more readily mobilized under the oxidizing conditions, suggesting that fermentative conditions promote more sustained Cr(VI) remediation.

## LA-ICPMS U-Pb ages of Paleo- and Mesoproterozoic granites in Bolivia

G.L. VARGAS-MATOS<sup>1</sup>, M.C. GERALDES<sup>1</sup>, R. MATOS<sup>2</sup>  
AND W. TEIXEIRA<sup>3</sup>

<sup>1</sup>UERJ, Faculdade de Geologia, Rua Sao Francisco Xavier  
524, Rio de Janeiro (RJ), 22241-000, Brazil

<sup>2</sup>UMCLA, Universidad Mayor San Andreas, La Paz, Bolivia

<sup>3</sup>USP, Universidade de Sao Paulo, Sao Paulo (SP) Brazil

Proterozoic granites of Bolivia new U-Pb zircon ages indicate an important change in chronostratigraphy of Bolivian Precambrian. The age of the Correroca Granite ( $1894 \pm 13$  Ma and  $1925 \pm 32$  Ma) suggest an important magmatic event which spatial distribution is bounded on the north by the San Diabolo shear zone, defining the oldest terrain with distinct geological story from other areas of the Bolivian pre-Cambrian. The San Pablo granite (ascribed as the Lomas Manechi magmatic event) yielded  $1617 \pm 14$  Ma, in agreement with the ages of the literature (1.67-1.62 Ga). The results of isotopic granitoids of Cachuela, Motacusal and Talcoso (San Ignacio orogeny), present U/Pb age between 1307 and 1333 Ma, suggesting an important period of generation of granitoids in the Bolivian pre-Cambrian.

The Sunsas magmatism presents predominantly crustal sources and presents temporal variation between 1071 Ma and 1047 Ma (Granites Naranjito, Taperas, Primavera and El Carmen).

The data here reported suggest a geological evolution for the Bolivian pre-Cambrian composed of four episodes of magmatism represented by the Correroca event, followed by San Pablo event. The younger San Ignacio event is represented by magmatic arc with important participation of older continental crust. Finally, the magmatism Sunsas is comprised of anarogenic (type A) and crustal rocks (S-type) representing an important collisional period in the SW Amazonian craton.

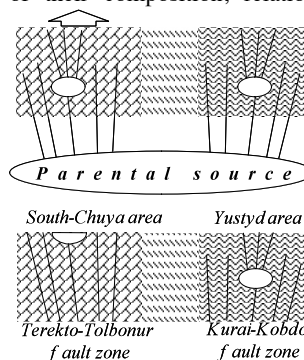
## Petrology of lamprophyres as a result of the study of minerals

ELENA VASYUKOVA

IGM SB RAS, av. ak. Koptuyuga, 3, Novosibirsk, Russia  
(lenav@inbox.ru)

Lamprophyres of the Chuya complex are one of the biggest displays of the alkali high potassium early meozoic magmatism of the Gorny Altay. Within this region dikes distributed unevenly, according to the fault zones and fractures. We have studied two largest and most saturated dikes local areas – South Chuya and Yustyd. The choice of these two areas is linked to the fact, that they are confined to two distinct fault systems, located in the different host rocks and associated with the different ore districts. In addition, rocks of different areas vary in the degree of carbonatization, phenocrysts and structural-textural features.

Petro- and geochemical characteristics of rocks from different local habitats were so similar, that allowed to assert a single maternal source. Phenocrysts of pyroxen, phogopite, containing chromium and possibly olivine suggest, that the parental melt was high-Mg and its geochemical characteristics indicate the involvement of enriched mantle. Trends in harker variation diagrams, morphology (type 'dike-in-dike') – all this does not contradict the hypothesis on the formation of the dikes as a result of fractionation. Studies of minerals have confirmed this suggestion. Most informative for petrological studies in this rocks are phlogopites and apatites. The composition of phlogopites reflects changes in the content of major elements, and apatites – of rare elements. In addition, their constituent volatiles significantly influenced the composition of the fluid phase of the rockforming melt. Study of their composition, relationships and restoration of the sequence of crystallization of minerals allowed to assume a model of formation of the Chuya lamprophyre complex, explain the differences between the two dikes areas.



The ultimate hypothesis is that the dikes South Chuya area formed at great depths directly from the source dyke Yustyd area are the result of crystallization of fractionated melt in the hypabyssal parts of the lithosphere, and associating with lamprophyre syenite massif is an intermediate chamber.

## Eu(III) interactions with calcium carbonate

AIKATERINI I. VAVOURAKI<sup>1\*</sup>,  
 ÁGELES FERNÁNDEZ-GONZÁLEZ<sup>2</sup>, MANUEL PRIETO<sup>2</sup>  
 AND PETROS G. KOUTSOUKOS<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, University of Patras,  
 Greece

(\*correspondence: kvavouraki@chemeng.upatras.gr)

<sup>2</sup>Department of Geology, Universidad de Oviedo, Spain

Understanding the interactions of radionuclides with mineral phases is important for the long-term storage safety of nuclear waste deposits which depends strongly on their interactions with the minerals. Calcite is a candidate mineral for use in nuclear waste repositories. Model studies involve nonradioactive trivalent lanthanides. In the present work Eu(III) interactions with calcite were investigated using two crystallization techniques which could yield complementary information. Counter-diffusion of ( $\text{Ca}^{2+}$ ,  $\text{Eu}^{3+}$ ) and ( $\text{Na}^+$ ,  $\text{CO}_3^{2-}$ ) ions was achieved through a porous silica hydrogel [1] in a U-shaped tube and aqueous solutions supersaturated with respect to calcite were prepared by mixing equimolar  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  solutions. The range of Eu(III) concentration was  $10^{-2}$ –50 mM. In the case of gels, Eu(III) was introduced into the sodium silicate solution used for the preparation of the silica gel to avoid formation of Eu(III) oxides. Crystals of calcium carbonate polymorphs in the presence of Eu(III) were formed in less than a month in the silica gel. Crystal growth proceeded and was finalized past a time period of one year. Additional crystallization experiments were carried out by vapor diffusion using the sitting drop crystallization method on a 'crystallization mushroom' [2]. Calcium carbonate precipitated in droplets containing  $\text{CaCl}_2$ : $(\text{NH}_4)_2\text{CO}_3$  ratio of 2.5 in the presence of Eu(III) concentration of 4–10 mM. The calcium carbonate polymorphs formed in the presence of Eu(III) were examined by Scanning Electron Microscope (SEM-EDS) and with electron microprobe (EMP) analysis. The extent of incorporation of Eu(III) into the calcium carbonate crystal structure is discussed in the perspective of using this mineral as a host for radionuclide disposal.

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## Bacterial and fungal communities colonizing mercury sulfide surfaces

A.I. VAZQUEZ-RODRIGUEZ<sup>1\*</sup>, C.M. SANTELLI<sup>2</sup>,  
 S.C. BROOKS<sup>3</sup> AND C.M. HANSEL<sup>1</sup>

<sup>1</sup>School of Engineering and Applied Sciences, Harvard  
 University, Cambridge, MA USA

(\*correspondence: avazquez@fas.harvard.edu)

<sup>2</sup>Department of Mineral Sciences, Smithsonian Institution,  
 Washington, DC USA

<sup>3</sup>Environmental Sciences Division, Oak Ridge National  
 Laboratory, Oak Ridge, TN USA

Soils and sediments, where mercury (Hg) can exist as Hg sulfide minerals (HgS), represent major reservoirs of Hg in aquatic environments. Due to their low solubility, primary and authigenic HgS (e.g. cinnabar and metacinnabar) have historically been considered insignificant sources of soluble Hg(II) to the environment. Recently however, the solubility of HgS was shown to be greatly enhanced in the presence of a natural microbial consortium [1]. The mechanisms for this enhanced solubility have yet to be assessed. Moreover, bacteria and fungi capable of colonizing HgS surfaces in the environment have not been identified, yet their proximity and association with the mineral makes them likely key players in effecting chemical changes that can impact dissolution.

To this end, we assessed the microbial diversity on HgS surfaces in the Hg-contaminated sediments and floodplain soils of the East Fork Poplar Creek in Oak Ridge, TN. Cinnabar and metacinnabar mineral sections were incubated at various depths, and hence redox conditions, in the creek channel, bank, and floodplain. Other metal sulfides, namely pyrite ( $\text{FeS}_2$ ) and sphalerite ( $\text{ZnS}$ ), were also incubated to distinguish the host metal effects on the colonizing community composition. Composition and diversity were determined after 6 weeks of incubation, via pyrosequencing using bacterial (16S rRNA) and fungal (ITS) primers.

Our results reveal a high diversity of microorganisms colonizing all the metal sulfide surfaces. The microbial community composition and phylogenetic diversity vary as a function of the host metal within the sulfide, as well as between the HgS polymorphs, cinnabar and metacinnabar. Oxidation rinds are observed on metacinnabar surfaces, the extent of which decreases with depth within the sediment. These communities have been cultivated and are being investigated for their ability to solubilize HgS. The results from this study will have large implications on the role that microbial communities play in the dissolution of HgS phases and hence mobility of Hg within the environment.

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## On the origins of prebiotic carbon containing rocks in the early Earth

ARON VECHT

Aron Vecht and Associates, London NW4 2AG, England  
(phosphors@vecht.com)

In 2007, we suggested that a paradigm shift was required to alter the generally accepted view of the organic origin of the carbon in earliest rocks [1]. To explain the distribution of deposits of methane (as hydrates), natural gas, oil, oil-tars, carbonatites as well as carbonates, we proposed the existence of stable minerals at depth which reacted when exposed to water and/or oxygen nearer the surface. We termed such rocks 'reactive minerals'. We chose carbides as examples e.g. Calcium Carbide or Aluminium Carbide. These would yield acetylene and methane respectively when exposed to water. These would in turn form carbonates under oxidizing conditions, or hydrocarbons and even graphite when exposed to a reducing environment. Under high temperatures carbonates would yield oxides while hydrocarbons would form carbon dioxide. We suggested that the existence of a considerable range of carbon containing compounds found in prebiotic rocks was not consistent with their organic origin.

More recently, evidence has been presented to support our suggestions.

1. The existence of a range of carbonate magma intrusions [2].
2. More detailed studies of  $^{13}\text{C}$  to  $^{12}\text{C}$  ratio. This was originally assumed to be evidence for the organic origin of carbonate deposits [3], however, more recently this conclusion has been questioned.

The oldest carbon containing rocks showing the existence of living systems is based on Stomatopoids and Prokaryotic cell structures. These are based on Chlorophyll and DNA systems respectively. Clearly such complicated organic structures must have developed from other organic synthetic systems. Thus Miller-Urey type systems [4] or Fischer-Tropsch catalytic reaction [5] have been proposed. Such complicated processes are unlikely to explain the large carbon containing deposits found with wide distribution. The simple carbon compounds we propose are much more likely to result in the variety and distribution of the range and extent of carbon compounds found on Earth.

The relationship between the earliest organic species and the earliest carbon containing rocks need considerable further study. Many assumptions are made without detailed information. Unfortunately, although detailed isotopic studies of the oldest rocks have been reported, the extent of carbon present (or absent) has so far been overlooked [6].

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## Power law behavior in continental crustal heat production and its implications to the thermal regime of the continents

NIMISHA VEDANTI, RAVI P. SRIVASTAVA, O.P. PANDEY  
AND V.P. DIMRI

National Geophysical Research Institute, Council of Scientific and Industrial Research, Hyderabad- 500606, India  
(nimisha@ngri.res.in)

The nature and distribution of radiogenic crustal heat production is directly related to the temperature-depth regime in the continental lithosphere. It depends upon the amount of Uranium, Thorium and Potassium present in the rock. It is a primary source of heat flow and contributes to as much as 50% to the observed heat flow at the surface. In the absence of direct sub-surface measurements, number of heat production models have been proposed, which includes widely used exponential model in which heat production diminishes exponentially with depth [1, 2], however this has not been the case. Our detailed study of the fractal behavior in the deep crustal heat production data from some of the prominent continental crustal section across the globe like Kaapvaal craton (south Africa), Baltic shield (Russia) and Dharwar craton (India) etc. exhibits inherent power law behavior in the deep continental heat production data, rather than exponential as has hitherto been believed [3]. This would mean that in case of power law distribution model, decay of heat production with depth within the crust will be slower. Consequently, more heat flow would be generated by heat producing elements within the crust and thus heat flow input from the mantle would be comparatively lower. This would affect rheological behavior of the crust. In comparison to exponential model, power law distribution conforms much better with geological observations and rock types, where metamorphic grade gradually increases with depth till Moho is reached and corresponding lithologies changes from felsic, to mafic. Thus, fractal models can be considered more realistic in defining the decay of heat producing elements with depth within the differentiated crust. Present findings will have significant impact in the estimation of lithospheric temperature-depth distribution.

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## Discovering environmentally-critical nanomineralogy: Highly reactive Mn-oxyhydroxide nanofiber nucleation and growth catalyzed by nanoematite

HARISH VEERAMANI<sup>1\*</sup>, URS DIPPON<sup>2</sup>,  
MITSUHIRO MURAYAMA<sup>1</sup>, RACHEL HENDERSON<sup>1</sup>,  
ANDREAS KAPPLER<sup>2</sup> AND MICHAEL F. HOCELLA, JR.<sup>1</sup>

<sup>1</sup>Department of Geosciences, Virginia Tech, Blacksburg, VA 24061, USA (\*correspondence: harish@vt.edu)

<sup>2</sup>Geomicrobiology, Center for Applied Geoscience (ZAG) Eberhard-Karls-University of Tübingen, Germany

Manganese oxides typically form by the oxidation of aqueous Mn(II) catalyzed by mineral surfaces and are non-specific but potent redox-active mineral components commonly found in the environment. They therefore participate in a wide array of reactions with organic and inorganic compounds. They often exhibit high sorptive reactivities and capacities exceeding those exhibited by iron oxides. When present, they can play a key role in the mobility and bioavailability of important aqueous ions.

The present study investigates abiotic Mn(II) oxidation catalyzed by nanoparticulate hematite in the presence of molecular oxygen in batch reactors. The kinetics of the reaction is studied as a function of the hematite particle size and the presence of organic ligands. The effect of organic ligands on the morphology of Mn-oxides is also studied.

Surface-area normalized rate constants suggest differences in reactivity of hematite depending on its particle size. The end product of Mn(II) oxidation, a higher valent manganese oxyhydroxide identified as the mineral hausmannite, has been characterized by employing a suite of analytical techniques including high-resolution TEM, EELS mapping, SAED and SEM. The resultant Mn-oxyhydroxides have a unique nanosized, fiber-like morphology. SEM analyses were used to describe the formation and growth of Mn-oxyhydroxides fibers over time. Mössbauer analysis on nanoparticulate hematite after complete Mn(II) oxidation indicate small detectable amounts of Fe(II) suggesting hematite reduction and resorption of ferrous iron.

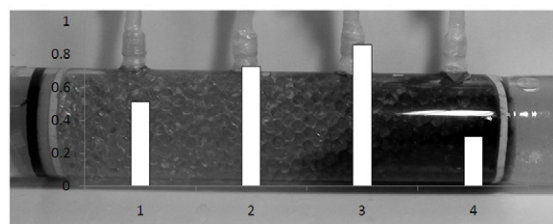
These findings suggest that the formation of Mn-oxides can be influenced by the bulk mineralogical and geochemical composition of the surrounding environment, as well as by the interfacial solute–solid nanochemistry of the solid-phase oxidant. This study further signifies the relevance of low-temperature interfacial geochemistry in the formation and the transformation of environmentally pertinent nanominerals.

## Arsenic partition in redox gradients systems with iron and sulfur presence

A.S. VEGA, S.E. ACEVEDO, E. LEIVA, P. RÍOS,  
G.E. PIZARRO AND P.A. PASTEN\*

Department of Hydraulic and Environmental Engineering  
Pontificia Universidad Católica de Chile Santiago Chile  
(\*correspondence: ppasten@ing.puc.cl)

In many cases the fate of arsenic (As) is controlled by its interaction with iron (Fe) and sulfur (S) species at the mineral-water interface. Although redox gradients are ubiquitous in aqueous systems, fewer controlled experimental studies have been performed on As-Fe-S systems. The interaction between diffusion-limited transport and the kinetics/equilibrium of chemical reactions was studied using redox gradient columns and batch sorption/coprecipitation experiments. The column was filled with a glass porous media, 1 mM FeCl<sub>2</sub> and 0.1 mM As(III) or As(V). Boundary redox conditions were controlled at each end (oxygen saturated water and 3 mM sulfide). Batch experiments used ferrihydrite and mackinawite as models for Fe and Fe/S precipitation under oxic and anoxic environments, respectively. A PHREEQC model was calibrated with the results from the batch experiments and it was used to assess As speciation scenarios in the column. Arsenic (0.1 mM) is effectively removed from solution by reaction with ferrihydrite (As(V): 99% As(III): 98%) and mackinawite (As(V): 45% As(III):93%) at oxic and anoxic conditions, respectively. Similar As removal from solution was observed when mackinawite and ferrihydrite were formed before and after As was added to the solution. The only exception was when mackinawite reacted with As(V). In the redox gradient column As is immobilized at oxic ( $pe = 0.3$ ) and anoxic ( $pe = -3$ ) conditions, whereas at intermediate redox potentials As is mobile (see Figure 1), showing that Fe and S have a buffer effect on the fate of As. The PHREEQC model shows that equilibrium conditions are not attained in the column.



Oxic boundary Anoxic boundary

**Figure 1:** Redox gradient column. At the oxic boundary As immobilization on Fe oxides was favoured while As immobilization on Fe-S minerals was favoured at the anoxic boundary. Bars depict the As concentration in solution. Fondecyt 1100943/2010

## Exploration of interactions involving human tooth enamel and dental composites using vertical scanning interferometry

MANUEL VEGA-ARROYO<sup>1,2</sup>, S. RAY TAYLOR<sup>2</sup>,  
ROLF S. ARVIDSON<sup>1\*</sup>, HEIDI B. KAPLAN<sup>3</sup>,  
GENA D. TRIBBLE<sup>2</sup> AND ANDREAS LUTTGE<sup>1</sup>

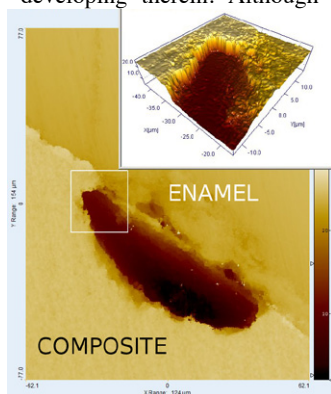
<sup>1</sup>Department of Earth Science MS-126, Rice University,  
Houston TX 77005, USA  
(\*correspondence: rsa4046@rice.edu)

<sup>2</sup>University of Texas Health Science Center at Houston –  
Dental Branch, Houston, TX 77030, USA

<sup>3</sup>Department of Microbiology and Molecular Genetics,  
University of Texas Medical School, Houston, TX 77030,  
USA

Although methacrylate resin-based dental composites are now used in the restoration of ~70% of the 120 million cavities (carious lesions) treated every year in the US, these materials have a limited service-life, requiring replacement after less than ~6 years (40% of a conventional amalgam). This replacement is most commonly necessitated because of secondary caries. Although the origin of these lesions at resin composite restoration sites is as yet unclear, they may be localized by leakage via microgaps between the cavosurface wall and the restoration. These microgaps result from shrinkage accompanying acrylate polymerization, thus yielding a protected microenvironment for growth of oral flora and subsequent chemical attack of the tooth (hydroxyapatite dissolution), and possibly the resin as well.

We present preliminary experimental results using restored teeth analyzed by vertical scanning interferometry (VSI, Fig. 1). VSI allows precise quantification of the geometry of the microgap environment and changes developing therein. Although the distribution of microgap



**Figure 1:** Microgap development at tooth-composite boundary.

volume is heterogeneous, the data clearly reveal the potential for micro-environments. Ongoing experiments include analysis of the chemical and mechanical response of these materials to imposed thermal and mechanical stresses, and *in vitro* analysis of microbial populations and attendant biofilm development.

## Grain-supported flow at magma transfer zones

N. VEGAS<sup>1\*</sup>, J. RODRIGUEZ<sup>2</sup>, J.M. TUBIA<sup>1</sup>, J.J. ESTEBAN<sup>1</sup>  
AND J. CUEVAS<sup>1</sup>

<sup>1</sup>Dpt. Geodinamica, Univ. Pais Vasco, UPV/EHU, E48940,  
Spain (\*correspondence: nestor.vegas@ehu.es)

<sup>2</sup>Dpt. Mineralogía-Petrología, Univ. País Vasco, UPV/EHU,  
E48940, Spain

Before extruding in volcanic systems, magma suffers a continued evolution during ascent from its source. Fingerprints of this magma transfer through the lithosphere are recorded by microstructures and textures in plutonic rocks.

At the most internal parts of the Variscan chain, high-K plutonic suites were emplaced following the roots of the orogen [1]. This singular high-K and Mg association of rocks (vaugnerites, appinites, redwitzites or durbachites) is related with vertical extrusion of lithospheric-mantle derived, high-K and Na melts [2, 3].

A widespread feature of these high-K suites is the development of sphene-centred ocellar textures in some synplutonic intrusions affected by mingling processes. The structural and petrological study of these textures indicates that they formed as an effect of Reynolds dilatancy in highly crystallised crystal mushes affected by grain-supported flow [4]. Fabrics deduced from field and ASM studies indicate oblate strain and compressive regime. These conditions favoured the vertical movement of hyperdense crystal mushes with non-newtonian behaviour. The strain partitioning in these magma transfer zones will promote melt migration to upper structural levels. Moreover, it will enhance the mingling process, favouring the large lithological variation observed in these suites.

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## Intracratonic carboniferous granites in the Paleoproterozoic crust of Lithuania: New SHRIMP U-Pb zircon ages

I. VEJELYTE<sup>1\*</sup>, K. YI<sup>2</sup>, M. CHO<sup>3</sup> N. KIM<sup>2</sup> AND T. LEE<sup>2</sup>

<sup>1</sup>Vilnius Univ., D. of Hydrogeology and Engineering Geology  
(\*correspondence:irma.vejelyte@gf.vu.lt), Lithuania

<sup>2</sup>Korean Basic Science Institute, Ochang, South Korea

<sup>3</sup>Seoul National University, Seoul, South Korea

Employing a Sensitive High-Resolution Ion Microprobe at Korea Basic Science Institute, we found Carboniferous granite previously unknown in the Paleoproterozoic crust of western Lithuania. The granite sample was recovered from a deep drill hole, Girkaliai-2, which is situated 3 km to the east of the Baltic Sea, within the Telsiai deformation zone. In the drill core, the analyzed granite forms a 10-cm wide dyke intruding the Paleoproterozoic charnockitic rocks. It is medium to fine-grained and consists of K-feldspar, plagioclase, biotite, and quartz. Accessory phases include monazite, zircon and opaque minerals. The contact between the granite and the host charnockite is straight and sharp. Two groups of zircon grains have been recognized in the granite. Zircons of major group are prismatic in shape and show concentric and oscillatory zoning characteristic of magmatic growth. Their U/Pb ratios are 0.81-2.15, and the U contents are 57-156 ppm. A weighted mean <sup>206</sup>Pb/<sup>238</sup>U age of 349.1±5.7 Ma (MSWD=3.2) was obtained from 12 spots. The second group of zircons yielded concordant U-Pb ages of 2042, 1880, 1846, 1726, 1630, and 1455 Ma. These grains represent xenocrysts entrapped from various country rocks during the granite emplacement. Our U-Pb zircon ages demonstrate that the Paleoproterozoic crust in western Lithuania has been affected by Early Carboniferous magmatism. The Girkaliai granitic dyke is similar to the 355 Ma diabase dykes in the eastern Baltic offshore [1], and the ca. 350 Ma alkaline-carbonatite intrusions in Poland such as Elk, Pisz and Tajno. Thus, all of these Carboniferous ages are attributed to the intracratonic magmatism associated with Paleozoic rifting in the East European craton [2]. This is a contribution to the project 'Precambrian rock provinces and active tectonic boundaries across the Baltic Sea and in adjacent areas' of the Visby Programme (the Swedish Institute).

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## Microbial sulphur isotope fractionation in a Mars analogue environment at Rio Tinto, SW Spain

ESTHER VELASCO<sup>1,2\*</sup>, PAUL MASON<sup>2</sup>, PIETER VROON<sup>1</sup>,  
WILFRED RÖLING, RICARDO AMILS<sup>3,4</sup>  
AND GARETH DAVIES<sup>1</sup>

<sup>1</sup>Faculty of Life and Earth Sciences, VU University of  
Amsterdam, The Netherlands

(\*correspondence: esther.velasco@falw.vu.nl)

<sup>2</sup>Department of Earth Science, Utrecht University, The  
Netherlands

<sup>3</sup>Centro de Astrobiología, Madrid, Spain

<sup>4</sup>CBM-SO, Autonoma University of Madrid, Spain

Sulphur isotopes are likely to be a key in future tool for the detection of past or present life on Mars, where abundant sulphate minerals are present. To investigate the link between the activity of sulphate reducing microorganisms and sulphur isotope fractionation, we incubated sediment from a modern hyper-acidic, Fe-rich subareal environment at Rio Tinto, SW Spain. This site has been frequently used as a geochemical analogue of Mars.

Sediments were sampled from the upper part of the Rio Tinto (Marismilla) as well as the estuary (Moguer). Laboratory incubation were carried out at 30°C using an artificial input solution with sulphate in excess and following techniques developed by Stam *et al.* [1]. The experiments were performed with an input solution at pH 7 and pH 3 and electron donors were provided by the natural substrate. Duplicate reactors were incubated for a total of 10 weeks. Initial data indicate moderate sulphate reduction rates of between 5 and 90 nmol cm<sup>-3</sup> h<sup>-1</sup> in Marismilla and between 5 and 45 nmol cm<sup>-3</sup> h<sup>-1</sup> in Moguer, independently of pH. Outflow solutions showed pH close to 7, regardless of inflow pH of 7 or 3, suggesting buffering within the sediment. Sulphur isotope fractionation was extreme in the Moguer estuary, extending beyond the maximum of 47‰ as predicted by the standard Rees model [2] of microbial sulphur isotope fractionation, suggesting that additional fractionation is possible [3] or indicating multiple cycles of reduction and oxidation of sulphate within the reactors. And inverse correlation between sulphate reducing rates and isotope fractionation was observed.

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## Mineral metastability and effective bulk composition: The effect of grain sizes and modal mineral amounts

S.O. VERDECCHIA<sup>1\*</sup>, J. RECHE<sup>2</sup>, E.G. BALDO<sup>1</sup>,  
E. SEGOVIA-DIAZ<sup>3</sup> AND F.J. MARTINEZ<sup>2</sup>

<sup>1</sup>CICTERRA (CONICET-UNC). Av. Veléz Sarsfield 1611,  
X5016CGA Córdoba, Argentina

(\*correspondence: sverdecchia@gmail.com)

<sup>2</sup>Departament de Geologia, Universitat Autònoma de  
Barcelona, 08193 Bellaterra, Spain

<sup>3</sup>Dpto. de Petrología y Geoquímica, CSIC-Universidad  
Complutense, 28040 Madrid, Spain

Large staurolite porphyroblasts (up to 2 cm) were recognized in quartz-mica schist of the Sierra de Ancasti (west-central Argentina) [1] with the mineral association: Crd-And-St-Grt-Bt-Ms-Pl-Qtz-Chl-Op. Textural relations suggest that the assemblage St-Grt-Bt was present in the metamorphic peak. Growth of late And or Crd porphyroblast is recognized as well. Two post-peak textural domains were identified: a) St being replaced by And without Crd, and b) Crd rich domains lacking And. A P-T pseudosection in the MnNCKFMASH system using XRF bulk composition allowed to estimate conditions of 590°C and 5.2kb for the St-Grt-Bt assemblage but post-peak textures and mineral compositions were not predictable. We assumed that the original XRF bulk composition was not valid during post-peak conditions not only because the cores of metastable porphyroblasts such as staurolite could have been isolated and excluded of the effective bulk composition [2] (EBC), but also, because heterogeneous distribution of staurolite could have affected the local EBC. Accordingly, post-peak textural relations (~580°C-3.5kb) developed during decompression were modeled using two bulk compositional domains defined on the basis of observed differences in staurolite mode. Two extreme cases were modelled: a) St poor - Crd rich domains lacking And; b) And + St rich domains lacking Crd. Results approximate real compositions and modal amounts observed in both post-peak textural domains. Thus, variation of EBC and generation of EBC domains through the PT path is a critical factor to consider for correct interpretation of metamorphic mineral and textural evolution and particularly for discrimination between polymetamorphic and single metamorphic episodes.

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## Evaluation of contaminant transport parameters at Leningrad Atomic Power Plant drain area

E.A. VERESCHAGINA

SpbSU, Saint-Petersburg, 199178 (ea.grigorieva@gmail.com)

The Leningrad Atomic Power Plant (Leningrad APP) drain area was studied. A hydrological study has been performed to demonstrate how contaminant transport proceeds in case of hypothetical disasters.

Gridded Surface Subsurface Hydrologic Analysis (GSSHA) model was chosen for the simulation of radionuclide and chemical transport. GSSHA is a physics based, fully distributed, hydrologic and sediment transport model. The distributed nature of the model confers significant potential advantages for the analysis of non-point source pollutant fate and control.

Precipitations falling on the watershed contain specified concentrations of contaminants for hypothetical disasters at Leningrad APP. As rainfall accumulates on the land surface, ponded surface water infiltrates, providing a source of contaminants into the soil column, and move as surface runoff to adjacent territory. Concentrations of contaminant are affected by decay and transformations.

The most part of the water ponded on the land surface infiltrates, removing contaminants. Water that infiltrates is assumed to contain the same concentration of dissolved contaminants as the ponded water. Infiltration was simulated using traditional Hortonian Green and Ampt (GA) approach.

Additionally, field experiments for testing the values of the Green and Ampt infiltration equation parameters were done for prevailing at the drain area soil types. The determined parameters were the effective capillary suction and the effective hydraulic conductivity.

Comparison of the model outputs with the experimental data indicates that the model can successfully describe cumulative infiltration in different soil types and contaminant transport.

## Using rare earth elements (REE) for tracing water masses

MARC VERHEUL<sup>1</sup> AND GERARD KLAVER<sup>2</sup>

<sup>1</sup>Deltares, Utrecht, The Netherlands

(marc.verheul@deltares.nl)

<sup>2</sup>BRGM, Orleans, France (G.klaver@brgm.fr)

Rare earth elements are a group of elements consisting of scandium, yttrium and the lanthanides. The concentrations in Dutch ground and surface water are low, at sub ppb ( $\mu\text{g}/\text{kg}$ ) level, but measurable with an optimised ICP-MS. The lanthanides show chemically nearly identical behaviour, which results in concentrations with a constant ratio between the different elements, although the absolute concentrations can vary by more than two orders of magnitude. The measured concentrations need to be divided by the levels in a reference clay mineral, yielding a flat line for samples with a clayey signature. Water with a calciferous influence is enriched with the heavier REE compared to the lighter REE. The slope can be expressed by the quotient of the sum of the normalised ytterbium and lutetium values and the sum of the normalised lanthanum and praseodymium values. The gadolinium anomaly (an enrichment) is caused by the application of gadolinium as a contrast agent during medical MRI-scans. This last anomaly is a clear indication of anthropogenically influenced (ground) water.

Due to absence of topography and constant water subtraction in the polderareas of the Netherlands, the hydrological system can be extremely complex locally. With REE-profiles and by combining all the characteristics of these REE-profiles, it is possible to make a water balance in these complex hydrological systems.

## A simple method for *in situ* zircon U-Th-He dating

PIETER VERMEESCH AND ANDY CARTER

Department of Earth and Planetary Sciences, Birkbeck,

University of London (p.vermeesch@ucl.ac.uk)

*In situ* U-Th-He dating of zircon by laser ablation offers significant advantages over the current practice of whole grain degassing and dissolution:

1. It dramatically increases sample throughput. Grains of zircon are notoriously hard to dissolve. Measuring their U and Th content requires dissolution in hydrofluoric acid at high temperature and pressure using a Parr bomb for up to 72 hours. In contrast, measuring the U and Th content by LA-ICP-MS can be done in a matter of minutes.
2. The process of in-situ measurements of U and Th content of grains yields U-Th-Pb ages as a by-product. Thus, in-situ dated zircon crystals are double-dated by default, offering exciting new research opportunities for detrital geochronology.

We here propose a simple four step procedure to measure *in situ* U-Th-He ages without the need to know any absolute concentrations or ablation pit volumes:

1. Polish and mount two sets of grains in indium: a standard of known U-Th-He age, and the sample of interest, whose age is unknown.
2. Ablate the grains with a UV laser and measure the raw helium signal (e.g., in units of mV or Hz) of the unknown sample along with helium measurements of the age standard.
3. Measure the U and Th signals of the standard and the unknown by EMPA, SIMS, or LA-ICP-MS in the same order as the helium measurements.
4. Given the known age of the standard and its raw U and Th signals, calculate the expected He signal of the standard. Dividing the measured by the expected He signal yields a 'gain factor' K. The U-Th-He age of the unknown is then obtained by applying this same gain factor to its raw He signal.

This new method eliminates the need for interferometric microscopy to measure ablation pit volume, largely avoids the challenges of measuring absolute U and Th concentrations by ICP-MS, and has relatively few sources of analytical uncertainty, potentially resulting in improved precision and accuracy over alternative analytical procedures.

## Modelling Li isotope signatures of waters altering a basaltic glass in under-saturated conditions

A. VERNEY-CARRON<sup>1</sup>, N. VIGIER<sup>1</sup> AND R. MILLOT<sup>2</sup>

<sup>1</sup>CRPG-CNRS, Vandœuvre lès Nancy, France

<sup>2</sup>BRGM, Orléans, France

In order to use lithium isotopes as tracers of silicate weathering, it is necessary to constrain the Li isotope fractionation caused by weathering processes (especially, mineral dissolution and secondary phase formation) as a function of environmental parameters.

Preferential uptake of <sup>6</sup>Li during the formation of clay minerals was quantified by several studies (e.g. [1]). Concerning leaching, experiments with a Li-rich basaltic glass in under-saturated conditions have shown that the  $\delta^7\text{Li}$  values of the leachates are lower than the fresh basaltic glass value during the early stages [2]. This was explained by a 2-step model: (1) Li is released in solution by diffusion, which leads to the formation of a leached layer. As <sup>6</sup>Li is lighter than <sup>7</sup>Li, the ratio of the diffusion coefficients of both isotopes ( $a=D_7/D_6$ ) is lower than 1. Thus, the solution is enriched in <sup>6</sup>Li and the leached layer in <sup>7</sup>Li. (2) The dissolution of the leached layer tends to increase the solution  $\delta^7\text{Li}$  value.  $D_7/D_6$  is also found to correlate with temperature.

In order to model natural data,  $D_7/D_6$ , but also the relative contribution of diffusion and dissolution rates has to be estimated. At  $T < 20^\circ\text{C}$ ,  $D_7/D_6$  is nil. However, it can be significant for hydrothermal fluids. Using diffusion and dissolution rates at high  $T^\circ$ , the model shows that the high dissolution rate masks the kinetic effect due to diffusion. In any case, the only way to produce  $\delta^7\text{Li}$  values in solution greater than that of the fresh mineral is to preferentially incorporate <sup>6</sup>Li into the secondary phases formed during the alteration.

[1] Vigier *et al.* (2008) *GCA* **72**, 780–792. [2] Verney-Carron *et al.* (2011) *GCA* (in press)

## The Pb age of the Earth from Neoproterozoic galenas

J. VERVOORT<sup>1\*</sup>, J. Blichert-Toft<sup>2</sup> AND F. ALBARÈDE<sup>2</sup>

<sup>1</sup>School of Earth and Environmental Sciences, Washington State University, Pullman, WA, USA 99164

(\*correspondence: vervoort@wsu.edu)

<sup>2</sup>Ecole Normale Supérieure, 69007 Lyon, France

Pb isotopes have provided the earliest estimates for the age of the Earth [1-3] and still provide important absolute age constraints on Earth's formation. Recent age determinations using the Pb isotope composition of the bulk silicate Earth range from 50 to 150 Ma after solar system formation [4-8]. Variation in present-day Pb isotope compositions in the silicate Earth, however, contribute to the uncertainty in these age determinations. Here we use the Pb isotope composition of galenas in volcanogenic massive sulfide (VMS) deposits in the Superior Province, Canada to determine the Pb age of the Earth. All deposits are Neoproterozoic (~2.7 Ga) and are derived from juvenile, mantle-derived volcanic rocks, as evidenced by their Nd and Hf isotopic compositions. Pb isotopes in the galenas are time invariant and thus provide a snapshot of the Neoproterozoic mantle from which they are ultimately derived.

A plausible scenario for Earth's Pb evolution is that it began with a low  $\mu$  in the solar nebula and increased progressively during accretion to the current value of ~ 8 for the silicate Earth [4-8]. Using a low average  $\mu$  from 4.56 to 4.52 Ga (< 0.7) with an increase to its current high  $\mu$  at 4.52 Ga, the galena Pb trend is nearly coincident with the 2.7 Ga Geochron. With these parameters there is no Pb paradox at 2.7 Ga. The timing of this process, however, is dependent on the early stage of Pb evolution on Earth: If  $\mu$  was lower during Earth's formation, the bulk of Pb loss occurred earlier; if  $\mu$  was higher, integrated Pb loss occurred later, but with maximum of ~4.48 Ga. Our estimate for the Pb age of the Earth of ~4.52 Ga is older than the range of ages based on the present-day silicate Earth. This age most likely dates Pb loss to the core [4-8] or to space during accretion [9], and may have been finally punctuated by a moon forming impact.

[1] Holmes (1946) *Nature* **157**, 680–684. [2] Houtermans (1946) *Naturwissenschaften* **33**, 185–186. [3] Patterson (1956) *GCA* **10**, 230–237. [4] Allegre *et al.* (1995) *GCA* **10**, 1445–1456. [5] Galer & Goldstein (1996) *AGU Monogr.* **95**, 75–98. [6] Halliday (2004) *Nature* **427**, 505–509. [7] Wood & Halliday (2005) *Nature* **437**, 1345–1348. [8] Allègre *et al.* (2008) *EPSL* **267**, 386–398. [9] Albarède *et al.* (2011) *MinMag*, this volume.

## Arsenic mobility in coal-combustion ashes mixed with agricultural soil

V. VESELSKÁ<sup>1\*</sup>, K. PEŤKOVÁ<sup>1</sup>, R.M. BOLANZ<sup>2</sup>,  
J. MAJZLAN<sup>2</sup>, E. JURKOVIČ<sup>1</sup>, B. LALINSKÁ<sup>3</sup>, E. HILLER<sup>1</sup>  
AND O. ĎURŽA<sup>1</sup>

<sup>1</sup>Department of Geochemistry, Comenius University,  
Bratislava, 842 15 Bratislava, Slovakia

(\*correspondence: veselska@fns.uniba.sk)

<sup>2</sup>Institute of Geosciences, Friedrich-Schiller University,  
Jena, Germany

<sup>3</sup>Department of Mineralogy and Petrology, Comenius  
University, Bratislava, 842 15 Bratislava, Slovakia

In this study, we focus on the influence of coal combustion residues (ashes) on soils. Ashes with elevated As content were buried in soils when a dam of an ash impoundment of the Nováky power plant (Slovakia) failed in 1965; subsequently, the ashes were covered by agricultural soil. In order to assess the arsenic mobility, we performed leaching studies with distilled water, ammonium nitrate, and acid ammonium oxalate solutions on ash-soil samples collected in three various depths intervals (0-30, 20-60 and 40-100 cm) at various locations in the 1965 ash spill.

Mild extractions with H<sub>2</sub>O and 1 M NH<sub>4</sub>NO<sub>3</sub> show that there is a potential to contaminate the surrounding environment with As due to relatively high concentrations of As measured in the leachates. However, in both extractions, the released As concentrations represent only a small percentage of the As<sub>TOT</sub> (5.3% and 0.3%, respectively).

Oxalate-extractable As fraction (73% of the As<sub>TOT</sub>) should be associated with the poorly crystalline Fe, Al, and Mn oxide phases, which represent 17%, 14%, and 63% of the total element concentrations in the samples, respectively. It could be assumed that released amounts of Si<sub>OX</sub> (484- 21, 319 mg/kg) and Al<sub>OX</sub> (10.04-22, 984 mg/kg) support a possibility of silicate leaching from amorphous glasses in this extraction step.

Single extractions were complemented with magnetic separation of heavy fraction, X-ray diffraction and electron microprobe analyses of ash-soil mixture. These studies show, that the magnetic fraction of the soils contains an average value of 0.15 wt% As and 0.08 wt% As in the non-magnetic fraction. In depths of > 40 cm, there were significant positive correlations between As and total Fe (r=0.71), as well as As and total Al (r=0.78). Positive correlation of r=0.94 was also found for As-Ca, indicating that Fe, Al, and Ca-rich minerals control the distribution of As and retain this element in the soils.

This study was supported by the project VEGA No. VEGA 1/1034/11.

## From compositional to P-T-deformation-t(relative age)-redox maps at the thin section scale

OLIVIER VIDAL, PIERRE LANARI, BENOIT DUBACQ,  
MANUEL MUNOZ AND ERIC LEWIN

Linking deformation with metamorphic conditions requires spatially continuous estimates of pressure (P) and temperature (T) conditions at least in two dimensions (P-T maps) that can be superposed to the observed structures of deformation at different scales.

We have developed an approach and a package of matlab scripts to produce EMP quantitative X-ray maps of composition at the thin section scale. These maps of mineral composition can be combined with a multi-equilibrium approach involving phyllosilicates to calculate P-T-deformation-t (relative age)-Fe<sup>2+</sup>/Fe<sup>3+</sup> maps, even for samples free of low variance parageneses. Various application examples show that in metapelites metamorphosed at < 550 °C, the composition of phyllosilicates does not change significantly by lattice diffusion with varying P and T. Different compositions of phyllosilicate grains coexisting metastably in the same thin section are therefore indicative of different P-T conditions of crystallization that were achieved at different times. The nucleation of new phyllosilicate grains with different compositions during P-T variation is activated by deformation, so that the location of the different phyllosilicate generations characteristic of different P-T conditions is correlated to the microstructures. In addition to historical information about the P-T and deformation history, the P-T-deformation-t-Fe<sup>2+</sup>/Fe<sup>3+</sup> maps highlight the evolution of redox condition and the heterogeneity of rheology at the thin section scale.

## Interaction of Se(IV)/Se(VI) species with granitic rock: Understanding of retention processes

K. VIDENSKA<sup>1\*</sup>, V. HAVLOVA<sup>2</sup>, M. GALIOVA<sup>3</sup>  
AND V. HAVRANEK<sup>4</sup>

<sup>1</sup>ICT Prague, Technická 5, 166 28 Prague 6, Czech Rep.

(\*correspondence: katerina.videnska@vscht.cz)

<sup>2</sup>NRI Rez plc., Husinec-Rez 130, 250 68 Rez, Czech Rep

<sup>3</sup>Masaryk University, Kotlářská 2, 61137 Brno, Czech Rep

<sup>4</sup>INP CAS, Husinec-Rez 130, 250 68 Rez, Czech Rep

### Introduction

The fission product <sup>79</sup>Se belongs between radionuclides considered in safety assessment of radioactive waste geological repository, namely due to relative long half life (3.56·10<sup>5</sup> yrs), anionic form in solution and biogenic character.

### Modelling

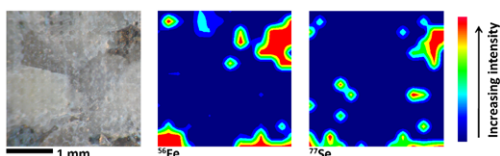
According to modelling (the Geochemist's Workbench) Se can be present at -II, 0, +IV and +VI oxidation states under granitic water conditions. Se (0) stability field would increase with increasing concentration of Se.

### Experimental

Se(IV) and Se(VI) as anionic species are not usually supposed to be strongly bound on mineral surfaces [1]. Series of batch sorption experiments with crushed granitic rock revealed different sorption properties of selenite Se(IV) and selenate Se(VI), with favourable attraction of Se(IV). The higher oxidation state of selenium and large grain size significantly decreased K<sub>D</sub>-values.

### Discussion

In order to identify potential retention mechanisms, LA-ICP-MS and PIXE measurement were performed on surface of granitic samples after contact with Se(IV) or Se(VI) solution. Surface maps revealed trend of Se increased concentration in presence of Fe.



**Figure 1:** LA-ICP-MS surface map of granite sample after contact with 2.10<sup>-5</sup> M Se(IV) solution.

The research was funded by Czech Ministry of Trace and Industry under contract No. FR-T11/362. MG acknowledge support from the MSMT (MSM 0021622412).

[1] Carbol & Enquist (2007) *SKB R 97*–13.

## Seawater-derived REY and HFSE systematics in Archean BIFs

S.VIEHMANN<sup>1,4\*</sup>, J.E. HOFFMANN<sup>1,2</sup>, C. MÜNKER<sup>2</sup>,  
B.W. ALEXANDER<sup>3,4</sup> AND M. BAU<sup>4</sup>

<sup>1</sup>Steinmann Institut, Universität Bonn, Germany

(\*correspondence: fumi@uni-bonn.de)

<sup>2</sup>Geologisch-Mineralogisches Institut, Universität zu Köln, Germany

<sup>3</sup>Inorganic Ventures Inc., Christiansburg, VA, USA

<sup>4</sup>Jacobs Universität Bremen, School of Engineering & Science, Bremen, Germany

The HFSE and REE-Y patterns of Banded Iron Formations (BIFs) can be used to place constraints on the trace element composition of Archean seawater [e.g. 1]. Here we report the first high-precision HFSE (Nb, Ta, Zr, Hf) and REE (Lu, Sm, Nd) concentration data for separated chert and magnetite mesobands of ca. 3.7 Ga old BIFs from Isua (SW Greenland) and ca. 2.7 Ga old BIFs from the Temagami Formation (Superior Province, Canada), all obtained by isotope dilution. Other trace element measurements were performed using Quadrupole ICP-MS.

PAAS-normalized REY signatures of both Archean BIFs are comparable to modern and other Archean seawater patterns (e.g. [2]) and show seawater-like positive La, Y, Gd anomalies. Positive Eu anomalies suggest an enhanced hydrothermal input in Archean oceans, and the constant lack of negative Ce anomalies indicates anoxic seawater conditions [3].

Superchondritic ratios of Nb/Ta and Zr/Hf in magnetite bands of the Isua BIFs (40.2 - 59.2; 44.9 - 53.7) point toward lower Nb/Ta and Zr/Hf ratios of Isua cherts (19.2 - 32.5; 31.3 - 46.1). Temagami BIFs display the same characteristic with superchondritic Zr/Hf ratios in magnetite samples (38.1 - 47.1) contrary to subchondritic Zr/Hf ratios in cherts (18.9 - 28.5). By contrast magnetite and chert layers of Temagami BIFs exhibit uniform Nb/Ta ratios (14.1 - 27.0). Compared to compositions of modern aqueous [e.g. 4] and hydrothermal reservoirs, HFSE ratios of the Archean BIFs lie between those fields. Therefore different depositional environments for Isua and Temagami BIFs are favoured and also a different behaviour of both geochemical twins (Nb-Ta and Zr-Hf) in different water depths and water masses of Archean seawater is suggested.

[1] Bau M. Alexander B. (2009) *Precam. Res.* **174**, 337-346.

[2] Planavsky N. *et al.* (2010) *GCA* **74**, 6387-6405. [3] Bau

M. Koschinsky A. (2009) *Geochem. J.* **43**, 37-47. [4] Firdaus

M.L. *et al.* (2011) *Nature Geosc.* **4**, 227-230.

## Iron isotope signature of Paleoproterozoic banded iron formation from Quadrilátero Ferrífero, Minas Gerais, Brazil

L.C. VIEIRA<sup>1\*</sup>, F. POITRASSON<sup>1,2</sup>, R.I.F. TRINDADE<sup>3</sup>  
AND F.F. ALKIMIM<sup>4</sup>

<sup>1</sup>Instituto de Geociências, Universidade de Brasília, Campus Darcy Ribeiro, 70904-970 Brasília-DF, Brazil  
(\*correspondence: lucieth@unb.br)

<sup>2</sup>Laboratoire Géosciences Environnement Toulouse, IRD-CNRS, 14-16, av. E. Belin, 31400 Toulouse, France

<sup>3</sup>Instituto de Astronomia Geofísica e Ciências Atmosféricas, Cidade Universitária, Rua do Matão 1226, Universidade de São Paulo, 05508-090 São Paulo-SP, Brazil

<sup>4</sup>Departamento de Geologia, Campus do Morro do Cruzeiro, Universidade Federal de Ouro Preto, 35400-000 Ouro Preto-MG, Brazil

The iron cycle study provides important insights into the early Earth System evolution history. The Precambrian record is marked by Banded Iron Formation (BIF) occurrences, which are the product of chemical precipitation from seawater, which were subsequently affected by diagenetic and metamorphic processes.

In Central Brazil, the Quadrilátero Ferrífero region comprises a large occurrence of Paleoproterozoic BIF with approximately 7000 km<sup>2</sup>, which hosts one of the largest iron ore deposits in the world. Some samples of the Quadrilátero Ferrífero's BIF were used in a preliminary investigation on the iron isotope signature recorded by these deposits.

We have analyzed a suite of samples by MC-ICP-MS using the nickel doping technique. Thirty three analyses of the Milhas hematite standard gave a  $\delta^{57}\text{Fe}$  value of  $0.766 \pm 0.088\%$  (2SD), relative to the IRMM-14 standard. On the USGS BIF reference rock we obtained  $\delta^{57}\text{Fe} = 0.903 \pm 0.042$  (2SE, n=6). Both values agree within uncertainties with previously published values. Our results on the Quadrilátero Ferrífero show large  $\delta^{57}\text{Fe}$  variations, between  $-1.493 \pm 0.034\%$  and  $-0.061 \pm 0.12\%$ . These different  $\delta^{57}\text{Fe}$  values were obtained for BIF samples which have different mineralogical associations. Samples with the lightest  $\delta^{57}\text{Fe}$  correspond to siliceous BIF whereas all other samples, are BIFs intermingled with carbonates. Such an isotopic range extending towards very light  $\delta^{57}\text{Fe}$  values have only been found in 2.5-2.7 Ga age BIFs, like those of the Quadrilátero Ferrífero.

## Biogeochemical characterization of geothermal fluids

ANDREA VIETH-HILLEBRAND, ALEXANDRA VETTER,  
ANKE SACHSE, STEFANIE HENNE, SIMONA REGENSPURG  
AND KAI MANGELSDORF

GFZ German Research Centre for Geosciences,  
Telegrafenberg, D-14473 Potsdam  
(vieth@gfz-potsdam.de)

Biogeochemical investigations on deep geothermal fluids are relatively rare, but are of great importance to characterize the geochemical origin of the fluid as well as the potential that biological processes will effect the working reliability of geothermal plants.

To characterize the natural variability in the inventory of dissolved organic carbon (DOC) compounds in geothermal fluids, samples from different geothermal plants in numerous geothermal regions of the world have been screened for the qualitative and quantitative composition of the DOC using size-exclusion chromatography. The characterization of the DOC as well as inorganic anions are valuable to evaluate if microbial processes will be relevant in the geothermal system as the DOC and several inorganic anions like nitrate and sulfate represent potential nutrients for the microbial ecosystem. The changes in composition of the microbial ecosystem in geothermal plants and heat storage systems were also characterized by bacterial membrane phospholipid fatty acids (PLFA) composition.

Here, we will present recent results on the screening of the DOC in selected geothermal fluids from a variety of geothermal plants and heat storage systems as well as the monitoring of fluid chemistry and PLFA composition in heat storage systems present in the North German Basin.

Samples from a solar assisted heat storage located in a quaternary freshwater aquifer in 15 to 30 m depth clearly show that the composition of the microbial ecosystem changes with respect to the seasonal changes of charge and discharge of heat. In wintertime, the PLFA composition of the indigenous microbial community showed an adaptation of the cell membrane during the discharge mode, when temperature decreases from 50 to 13.7°C during time of heat extraction.

One deep heat storage in the North German Basin (1250 m depth) where surplus heat from a gas and steam cogeneration plant is stored in summertime and which is used in wintertime for district heating shows changing PLFA patterns that clearly indicate different composition of the microbial communities on the warm and cold side.

## Isotopic tracing of lithium sources in the Seine River, Paris (France)

N. VIGIER<sup>1</sup>, J. GAILLARDET<sup>2</sup>, P. LOUVAT<sup>2</sup> AND J. CHEN<sup>2</sup>

<sup>1</sup>CRPG-CNRS, Nancy Université, 15 rue Notre-Dame-des-Pauvres B.P. 20 F-54501 Vandœuvre lès Nancy

<sup>2</sup>IPGP, CNRS, 75252 Paris, France

Li isotopes have recently been used for tracing chemical erosion of silicate lithologies in present-day river basins and in the past, through oceanic records. Silicate weathering is a significant sink of atmospheric CO<sub>2</sub>, but classical methods are insufficient for determining alteration rates and control laws with sufficient precision to be used in modeling of geochemical cycles and climate at large scale.

Most of the published studies show that dissolved lithium mainly come from silicate lithologies, even in mixed lithology basins (e.g. Kisakurek *et al.* 2005). However, recently a couple of studies have also shown that anthropogenic input might impact the Li isotopic composition of natural waters. Indeed, some rain waters display unusually high  $\delta^7\text{Li}$  and fertilizers may also be highly enriched in  $^7\text{Li}$  (Millot *et al.* 2010). Analyses of commercial solutions show that their  $\delta^7\text{Li}$  are particularly high relative to the range estimated for natural systems (Tomascak, 2004).

In order to estimate the order of magnitude of Li contamination of natural waters from anthropogenic sources, the Seine River in Paris, the largest urban area in France, has been sampled at various seasons. Li isotopes were measured in the filtered fractions (<0.2 $\mu\text{m}$ ) by MC-ICP-MS, after the Li separation procedure described in Vigier *et al.* (2009).

The  $\delta^7\text{Li}$  measured in the dissolved fractions of the Seine River range between 8.6‰ and 14.2‰. This range is within that determined for rivers located far from human activity. However, these values are low when compared to the published values for carbonate and evaporite lithologies (~30‰). This may mean that, even in a basin dominated by this kind of lithology, dissolved Li mainly comes from minor silicate phases. This is consistent with the low Li levels in carbonates. Another possibility is that anthropogenic inputs are significant and have on average a low  $\delta^7\text{Li}$  in the Paris area. Some streams draining rooves and roads display a wide range of  $\delta^7\text{Li}$  (from 25‰ to -17‰), with an average of 7‰. A positive correlation between  $\delta^7\text{Li}$  and discharge in the Seine waters does suggest a role of anthropogenic components, such as for Zn (Chen *et al.* 2008). More investigation is needed in order to better determine the isotope composition of each potential endmember.

## FTIR study of OH-OD exchange in Fe-free ringwoodite-wadsleyite samples

E. VIGOUROUX<sup>1</sup>, J. INGRIN<sup>1</sup>, N. BOLFAN-CASANOVA<sup>2</sup> AND D. FROST<sup>3</sup>

<sup>1</sup>UMET - UMR CNRS 8207 - Université Lille 1 – Cité Scientifique, 59655 Villeneuve d'Ascq, France  
(eric.vigouroux@ed.univ-lille1.fr,  
jannick.ingrin@univ-lille1.fr)

<sup>2</sup>LMV - UMR CNRS 6524 - Université Blaise Pascal – 5 rue Kessler, 63038 Clermont-Ferrand, France

<sup>3</sup>BGI – Bayreuth University– Universitätsstrasse, 95447 Bayreuth, Germany

Mantle ringwoodite and wadsleyite may incorporate large amount of H in their structure (up to several wt % H<sub>2</sub>O). A good knowledge of hydrogen diffusion in these mineral phases and its relationship with their electrical conductivity is critical to estimate the real amount of water present in the transition zone. We synthesized ringwoodite and wadsleyite in multi-anvil presses up to 21 GPa and 1100 °C from forsterite powder surrounded by a small amount of brucite. The grain size of the ringwoodite samples ranged between 30 and 70  $\mu\text{m}$ , while wadsleyite samples had grains sizes smaller than 20  $\mu\text{m}$ . The samples incorporated moderate amount of water in the range of 0.1 to 0.2 wt% H<sub>2</sub>O as confirmed by FTIR analyses performed on double face polished thin slices of few hundred microns.

In order to measure H diffusion rate in ringwoodite, we annealed a 106  $\mu\text{m}$  thick slice for up to 80 hours in a OD enriched atmosphere at 400°C and we followed step by step the OH-OD exchange by FTIR. The main OH band in ringwoodite, the OH broad band at 3120 cm<sup>-1</sup>, decreased rapidly but no equivalent OD band was produced. It suggests that, in ringwoodite, the mobility of H linked to this defect, is high and the removing of hydrogen from the crystals are not limited by D self-diffusion (ringwoodite was not destabilized even after 80 hours annealing, as confirmed by Raman and FTIR analyses). The effective diffusion coefficient through the thin section is of the order of 2 10<sup>-14</sup> m<sup>2</sup>s<sup>-1</sup>, and the corresponding intra-crystalline diffusion coefficient is around 3 10<sup>-15</sup> m<sup>2</sup>s<sup>-1</sup> assuming an average grain size of 40  $\mu\text{m}$ . These results are ten times faster than the diffusion coefficient in wadsleyite extrapolated at 400°C from the experiments of Hae *et al.* 2006 performed in wadsleyite [1].

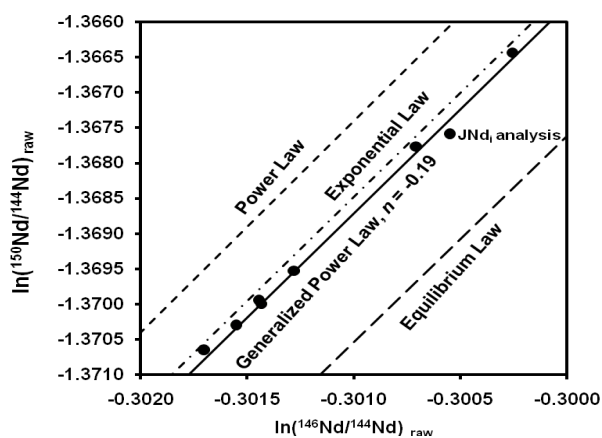
[1] Hae *et al.* (2006) *Earth Planet Sci Let* **247**, 141–148.

## Estimation of mass discrimination in MC-ICP-MS Nd isotope analysis using generalized power law

B. VIJAYA GOPAL, B. SREENIVAS  
AND Y.J. BHASKAR RAO

National Geophysical Research Institute (CSIR), Hyderabad  
500007, India (bvijayagopal@ngri.res.in)

The multi collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) is known for large mass discrimination when compared to Thermal Ionization Mass Spectrometer (TIMS), but remains time-independent. An exponential law is routinely used to correct for this mass discrimination in MC-ICP-MS analysis. Although, this resulted in precisions of < 50 ppm when compared to TIMS analysis, the fringe isotope ratios, eg.  $^{150}\text{Nd}/^{144}\text{Nd}$  seems to deviate by > 500 ppm. Thus, a generalized power law (GPL; [1]) was introduced. Applying GPL for Nd isotope analysis of JMC Nd, it was shown that an exponent variable ( $n$ ) of -0.23 is more effective in correcting the measured Nd isotope ratios using Nu Plasma MC-ICP-MS [2]. Also it was observed that variable  $n$  for various instruments generally ranges between -0.2 and -0.5. In this work, we estimated the  $n$  value for Nd isotope compositions of  $\text{JNd}_i$  measured on Nu HR MC-ICP-MS and found that GPL with a  $n$  value of -0.19 is more effective (Fig. 1). This value of  $n$  appears similar to the one obtained by Wombacher and Rehkämper [2].



**Figure 1:** Analysis of  $\text{JNd}_i$  with various laws for correction

[1] Maréchal, C.N. Télouk, M & Alberède, F. (1999) *Chem. Geol.* **156**, 251–253. [2] Wombacher, F & Rehkämper, M. (2003) *JAAS*, **18**, 1371–1375.

## REE distribution for the Arkachan large intrusion-related Gold deposit: Evidence for fluid origin

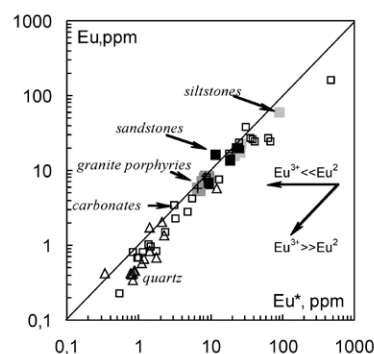
O.V. VIKENT'EVA\*, G.N. GAMYANIN  
AND N.S. BORTNIKOV

IGEM RAS, Moscow 119017, Russia

(\*correspondence: ovikenteva@rambler.ru)

The Arkachan gold deposit is located in the tin metallogenic zone of Mesozoic Verkhoyansk belt (400 km to the North of Yakutsk) and hosted by sandstones and siltstones  $\text{C}_{2-3}\text{-P}_1$ . There is granite intrusion 2 km beneath the deposit. REE were determined by ICP-MS for unaltered and altered host rock, for quartz and carbonate and for fluid inclusions.

The REE total content increases from unaltered to altered host rocks from 90 to 200 ppm and from 170 to 830 ppm for sandstones and siltstones, respectively. All studied host rocks, ore carbonate and quartz are enriched in LREE, but carbonates from altered terrigenous rocks has  $\text{La}/\text{Yb} < 1$ . Host rock alteration produced by acidic high temperature fluids and REE distribution were controlled by the sorption. Role of the complexation is increased at ore quartz and carbonate precipitation. Values of tetrad effect, more pronounced for the third tetrad are 1.2-1.5. Distinct negative Eu anomaly ( $\text{Eu}/\text{Eu}^* = 0.4-0.7$ ) prevails in the rocks and minerals (Fig.1).



**Figure 1:** Plot of chondrite-normalized Eu concentrations versus calculated  $\text{Eu}^*_n$  values, where  $\text{Eu}^*_n = (\text{Sm}_n(\text{Tb}_n \cdot \text{Eu}_n)^{1/2})^{1/2}$ .

Fluids with deficient of Eu derived from granitic plutons. The  $\text{Eu}/\text{Eu}^*$  values for the some samples, e.g. for late quartz, are 1-1.4, specified by a relatively reduced hydrothermal fluid with  $\text{Eu}^{3+} \ll \text{Eu}^{2+}$ . The inverse relationship of  $\Sigma\text{REE}$  and of  $\text{Eu}/\text{Eu}^*$  indicates a substantial role of magmatic fluid in the formation of the altered rocks. The hydrothermal fluids of the Arkachan deposits are known to be a mixture of  $\text{H}_2\text{O} + \text{CO}_2 + \text{NaCl}$  with salinity of 3.7 to 26.3 wt % NaCl-equiv. leaving chloride as the most likely candidate for the REE-transporting agent. LREE depletion of the siderite might be a result of the mineralogical control.



## Ore-magmatic hydrothermal systems of massive sulphide deposits of Southern Urals: Melt and fluid inclusion data

I.V. VIKENTYEV<sup>1\*</sup>, V.S. KARPUKHINA<sup>2</sup>, V.B. NAUMOV<sup>2</sup>  
AND A.Y. BORISOVA<sup>3,4</sup>

<sup>1</sup>IGEM RAS, Moscow 119017, Russia

(\*correspondence: viken@igem.ru)

<sup>2</sup>GEOKHI RAS, Moscow 119991, Russia

(naumov@geokhi.ru)

<sup>3</sup>GET-OMP, Toulouse 31400, France

(borisova@lmtg.obs-mip.fr)

<sup>4</sup>Geological Department, MSU, Moscow 119899, Russia

According to existing models [1], the formation of the volcanogenic massive sulphide (VMS) deposits of the Urals is related to shallow chambers of acidic magma. The ore bodies are hosted by locally altered felsic rocks. All economic VMS deposits are located at some lithostratigraphic levels corresponding to two major and a few local stages of Lower Silurian and Middle Devonian volcanism. Melt inclusions (MI) and high density fluid inclusions (FI) in quartz phenocrysts were studied in 200 samples of dacite, rhyodacite and rhyolite.

Two main types of MI have been discovered: the most widespread devitrified inclusions, and rarely found glasses, some of them contain the ore globules of magnetite and also sulphides, represented by pyrrhotite, pentlandite, chalcopyrite and bornite, defined by electron microprobe. Melting of glasses occurred at 600-720°C, homogenization at 850-1130°C, whereas devitrified inclusions at 750-820°C and 950-1210°C accordingly. MI were analyzed for major elements and F, Cl by electron microprobe and H<sub>2</sub>O by secondary ion microprobe. The concentrations of volatiles in the MI are (in wt%) are H<sub>2</sub>O up to 6.5, Cl up to 0.28, F up to 0.42 contents; the average content of sulfur is 0.025 wt%.

FI in quartz phenocrysts are round to negative crystal shaped, from 25 to 100  $\mu\text{m}$ , with gas bubbles from 8 to 40  $\mu\text{m}$ . The homogenization of the FI occurred at 124-250°C in liquid phase. The freezing temperatures of FI range from -14 to -37°C. Salinities are from 1.2 to 6.2 wt% NaCl, density of aqueous fluids from 0.80 to 0.94 g/cm<sup>3</sup>, calculated pressure from 680 to 850 MPa. Micro-Raman investigation demonstrated a presence of liquid H<sub>2</sub>O only. Evaluated by LA-ICP-QMS at GET [2] contents in the magmatic fluid are: Cu 0.03-2.1 wt%, Zn 0.008-1.7 wt%, K 0.08-2.0 wt%, Fe 0.1-1.3 wt%, B 40-1600 ppm, Ba 20-2200 ppm, Sn 4-1600, Pb 14-740 ppm, Ag 4-200 ppm, Au 4-8 ppm.

[1] Baranov *et al.* (1988) *Proc. 7<sup>th</sup> IAGOD Symp*, 449-460.

[2] Borisova *et al.* (2010) *Geostand. Geoanal. Res.*, **34**, 245-255.

## Alterations to nanoparticle associated proteins

P.J. VIKESLAND, M.S. HULL, M. CHAN, R. KENT  
AND P. PATI

Virginia Tech, Blacksburg, VA 24061, USA (pvikes@vt.edu, mahull@vt.edu, mychan@vt.edu, ronkent40@gmail.com, param@vt.edu)

Engineered nanoparticles are often either purposely stabilized with proteins or acquire a protein 'halo' while in geologic or biologic media. The presence of this protein coat is generally thought to stabilize nanoparticles and make them resistant to aggregation and deposition phenomena. Our work has systematically examined the gold nanoparticle/protein interface in an effort to quantify the strength and stability of these interactions and to define the chemical and morphological transformations of the protein coat. Bovine serum albumin (BSA) was chosen as a representative protein and gold nanoparticles serve as a model nanoparticle system. Gold is an ideal model nanoparticle since it can be readily produced as monodisperse suspensions of varying size and variable surface functionality. Furthermore, gold is amenable to a number of surface plasmon enabled spectroscopies that facilitate quantitative evaluation of the protein/gold interface.

This presentation will highlight studies conducted to 1) quantify BSA binding to gold nanoparticle surfaces, 2) evaluate how BSA conformation changes in response to variations in solution chemistry, 3) determine the stability of the BSA coating under flow conditions, and 4) elucidate the chemical and biological reactivity of the BSA coating. These experiments collectively rely upon UV-Vis measurements of changes in the surface plasmon band location and intensity, surface enhanced Raman spectroscopy to evaluate changes in BSA conformation and chemistry, and deposition and flow-cell AFM studies that define the stability of the BSA-gold nanoparticle interaction.

The current work has led to an improved understanding of protein/nanoparticle interactions and has helped define the chemical and morphological transformations that surface associated proteins are subject to. The collected results have important implications on the ultimate fate, transport, and toxicity of nanoscale particles released to aquatic environments.

## Optimizing the use of magnetite from an iron mine for reduction of aqueous Cr(VI)

M. VILLACÍS-GARCÍA<sup>1</sup> AND M. VILLALOBOS<sup>1,2\*</sup>

<sup>1</sup>Environmental Bio-Geochemistry Group, Chemistry School

<sup>2</sup>Earth Sciences Graduate Program, Geology Institute, UNAM, Coyoacan, C. U., Mexico 04510, D.F

(\*correspondence: mariov@geologia.unam.mx)

### Introduction

Magnetite is an inverse spinel ferrite that contains in its structure both Fe<sup>3+</sup> and Fe<sup>2+</sup> [1], and may therefore act as a reducing agent. This behavior has been applied in remediation of contaminated water with oxidized metal species that upon chemical reduction become immobile [2]. In this paper we present an investigation using natural samples of this mineral from an Fe mine deposit in Mexico towards the reduction of Cr(VI) to Cr(III), with the final aim to understand the geochemical conditions of optimal performance for applying it to real pollution scenarios. The most important problem to solve for optimal implementation, is the rapid surface passivation of the mineral due to complete oxidation of superficial Fe<sup>2+</sup>, which results in very low Cr(VI) reduction yields.

### Methodology

Investigations were performed with magnetite of various particle sizes, both natural and synthetic. Batch experiments were performed with a solid concentration of 6 g L<sup>-1</sup> and concentrations of Cr(VI) of 5-10 mg L<sup>-1</sup> and up to 50 mg L<sup>-1</sup>. Mixtures of magnetites with low amounts of Fe (0) were also investigated, which presumably replenish superficial magnetite Fe(II) [3].

### Discussion of Results

The reduction capacity of magnetite increased with decreasing particle size, but the overall reduction rates and yields were relatively low. Small weight percentages of Fe (0) (1-5%) mixed with magnetite, which in the absence of magnetite showed no reduction capacity, significantly increased both rates and yields. We report the optimization of the magnetite/Fe (0) ratio as a function of particle size, and pH, and confirmed the surface-mediated reduction mechanism.

[1] Liu *et al.* (2006) *Mater. Lett.* **60**, 2979–2983.

[2] Kendelewicz *et al.* (2000) *Surf. Sci.* **44**, 55–60. [3] Coelho *et al.* (2008) *Chemosphere* **71**, 90–91.

## A unified surface structural model for ferrihydrite: Proton, electrolyte, and arsenate adsorption

M. VILLALOBOS<sup>1\*</sup> AND J. ANTELO<sup>2</sup>

<sup>1</sup>Environmental Bio-Geochemistry Group, Chemistry School, and Earth Sciences Graduate Program, Geology Institute, UNAM, Coyoacan, CU, Mexico 04510, D.F

(\*correspondence: mariov@geologia.unam.mx)

<sup>2</sup>Soil Science and Agricultural Chemistry Dept., University of Santiago de Compostela, Spain

### Introduction

Ferrihydrite (FH) is a common hydrous ferric oxide nanomineral of 'young' formation in aqueous geochemical environments. Its small particle sizes (1.5-5 nm) [1, 2] expose a very high specific surface area at the mineral/water interface, and this may have considerable influence on the transport and fate of a variety of trace and major elements through diverse sorption processes. In particular, arsenate anions show a very high affinity for FH, and their fate in contaminated environments is almost invariably associated to Fe(III) oxide surfaces [3, 4]. The extremely small FH nanoparticles, which show high particle aggregation when dried, preclude experimental determination of important surface parameters for the thermodynamic description of its adsorption behavior. In the present work we have compiled eight sets of published acid-base surface titration data for synthetic preparations of FH across a wide range of particle sizes, and two sets of arsenate adsorption data, and unified their description through a face-distribution site-density model developed previously for goethite.

### Discussion of Results

We show that the surface proton charge behavior of FH in conjunction with its As(V) adsorption behavior may be adequately described using the affinity constants derived for goethite, by assuming the FH surface to be composed predominantly of a surface site configuration equal to that of the (010) goethite face (*Pnma* space group). Also, through the applied model the available specific surface area of each FH preparation in aqueous suspension may be successfully derived, showing values between 330 and 1120 m<sup>2</sup>/g. The implications of the results reported here are highly relevant for predictive purposes of FH surface reactivity in general.

[1] Murphy *et al.* (1976) *J. Colloid Interface Sci.* **56**, 270–283.

[2] Janney *et al.* (2000) *Clay Clay Min.* **48**, 111–119. [3] Arai *et al.* (2006) *ES&T* **40**, 673–679. [4] Slowey *et al.* (2007) *Appl. Geochem.* **22**, 1884–1898.

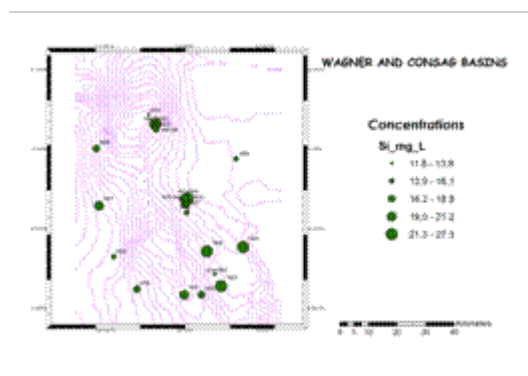
## Variation of silica and diatoms in Wagner and Consag Basins in the North part of California Gulf, Mexico

RUTH ESTHER VILLANUEVA-ESTRADA<sup>1\*</sup>,  
ALEJANDRO ESTRADAS-ROMERO<sup>1</sup>,  
ROSA MARÍA PROL-LEDESMA<sup>1</sup>,  
MARÍA EUGENIA ZAMUDIO-RESENDIZ<sup>2</sup>,  
DAYAN RODRÍGUEZ<sup>1</sup>, EZEQUIEL TOBON<sup>1</sup>  
AND RENTERIA JAZMIN<sup>1</sup>

<sup>1</sup>Instituto de Geofísica, Universidad Nacional Autónoma de México (\*correspondence: ruth@geofisica.unam.mx)

<sup>2</sup>Instituto de Ciencias del Mar y Limnología, Universidad Nacional Autónoma de México

In this work we present preliminary results about the abundance and species richness of diatom in sediments related with the chemistry of pore water. The oceanographic cruise (WAG-02) was done at the end of July 2010 in the Wagner and Consag basins of the Northern part of Gulf of California. The study area is characterized by pockmarks, mud volcanoes and gas vents at depths of 65 to 150 m approximately [1].



**Figure 1:** Spatial distribution of silica concentrations in pore water.

### Discussion of Results

The presence of silica in the Wagner Fault could be high productivity waters in the zone, dissolution of minerals and the hydrothermal activity.

[1] Canet, C. *et al.* (2010) *Sedimentary Geology* **228**, 292–303. [2] Battarbee, R.W. (1986) 527–570.

## Os isotopes in sulfides from xenoliths of the Campos de Calatrava Volcanic Field, Central Spain

C. VILLASECA<sup>1</sup>, J.M GONZÁLEZ-JIMÉNEZ<sup>2</sup>,  
W.L. GRIFFIN<sup>2</sup>, E. ANCOCHEA<sup>1</sup>, F. GERVILLA<sup>3</sup>,  
S.Y O'REILLY<sup>2</sup>, N.J. PEARSON<sup>2</sup> AND E. BELOUSOVA<sup>2</sup>

<sup>1</sup>Dpt. Petrology and Geochemistry, UCM-CSIC, Madrid, Spain (granito@geo.ucm.es, eancochea@geo.ucm.es)

<sup>2</sup>GEMOC ARC National Key Centre, Sydney, Australia (jose.gonzalez@mq.edu.au., bill.griffin@mq.edu.au, sue.oreilly@mq.edu.au, npearson@mq.edu.au, elena.belousova@mq.edu.au)

<sup>3</sup>Dpt. Mineralogy & Petrology, University of Granada, Spain (gervilla@ugr.es)

The Campos de Calatrava Volcanic Field (CCVF) comprises more than 200 volcanic centers with ultra-potassic to more Na-rich alkaline magmas that intruded the easternmost branch of the Hercynian Iberian Massif, in central-south Spain, ca. 8.7-0.7 Ma ago. Small lherzolite-wherlite xenoliths are embedded in pyroclastic deposits of volcanic centers. These xenoliths are spinel-bearing varieties; garnet is absent in the lherzolite suite. The presence of interstitial volatile-rich minerals (i.e. amphibole and phlogopite) and the distribution of trace elements in them suggest mantle metasomatism by subduction-related melts [1].

Fe-rich monosulphide solid solution (Fe-rich Mss) (<16.67 at% Ni) is the only sulphide present in the xenoliths. *In situ* LA-MC-ICPMS analyses reveal that sulfides included in primary silicates are Os-poor (<15 p. p. m.), making it difficult to obtain precise Re-Os isotope data. In contrast, sulfides sitting in open fractures or included in metasomatic silicates have higher Os contents (up to 89 p. p. m.). The Re-Os data show large variations in <sup>187</sup>Os/<sup>188</sup>Os (0.1142-0.1241) and <sup>187</sup>Re/<sup>188</sup>Os (0.02-0.12).  $T_{MA}$  and  $T_{RD}$  (Re depletion) model ages, compared with PUM at the present day, range from 1.0 to 2.3 Ga and from 0.75 to 2.1 Ga respectively. One grain has <sup>187</sup>Os/<sup>188</sup>Os = 0.1270 and <sup>187</sup>Re/<sup>188</sup>Os = 0.05;  $T_{MA}$  and  $T_{RD}$  are 0.4 and 0.35 Ga.

The differences in Re-Os systematics of sulfides reflect a probable metasomatism at 1 Ga ago. This metasomatic event is also recognised in Nd  $T_{DM}$  ages from spatially associated gabbros of the Hercynian orogen in central Spain (Fernández-Suárez *et al.* 2011).

[1] Villaseca, C. *et al.* (2010) *Geol. Soc. London Special Publ.* **337**, 125–152. [2] Fernandez-Suárez *et al.* (2011) *Lithos* doi: 10.1016/j.lithos.2010.09.010.

## Novel insights into the ion sorption properties of calcite in aqueous solutions using cavity ring-down spectroscopy

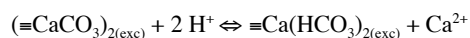
A. VILLEGAS-JIMÉNEZ<sup>1\*</sup>, R.M. HAZEN,<sup>1</sup>  
AND D.A. SVERJENSKY<sup>2</sup>

<sup>1</sup>Carnegie Institution of Washington, Geophysical Laboratory,  
Washington, D.C. 20015, USA

(\*correspondence: adriano@gl.ciw.edu)

<sup>2</sup>Johns Hopkins University, Earth and Planetary Sciences,  
Baltimore, MD 21218, USA

Despite significant advances on the elucidation of the structure of the calcite-water interface, much controversy still surrounds some of its most fundamental physical-chemical properties [e.g. the pH of the isoelectric point, the point of zero net surface charge, the proton and lattice-derived ion sorption properties]. This is largely due to the lack of suitable experimental approaches allowing a rigorous characterization of calcite surface equilibria over expanded compositional ranges. Electrokinetic techniques do not allow direct probing of surface reactions whereas conventional wet-chemical approaches (batch and titration) fail to control or monitor CO<sub>2(g)</sub> exchange across the air-water interface which leads to large uncertainties in the computed (ad)sorption data. Recently, a novel titration protocol that addresses this difficulty was developed and tested over a relatively wide range of chemical conditions [1]. The new data was interpreted in terms of the following 2H<sup>+</sup>/Ca<sup>2+</sup> ion exchange equilibrium:



If true, this mechanism may impact the aqueous speciation of carbonate-rock systems with restricted CO<sub>2(g)</sub> ventilation via the buffering of pH and calcite dissolution. It follows that a careful verification of this reaction is warranted. To this end, and to gain further insight into the ion sorption properties of CaCO<sub>3(s)</sub> in aqueous solutions, we are conducting new titrations of high-purity, additive-free, synthetic calcite and aragonite powders over a broader range of conditions using a novel titration approach that allows, for the first time, a reliable monitoring of the chemistry of the CaCO<sub>3(s)</sub>-H<sub>2</sub>O<sub>(l)</sub>-CO<sub>2(g)</sub> system. Accurate *p*CO<sub>2</sub> measurements are obtained via a gas-recirculation device and a last-generation cavity ring-down laser spectrometer which avoids interferences from water vapor with negligible sample perturbation, a notable advantage over IR spectrometer-based strategies. Our approach yields very high-quality data suitable for the calibration of ion sorption models for CaCO<sub>3(s)</sub> surfaces.

[1] *Phys. Chem. Chem. Phys.* (2009) **11**, 8895–8912.

## Molybdenum isotopes in the altered oceanic crust, a novel proxy for recycling?

F. VILS<sup>1\*</sup>, T. ELLIOTT<sup>1</sup>, M. WILLBOLD<sup>1</sup>, M. HARRIS<sup>2</sup>,  
C. SMITH-DUQUE<sup>2</sup>, R. COGGON<sup>3</sup> AND D. TEAGLE<sup>2</sup>

<sup>1</sup>University of Bristol, BS8 1RJ Bristol, United Kingdom

(\*correspondence: flurin.vils@bristol.ac.uk)

<sup>2</sup>National Oceanography Centre Southampton, University of  
Southampton, SO14 3ZH Southampton, United Kingdom

<sup>3</sup>Imperial College London, SW7 2AZ, United Kingdom

During movement of the oceanic crust away from mid-ocean ridges, hydrothermal alteration of the oceanic crust results in a distinct elemental and isotopic signal. The change in isotopic composition compared to unaltered MORB is an important tracer for the involvement of fluids released from the altered oceanic crust at the base of arc volcanoes during subduction. Any isotopic system not fractionated during dehydration reaction and inert to diffusion is therefore a valuable tracer to shallow or deep recycling of subducted material. Recent studies showed that Mo isotopes could be such a novel proxy [1, 2, 3] as measured Mo isotope values in arc and ocean island basalts differ significantly from mantle values (estimated to be similar to continental crust 0‰ δ<sup>97/95</sup>Mo). This study investigates the change in Mo isotopes through the altered oceanic crust to better constrain the input into the subduction zone.

Samples of the altered oceanic crust across the Pacific Ocean have been measured for Mo isotopes and Mo concentrations (ODP Sites 1179, 1301, 1256). Combined the studied samples show a decreasing down-hole trend varying over 1‰ δ<sup>97/95</sup>Mo. The heavier isotope ratio in the upper part of the crust might be the source region for the heavy isotope ratio seen in the Mariana arc [2] and the lighter isotope ratio further down-hole might be the source for the light isotope ratio seen in ocean islands basalts [1, 3]. To further constrain this down-hole trend over a complete section of the altered oceanic crust (through pillow basalts, sheeted dyke complex, and gabbros), additional Mo isotope and concentration measurements on the deepest ODP hole (Site 1256) are currently in process.

[1] Willbold *et al.* (2009) *GCA* **73 suppl.** A1444.

[2] Freymouth *et al.* (2011) this volume. [3] Lai *et al.* (2011) this volume.

## Heavy metals and arsenic in the soils in the area of Narva power plants: Distribution and controlling factors

L.-E. VINNE\*, L. BITYUKOVA AND H. SCHVEDE

Institute of Geology at Tallinn University of Technology,  
Tallinn, Estonia

(\*correspondence: liis-erliken.vinne@gi.ee)

Two world's largest oil shale-fired thermal power plants located in the North-eastern Estonia are the main sources of air pollution in Estonia. Up to 50 thousand tonnes of combustion ashes are emitted to the atmosphere annually.

Oil shale contains most of the naturally occurring chemical elements at least in trace amounts. Trace species may be realised during combustion and can pose an environmental and human risk. Soils have been considered as one of the main recipients of pollutants.

To evaluate potential hazard of contamination in the area influenced by the Narva Power Plants the geochemical mapping was carried out. Geochemical maps created basing on the ICP-MS data for major and trace elements allow illustrating spatial distribution of elements studied and outline the areas with uncommon concentrations in the soils. Well-defined areas with the highest values of elements are observed generally along the seacoast zone and to the east of the Narva region that reflect the incorporation of the Lower Ordovician shale bedrock naturally enriched in potentially toxic elements.

Mobility and availability of arsenic and heavy metals in soils was evaluated by the two-steps (milliQ water and sodium acetate) sequential extraction. The results showed that heavy metals and arsenic are leached in low quantities and attributed generally to mineral phase in the soils. The water soluble fractions are negligible (<1%). The Na-acetate extractable concentrations of Cd, Co, Cr, Pb and Zn are much higher than those obtained using water extraction. Extractability of elements depending on pH, grain size composition and soil types also as elements contribution from very various parent materials will be discussed in the presentation.

## Thermodynamics of solid solutions of carbonates with non-isostructural end-members: The prediction of solubility limits with the single defect method

V.L. VINOGRAD<sup>1</sup>, M.I. LUCHITSKAIA<sup>2</sup> AND B. WINKLER<sup>2</sup>

<sup>1</sup>Institute of Energy and Climate Research (IEK6),  
Forschungszentrum Jülich, 52425, Germany  
(v.vinograd@fz-juelich.de)

<sup>2</sup>Institute of Geosciences, University of Frankfurt, Frankfurt  
a.M., 60438, Germany

Carbonates are considered as sorbents for various contaminants dissolved in aqueous solutions. Numerous studies suggested that carbonates can retain significant amounts (up to thousands of ppm) of  $\text{SO}_4^{2-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{HAsO}_3^{2-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{CrO}_4^{2-}$ , while concurrent spectroscopic and surface diffraction studies have shown that these anions, indeed, replace  $\text{CO}_3^{2-}$  units of the carbonates. The question is, can these experimental results be considered as a proof for the formation of thermodynamically stable solid solutions? Our approach to the problem is based on the assumption that the solute components obey Henry's law. This is equivalent to assuming that the enthalpy of mixing of a diluted solid solution can be approximated as a linear function of the mole fraction of the solute. The extrapolation of this line to 100% of the solute component allows defining the enthalpy of the virtual (solute) end-member, which within the same assumption forms a perfectly ideal solution with the host. We have been able to calculate the total energies of virtual end-members from the total energy of the host (carbonate) and the energies of supercells of the host with a single  $\text{CO}_3^{2-}$  unit replaced by an anion of the solute end-member. The energies were calculated from first principles. The standard enthalpies of the virtual end-members were then calculated relative to reference compounds with the same composition, whose standard thermodynamic properties are well defined. Our calculations predict vanishingly small concentrations of  $\text{SO}_4^{2-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{HAsO}_3^{2-}$  and  $\text{HPO}_4^{2-}$ . This suggests that carbonate 'solid solutions' formed by co-precipitation with these components are not stable in the thermodynamic sense. Experimental approaches to testing this hypothesis are discussed.

## Thermodynamics of rutile- and $\alpha$ -PbO<sub>2</sub>-type solid solutions from quantum-mechanical calculations

V.L. VINOGRAD<sup>1</sup> AND B. WINKLER<sup>2</sup>

<sup>1</sup>Institute of Energy and Climate Research (IEK6),  
Forschungszentrum Jülich, 52425, Germany  
(v.vinograd@fz-juelich.de)

<sup>2</sup>Institute of Geosciences, University of Frankfurt, Frankfurt  
a.M., 60438, Germany

Recent progress in analytical techniques sensitive to ppm-range concentrations attracted the interest of petrologists to geothermobarometry based on trace element partitioning between various minerals [1]. Current approaches for the calibration of such geothermobarometers are purely phenomenological. Indeed, the thermodynamic mixing properties of solid solutions, whose concentration ranges do not exceed 1000 ppm, cannot be easily measured and thus typically are not known. We propose to use atomistic model simulations for the calibration and extrapolation of such geothermobarometers. In this report we will present the results of density functional theory based simulations of TiO<sub>2</sub>-SiO<sub>2</sub> and TiO<sub>2</sub>-ZrO<sub>2</sub> solid solutions with rutile and  $\alpha$ -PbO<sub>2</sub>-type structures obtained using the double-defect method [2]. The results will be discussed in relation to Zr-in-rutile thermometry and Si-in-rutile barometry. The pressure effects of Ti-in-quartz and Ti-in-zircon thermometers have also been modeled.

[1] T. Zack, R. Moraes, A. Kronz (2004) *Contrib. Mineral. Petrol.* **148**, 471–488. [2] V.L. Vinograd, B. Winkler (2010) *Reviews in Mineralogy & Geochemistry* **71**, 451–475.

## Factors affecting the physical phase state of SOA particles from biogenic and anthropogenic precursors

A. VIRTANEN<sup>1\*</sup>, E. SAUKKO<sup>1</sup>, A. LAMBE<sup>2</sup>, P. MASSOLI<sup>3</sup>,  
T. ONASCH<sup>3</sup>, J. WRIGHT<sup>2</sup>, D.R. CROASDALE<sup>2</sup>,  
A. LAAKSONEN<sup>4</sup>, P. DAVIDOVITS<sup>2</sup> AND D. WORSNOP<sup>3</sup>

<sup>1</sup>Tampere University of Technology, Department of Physics,  
P.O.Box 692, 33101 Tampere, Finland  
(\*correspondence: annele.virtanen@tut.fi)

<sup>2</sup>Boston College, Department of Chemistry, 2609 Beacon  
Street, Chesnut Hill, MA 02467-3860, USA

<sup>3</sup>Aerodyne Research, 45 Manning Road, Billerica, MA 08121-  
3976, USA

<sup>4</sup>Finnish Meteorological Institute, P.O. Box 503, 00101  
Helsinki, Finland

SOA formation and properties are widely studied to clarify the role of SOA in radiative forcing and climate. However, very limited information is available on the morphology and phase state of SOA particles. Verifying the physical phase state of SOA particles gives new and important insight into their formation and growth process and essential information on their implications in the atmosphere [1, 2].

According to our recent results [3], pine derived SOA particles in chamber conditions as well as atmospheric SOA particles formed in boreal forest can be amorphous solid in their physical state at least several hours after their formation. However, it is not known yet how general the observation is and what the atmospheric implications are.

In this study we have investigated the physical phase state of SOA particles formed in Boston College flow tube from various precursor VOCs representing both biogenic and anthropogenic sources. In addition, the phase change was investigated as a function of particle oxidation level (O:C) and flow tube SO<sub>2</sub> concentrations.

According to our results the solid phase is the dominating phase state of formed SOA in the case of both biogenic and anthropogenic precursors at least up to relative humidity (RH) values of 55-70%. At higher RH values the humidity induced phase transition takes place and particles liquefy. We find that the O:C ratio of particles as well as chamber SO<sub>2</sub> concentration have an effect on the phase of SOA particles.

[1] Zahardis *et al.* (2007) *Atmos. Chem. Phys.* **7**, 1237-

[2] Zobrist *et al.* (2008) *Atmos. Chem. Phys.* **8**, 5221-

[3] Virtanen *et al.* (2010) *Nature*, **467**, 467.

## The delivery of organic material to the early solar system

R. VISSER<sup>1\*</sup>, E.F. VAN DISHOECK<sup>2,3</sup>, S.D. DOTY<sup>4</sup>  
AND E.A. BERGIN<sup>1</sup>

<sup>1</sup>Dept. of Astronomy, University of Michigan, 500 Church Street, Ann Arbor, MI 48109-1042, USA

(\*correspondence: visserr@umich.edu)

<sup>2</sup>Leiden Observatory, Leiden University, P.O. Box 9513, 2300 RA Leiden, the Netherlands

<sup>3</sup>Max-Planck-Institut für Extraterrestrische Physik, Giessenbachstrasse 1, 85748 Garching, Germany

<sup>4</sup>Dept. of Physics and Astronomy, Denison University, Granville, OH 43023, USA

The solar nebula, in which the Earth and all other solar-system bodies were formed, was a complex chemical mixture of gas and dust. In order to fully understand the nebula's chemical composition at the time the solid bodies were formed, one has to go back in time and retrace the chemistry to the molecular cloud that collapsed to form the solar nebula. Here we present recent astrochemical observations and models that aim to do just that [1, 2, 3]. The main focus is on water and on simple organic compounds like methanol (CH<sub>3</sub>OH) and dimethyl ether (CH<sub>3</sub>OCH<sub>3</sub>), which are tracers of the organic complexity that likely aided the eventual formation of life. The models predict that water and simple organics were already formed abundantly at an early time. As the parent molecular cloud collapsed and evolved into the early solar system, changes in density, temperature and radiation led to further chemical processing. The abundances of several key species in this simulated solar nebula match those observed in comets [4], but others are off by orders of magnitude. We discuss what both the good and the poor matches mean for the delivery of organic material to the Earth and elsewhere.

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[2] Visser *et al.* (2009) *Astron. Astrophys.* **495**, 881–897.

[3] Visser *et al.* (2011) *Astron. Astrophys.* submitted.

[4] Bockelée-Morvan *et al.* (2000) *Astron. Astrophys.* **353**, 1101–1114.

## Raman spectroscopy of endoevaporitic microbial communities from the Atacama Desert

PETR VÍTEK<sup>1\*</sup>, HOWELL G.M. EDWARDS<sup>2</sup>,  
JAN JEHLIČKA<sup>1</sup>, ELIZABETH CARTER<sup>3</sup>, CARMEN ASCASO<sup>4</sup>  
AND JACEK WIERZCHOS<sup>4</sup>

<sup>1</sup>Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University in Prague, Albertov 6, 128 43 Prague 2, Czech Republic

(\*correspondence: vitek2@natur.cuni.cz)

<sup>2</sup>Centre for Astrobiology and Extremophiles Research, School of Life Sciences, University of Bradford, Bradford BD7 1DP, United Kingdom

<sup>3</sup>Vibrational Spectroscopy Facility, School of Chemistry, University of Sydney, Sydney, NSW 2006, Australia

<sup>4</sup>Museo Nacional de Ciencias Naturales, CSIC, c/ Serrano 115 dpdo., 28006 Madrid, Spain

Geobiological systems with emphasis on halite and gypsum crusts from the Atacama Desert, one of the driest places on Earth, were studied. Raman spectroscopic analysis revealed variations in pigment composition within various endolithic colonies, allowing in some cases suggestions to be made about survival strategies.

Scytonemin, an effective extracellular UV-protectant, was found in cyanobacterial colonies within halite and gypsum crust from the hyperarid core of the Atacama Desert using Raman spectroscopy. The amount of scytonemin present differed depending on the particular microhabitat. Substantial differences are proposed to reflect a variable biosynthesis due to the amount of light available inside the halite and gypsum crust.

Raman spectroscopic analyses of the endoevaporitic colonies from Ca-sulphate exhibited systematic variations in carotenoid composition together with the presence/absence of a phycobiliprotein signal (indicative for cyanobacteria). The cyanobacterial signal was accompanied by two clearly distinguishable  $\nu(\text{C}=\text{C})$  carotenoid bands at  $\sim 1516$  and  $1498 \text{ cm}^{-1}$ , pointing to carotenoids of different chain length. Within the colonies living closer to the surface, scytonemin was also identified. The Raman signal of algal colonies from near the rock surface exhibited a  $\nu(\text{C}=\text{C})$  carotenoid band at  $\sim 1525 \text{ cm}^{-1}$  accompanied by chlorophyll, whereas the same carotenoid band obtained from red algae is shifted towards lower wavenumbers with the spectra lacking chlorophyll.

Fast Raman mapping of the green algal colonies exhibited great potential of the method for the study of endolithic communities in their original habitats.

## Readily available acidity in schwertmannite

CHAMINDRA VITHANA<sup>1,2\*</sup>, LEIGH SULLIVAN<sup>1,2</sup>,  
RICHARD BUSH<sup>1,2</sup> AND ED BURTON<sup>1,2</sup>

<sup>1</sup>Southern Cross GeoScience, Southern Cross University,  
Australia (\*correspondence: c.vithana.10@scu.edu.au)

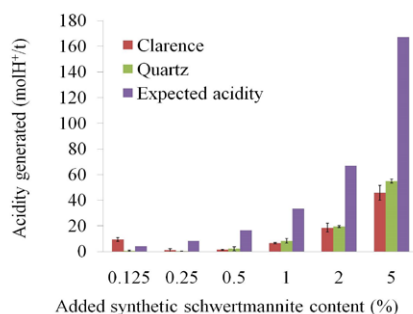
<sup>2</sup>CRC CARE, Building X, University of South Australia,  
Mawson Lakes SA 5095, Australia

### Introduction

Schwertmannite and jarosite are considered as less soluble ironhydroxy sulfate minerals which are present in highly acidic environments (pH < 3). These minerals release acidity in the long run as they weather by hydrolysis [1]. However, 1M KCl extraction of soil samples (Clarence and Quartz) spiked with those two minerals showed that schwertmannite has some acidity that may be readily available.

### Results and Discussion

Unlike jarosite, schwertmannite released acidity during 1M KCl extraction. It was found that the measured acidity in schwertmannite added samples was ~1/3 of the expected total inherent acidity (Figure 1). This acidity release was also associated with the release of surface bound sulfate from schwertmannite. It was found that ~30% of sulfate in schwertmannite was able to be released by 1M KCl, an amount that matches other observations [2].



**Figure 1:** Acidity generated vs expected acidity

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[2] Bigham *et al.* (1990) *Geochim. Cosmochim. Acta* **54**, 2743–2758.

## Dust from copper smelters in the Zambian Copperbelt

M. VÍTKOVÁ<sup>1\*</sup>, V. ETTLER<sup>1</sup>, F. VESELOVSKÝ<sup>2</sup>,  
B. KRÍBEK<sup>2</sup> AND O. ŠEBEK<sup>3</sup>

<sup>1</sup>Institute of Geochemistry, Mineralogy and Mineral  
Resources, Charles University in Prague, Albertov 6,  
128 43 Prague 2, Czech Republic  
(\*correspondence: vitkova3@natur.cuni.cz,  
m.vitkova@seznam.cz)

<sup>2</sup>Czech Geological Survey, Geologická 6, 152 00 Prague 5,  
Czech Republic

<sup>3</sup>Laboratories of the Geological Institutes, Charles University  
in Prague, Albertov 6, 128 43, Prague 2, Czech Republic

Smelting activities in the Copperbelt Province (Zambia) have produced huge amounts of various wastes. Dust particles emitted during the ore and slag processing pose high risk of environmental pollution in this area [1, 2]. Three types of dusts identified as possible sources of contamination were studied: (A1) dust from slag crushers, (A2) fly ash trapped by filters originating from processing of the slags and (B) electrostatic precipitator dust from smelting of Cu and Co-rich ores. Bulk chemical analyses and mineralogical investigation using XRD, SEM/EDS and TEM were performed. The samples were enriched with various levels of metals and metalloids. Maximum concentrations of 256 g Cu/kg (B), 8.9 g Co/kg (A1), 4.7 g Pb/kg (A2) and 19.8 g Zn/kg (A2) were determined. Based on XRD analysis, the composition of dust A1 generally corresponds to silicate slags [3] with dominating Ca-Fe pyroxenes, quartz (SiO<sub>2</sub>), fayalite (Fe<sub>2</sub>SiO<sub>4</sub>) and cuprospinel (CuFe<sub>2</sub>O<sub>4</sub>). Calcite (CaCO<sub>3</sub>), Ca-Fe pyroxenes and quartz represented the main phases of fly ash A2 with minor ZnS and elemental Cu and a significant portion of amorphous/glassy fraction. Chalcantinite (CuSO<sub>4</sub>·5H<sub>2</sub>O), magnetite (Fe<sub>3</sub>O<sub>4</sub>) and delafossite (CuFeO<sub>2</sub>) dominated in dust B. Detailed mineralogical investigations revealed the presence of Cu sulphides in the studied samples and possible substitutions of metals in the pyroxene structure. Elevated concentrations of Cu, Co and Zn were detected in the silicate glass. *In situ* weathering processes may result in the release of contaminants into the environment (e.g. soils) depending on the stability of phases present in the dust.

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## Sedimentary and chemical weathering fluxes at the outlet of the granitic Strengbach catchment (Vosges massif, Eastern France)

DANIEL VIVILLE\*, FRANÇOIS CHABAUX, PETER STILLE, MARIE-CLAIRE PIERRET, SOPHIE GANGLOFF AND SYLVAIN BENARIOUMLIL

EOST-LHYGES (CNRS/Uni. Strasbourg), 1, rue Blessig, F-67084 Strasbourg Cedex, France (\*correspondence: dviville@unistra.fr)

Understanding the relationship between chemical weathering and physical erosion rates is an important issue of Surface and Environmental Science. The determination of the relationships and parameters controlling chemical weathering and physical erosion can be achieved, among others, by comparing weathering and erosion fluxes measured at the outlet of small experimental watersheds. Astonishing is the fact, that numerous studies of chemical weathering fluxes exist and that only a few focused on erosion fluxes. This is for instance the case for the Strengbach catchment, for which geochemical budgets have been established since the mid 80ties but physical erosion rates only since very recently.

The aim of this study is to assess the physical erosion rate of the granitic Strengbach catchment (0.8 km<sup>2</sup>, Vosges Massif, Eastern France) with the dissolved flux carried by the streamlet.

The results show that the erosion rate (about 5 T. km<sup>-2</sup>. yr<sup>-1</sup>) is at least equivalent to the chemical weathering rate and could be twice depending on the weathering rate retained corrections (atmospherical, biological). They also indicate that the erosion rate based on the lonely suspended matters calculation induces an underestimation of about 30%.

On the basis of this work, it appears that the weathering and erosion budgets determined on the Strengbach catchment do not differ significantly from other granitoids catchments studied previously.

## Marine Mo isotope inventory: The role of igneous rock weathering

A.R. VOEGELIN<sup>1\*</sup>, TH.F. NÄGLER<sup>1</sup>, N. NEUBERT<sup>2</sup>, T. PETTKE<sup>1</sup>, M. STEINMANN<sup>3</sup> AND O. POURRET<sup>4</sup>

<sup>1</sup>Institut für Geologie, Universität Bern, Switzerland (\*correspondence: voegelin@geo.unibe.ch)

<sup>2</sup>Institut für Mineralogie, Leibniz Universität Hannover, Germany

<sup>3</sup>UMR 6249 Chrono-Environment, Université de Franche-Comté, France

<sup>4</sup>HydriSE, LaSalle Beauvais, 60026 Beauvais cedex, France

The marine isotope inventory strongly depends on fractionation processes during continental rock weathering and subsequent river transport. Concerning molybdenum (Mo), the riverine contribution accounts for the largest part of the marine budget (e.g. [1]). Models of oceanic Mo cycling thus strongly depend on understanding continental processes causing Mo isotope fractionation.

This study investigates the effect of igneous crustal rock weathering on aquatic  $\delta^{98/95}\text{Mo}$  signals by comparing stream water and bedrock (basalt, granite, gneiss) Mo isotope data to results of laboratory leach experiments. Stream waters analyzed here are enriched in the heavy isotopes, a result in line with findings of previous studies [2-4]. To date, weathering of magmatic rocks has not been associated with resolvable Mo fractionation, as their  $\delta^{98/95}\text{Mo}$  show little variability ( $\delta^{98/95}\text{Mo} = -0.1$  to  $0.3\%$ , [5]). Incongruent mineral weathering and/or adsorption/resorption processes are the most likely factors to have caused the observed signals, while soil retention and adsorption of light Mo to the particulate load play a secondary role. This interpretation, based on water and bedrock samples, is supported by data of bedrock leach experiments, where leach solutions show a moderate fluctuation in  $\delta^{98/95}\text{Mo}$  between 0.5 and 1‰. This is nearly identical to the variability found in the stream waters (0.6-1.1‰). Sulfide oxidation was proposed to be an important factor controlling stream water Mo isotopic composition in a catchment underlain by sedimentary rocks [4]. Considering that silicate rocks may contain sulfides with variable isotope signatures, their incongruent dissolution could generate the observed aqueous  $\delta^{98/95}\text{Mo}$  signals.

[1] McManus *et al.* (2002) *Geochem. Geophys. Geosyst.* **3**, 1078. [2] Archer & Vance (2008) *Nature Geosci.* **1**, 597-600. [3] Pearce *et al.* (2010) *EPSL* **295**, 104-114. [4] Neubert *et al.* (2011) *EPSL* **304**, 180-190. [5] Siebert *et al.* (2003) *EPSL* **211**, 159-171.

## Nanoparticulate Fe(III)-precipitates forming by Fe(II) oxidation in water

A. VOEGELIN\*, S. SCHWARZ, S.J. HUG AND R. KAEGI

Eawag, Swiss Federal Institute of Aquatic Science and Technology, CH-8600 Dübendorf, Switzerland  
(\*correspondence: andreas.voegelin@eawag.ch)

The oxidation of dissolved Fe(II) at oxic/anoxic boundaries leads to the precipitation of nanoparticulate Fe(III)-phases that profoundly impact the biogeochemical cycling of Fe and the fate of other major and trace elements in environmental systems. Despite the importance of Fe(III)-precipitates as immobilizing sorbents or colloidal carriers for contaminants and nutrients, numerous questions relating to their formation, their structural diversity and resulting differences in reactivity remain to be resolved.

Our recent work on Fe(III)-precipitates formed in aerated Fe(II)-containing aqueous solutions at pH 7 indicated the importance of Fe(III)-phosphates [1, 2]: At molar dissolved P/Fe (II) ratios >0.5, we observed exclusive formation of amorphous Fe(III)-phosphates that also incorporated substantial amounts of Ca. At P/Fe(II) <0.5, we concluded from X-ray absorption spectroscopy data that Fe(III)-phosphate formed until P was depleted, followed by the formation of other Fe(III)-phases (Si-rich hydrous ferric oxide at Si/Fe > 0.5, 2-line ferrihydrite at Si/Fe ~0.2-0.5, or lepidocrocite at Si/Fe <0.2) [1]. Electron microscopy data suggested that the different Fe(III)-phases became mixed in nanoparticles with diameters of a few 10-100 nm [2].

In continuing work, we aim (i) to resolve the composition and structure of Fe(III)-phosphates and the mode of cation and anion incorporation (Ca versus Mg, phosphate versus arsenate), (ii) to evaluate the transformation of different types of fresh precipitates during aging, and (iii) to assess how the different types of fresh Fe(III)-precipitates and their aging products affect other major and trace elements in aquatic systems. This work is based on controlled laboratory experiments in synthetic aqueous solutions, complemented by studies on real systems such as diagenetic Fe accumulations in lake sediments or As-removal units for drinking water treatment.

[1] Voegelin *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 164–186. [2] Kaegi *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 5798–5816.

## The partitioning of volatile elements between metal and silicate at high pressures and temperatures

A.K. VOGEL<sup>1\*</sup>, D.C. RUBIE<sup>1</sup>, D.J. FROST<sup>1</sup>  
AND H. PALME<sup>2</sup>

<sup>1</sup>Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

(\*correspondence: antje-kathrin.vogel@uni-bayreuth.de)

<sup>2</sup>Forschungsinstitut und Naturmuseum Senckenberg, D-60325 Frankfurt, Germany

Volatile elements are depleted in the Earth's mantle and in nearly all other solid objects of the inner solar system (Moon, Mars, meteorites), most probably because they failed to condense at high temperatures. In some cases evaporation before or during accretion may also have occurred. Many of these elements were additionally affected by core formation. To disentangle primary depletion and depletion by core formation and to provide additional clues for the processes of core formation we studied the metal - silicate partitioning behaviour of the volatile siderophile elements Sn, Pb, P, Cu and Ge, covering a range of 650 K in condensation temperatures.

Experiments were performed over a pressure and temperature range of 10.5 GPa to 23 GPa and 2273 K to 2673 K respectively using a multi-anvil apparatus. The oxygen fugacity varied from -2.0 to -2.4 log units relative to the iron-wüstite-buffer. The starting materials consisted of 3 parts (by weight) silicate (peridotitic composition) and 1 part (by weight) metal, with the latter consisting of 95 wt% Fe, and 1 wt% of P<sub>2</sub>O<sub>5</sub>, Cu, GeO<sub>2</sub>, SnO and Pb<sub>3</sub>O<sub>4</sub> respectively. To consider the effect of S one experiment was performed with 10wt% S added as FeS to the metal phase of the starting material. Analyses of the metal phases were performed with an EPMA, the compositions of the silicate phases were analyzed by LA-ICP-MS.

The volatile elements Sn and Pb are similarly depleted in the Earth's mantle, which requires similar effective partition coefficients ( $D^{\text{met/sil}}$ ) during core formation. However, at low pressures the partition coefficients of Sn and Pb differ by up to two orders of magnitude. Our results show that the liquid metal - liquid silicate partition coefficients of Sn and Pb converge with increasing pressure, indicating that equilibration pressures of at least 30 GPa were necessary to avoid fractionating them in the Earth's mantle.

We found that 10 wt.% S in the metal phase has hardly any influence on the  $D^{\text{met/sil}}$  of Pb but lowers the value for Sn by about 0.6 orders of magnitude.

## Isotope reference materials for present and future isotope research

JOCHEN VOGL\* AND WOLFGANG PRITZKOW

BAM Federal Institute for Materials Research and Testing,  
Berlin, Germany (\*correspondence: jochen.vogl@bam.de)

The variation of isotope abundance ratios is increasingly used to unravell natural and technical questions. In the past the investigation and interpretation of such variations was the field of a limited number of experts. With new upcoming techniques and research topics in the last decades, such as provenance and authenticity of food, the number of published isotope data strongly increased. The development of inductively coupled plasma mass spectrometers (ICPMS) from an instrument for simple quantitative analysis to highly sophisticated isotope abundance ratio machines influenced this process significantly. While in former times only experts in mass spectrometry were able to produce reproducible isotope data, nowadays many laboratories, never been in touch with mass spectrometry before, produce isotope data with an ICPMS. Especially for such user isotope reference materials (IRM) are indispensable to enable a reliable method validation. The fast development and the broad availability of ICPMS also lead to an expansion of the classical research areas and new elements are under investigation. Here all users require IRM to correct for mass fractionation or mass discrimination or at least to enable isotope data related to a common accepted basis. Despite this growing interest suitable IRM are still lacking for a number of isotope systems such as magnesium.

For all isotope abundance ratio applications reference materials are necessary either for correction of mass fractionation/mass discrimination, for method validation or to provide a common accepted basis. The production of these urgently needed IRM, however, has stagnated within the past decades. Reasons might be that the scientific relevance often has not been realized; time and effort seemed not in balance with the scientific gain. Recently the situation has changed slightly, as researcher at NIST resumed their work and BAM and NRC started working on IRM.

The needs for present research on isotope variations are being considered and are compared to the limitations of current isotope reference materials within this presentation. The resulting disagreement between both is being discussed and solutions will be provided.

## Geochemical consequences of thermomechanical processes in subduction zones. Implications for crustal making processes

KATHARINA VOGT<sup>1</sup>, TARAS GERYA<sup>1,2</sup>  
AND ANTONIO CASTRO<sup>3</sup>

<sup>1</sup>Swiss Federal Institute of Technology (ETH-Zurich), 8092  
Zurich, Switzerland

<sup>2</sup>Moscow State University, 119899 Moscow, Russia

<sup>3</sup>University of Huelva, 21071 Huelva, Spain

We have analyzed the dynamics of crustal growth processes at active continental margins based on a 2D coupled petrological-thermomechanical numerical model of an oceanic-continental subduction zone. The model includes spontaneous slab retreat and bending, dehydration of subducted crust, aqueous fluid transport, partial melting, melt extraction and melt emplacement in form of both extrusive volcanics and intrusive plutons.

Our results show that the rate of crust formation and the composition of newly formed crust are strongly depended on the degree of rheological weakening induced by fluids percolating from the subducting slab and upwards propagating melts. Subsequently we could identify the following geodynamic regimes: (i) stable arcs (ii) compressional arcs with plume development and (iii) extensional arcs.

Crust formation in stable arc settings is characterized by flattened intrusions and low crustal growth rates. At first dacitic melts are produced due to partial melting of the slab nose, followed by flux melting of wet peridotite. In compressional arcs the emplacement of hybrid plumes adds additional material to the continental crust. Partially molten rock melanges composed of basalts and sediments accumulate at asthenospheric depth forming plumes, which rise through the mantle prior to emplacement. We have calculated the isotopic initial ratios of Sr and Nd in the plume during the simulations, showing that the geochemical signature varies strongly with the basalt/(basalt+sediment) fraction in the plume. These signatures are transferred to andesitic magmas and finally confirm the geochemical signatures of the continental crust.

Crustal growth in extensional arc settings is accomplished by decompression melting of dry peridotite, leading to elevated crustal growth rates.

## Experimental weathering of micas in acid soils conditions: Contribution of boron isotopes

A. VOINOT<sup>1,2</sup> \*, D. LEMARCHAND<sup>1</sup>, M-P. TURPAULT<sup>2</sup>  
AND F. CHABAUX<sup>1</sup>

<sup>1</sup>LHYGES, CNRS-UDS, Strasbourg, France

(\*correspondence: alexandre.voinot@etu.unistra.fr)

<sup>2</sup>BEF, INRA, Champenoux, France

Soil minerals evolve by contact with weathering agents (protons, organic acids and ligands) supplied by atmospheric inputs or produced by coexisting living organisms. Determination of their relative contribution and seeing if they interact with soil minerals through different mechanisms is a key step toward identification of the pedogenic processes in action and soil sustainability.

In order to test if different weathering agents can induce specific and traceable mechanisms (dissolution vs. transformation), we lead a series of laboratory experiments intended to investigate the behavior of phyllosilicate minerals in contact with 3 different chemical reactants: HCl (protons), citric acid (organic acids) and siderophores (ligands). These experiments were performed at 2 different pH conditions (pH3 and pH4.5) for 37 days at 20°C in a continuous flow system. Biotite was selected as test mineral because it is a common and reactive mineral in soils. To trace weathering reactions, we monitored the boron chemical and isotopic compositions in the outflowing solutions. The choice of B as weathering proxy is based on its balanced distribution between minerals sites (interlayers and tetrahedral sites). Moreover, each of these sites have distinct B isotopic signatures [1], in line with the large isotopic fractionation generated by weathering reactions [2].

Comparison of B and major elements in solution reveals that all experiments conducted at pH3 and citric acid at pH4.5 lead to predominant dissolution reactions. By contrast, reactions conducted at pH4.5 with HCl and siderophores show a large removal of isotopically fractionated boron, indicating a predominant contribution of interlayer sites and a large transformation (vermiculitization) of the biotite.

[1] L. B. Williams *et al.* (2001) *Geochimica et Cosmochimica Acta* **65**, 1769–1782. [2] D. Cividini *et al.* (2010) *Geochimica et Cosmochimica Acta* **74**, 3143–3163.

## Proterozoic magmatism

O. VOLCAN

oasisvolcan@yahoo.com

Proterozoic magmatism along the margin of the Yangtze Block is extensive and provides important evidence in the plate tectonic reconstructions for the Proterozoic. The wangcang area on the northwestern margin of the Yangtze Block consists of complex Archean to early Proterozoic crystalline basement and a suite of high-grade metamorphic rocks surrounded by late Neoproterozoic to Phanerozoic sedimentary covers. In the the northwestern margin of the Yangtze craton there were found many bodies as tectonic blocks of greenschist rocks, which were named Hekou Formation. Single-grains zircon U–Pb TIMS dating of andesite-dacite indicates that the Hekou Formation erupted at  $882 \pm 69$  Ma. This is a new time for volcanics rocks found along the margin of the Yangtze Block.

## Spatial pollution gradients in Central Europe after 25 years of decreasing industrial emissions

P. VOLDRICHOVA<sup>1,2\*</sup>, M. NOVAK<sup>1</sup>, L. ERBANOVA<sup>1</sup>,  
E. PRECHOVA<sup>1</sup>, F. VESELOVSKY AND V. BLAHA<sup>1</sup>

<sup>1</sup>Department of Geochemistry, Czech Geological Survey,  
Geologická 5, 152 00 Prague 5, Czech Republic  
(\*correspondence: petra.voldrichova@geology.cz)

<sup>2</sup>Department of Analytical Chemistry, Faculty of Science,  
Charles University in Prague, Albertov 6, 128 43 Prague  
2, Czech Republic

Industrial pollution in the Czech Republic (Central Europe) peaked in the mid-1980s. Soft coal combustion in the north of the country was one of the largest sources of many trace elements for the atmosphere and ecosystems. Introduction of more advanced technology in the 1990s led to a steep decrease in nationwide industrial emission rates of pollutants. In the mid-1980s, the Northern Czech Republic was 4 to 10 times more polluted than the Southern Czech Republic, which is less industrialized. In 2009, we established a new network of 10 monitoring stations near the borders between the Czech Republic, Germany, Austria and Poland. Samples of vertical and horizontal atmospheric deposition (snow and ice accretions, respectively) are collected each winter (Oct. 15- April 15). Monitoring sites are situated on mountaintops at an elevation of 1000 m. All samples are treated in a clean laboratory (class 7). Concentration of 19 elements (Al, As, Bi, Be, Cu, Co, Cr, Cd, Fe, Mn, Ni, Pb, Sb, Sc, Ti, Th, U, V, and Zn) is determined using SF ICP MS. Preliminary data from 2009 suggest that, for most of the environmentally relevant elements, spatial pollution gradients differ from previous decades. For example, for arsenic (As) and lead (Pb), the eastern part of the country (Jeseniky and Beskydy Mts.) exhibits the highest pollution loads. At the same time, the northern and southern part of the country show lower pollution loads. The northern part of the country, situated near a cluster of coal-burning power plants, experienced a faster decrease in pollution rates over the past 25 years than the south; its current atmospheric deposition is not significantly higher than in the south. For antimony (Sb), all 10 sites have similar atmospheric inputs. For zinc (Zn), the highest concentrations in atmospheric input were found in the northwest. Novohradské Mts. (south) have similar Zn inputs as Jizerské Mts. (north). Overall, pollution levels are up to 20 times lower compared to the late 1980s. They are more site-specific, and reflect temporal changes in operation of distant vs. local point sources of pollution.

## The Paleozoic $\delta^{88/86}\text{Sr}_{\text{seawater}}$ record – Quantifying carbonate production rates at mass extinction events

H. VOLLSTAEDT<sup>1\*</sup>, A. EISENHAEUER<sup>1</sup>, F. BÖHM<sup>1</sup>,  
J. FIETZKE<sup>1</sup>, A. KRABBENHÖFT<sup>1</sup>, V. LIEBETRAU<sup>1</sup>,  
J. FARKAS<sup>2</sup> AND J. VÉIZER<sup>3</sup>

<sup>1</sup>Leibniz-Institut für Meereswissenschaften (IFM-GEOMAR),  
Wischhofstr. 1-3, D-24148 Kiel, Germany  
(\*correspondence: hvollstaedt@ifm-geomar.de)

<sup>2</sup>Czech Geological Survey, Geologická 6, 152 00 Praha 5,  
Czech Republic

<sup>3</sup>University of Ottawa, Dept. of Earth Sciences, 140 Louis  
Pasteur, Ottawa, Canada K1N 6N5

Within the Phanerozoic Eon strata boundaries are often associated with the extinction of marine organisms. The reasons for these events are still discussed and a quantification of observed changes in the marine carbonate system is missing.

Strontium (Sr) is one of the most important divalent cations in calcium carbonate minerals and a carrier of important proxy information. In terms of the Sr output flux of the ocean ( $\delta^{88/86}\text{Sr}_{\text{seawater}}$ :  $\sim 0.39\%$ ), isotopically light carbonates ( $\delta^{88/86}\text{Sr}_{\text{carbonates}}$ :  $\sim 0.15 - 0.25\%$ ) represent the major Sr sink. Consequently, variations in Sr/Ca and paired  $^{87}\text{Sr}/^{86}\text{Sr}$ - $\delta^{88/86}\text{Sr}$  values are a suitable tool to investigate the global carbonate budget throughout Earth's history including the biotic turnover of calcifying organisms at stratigraphic boundaries. Latter processes are expected to have a large influence on Sr geochemistry and isotope composition of seawater.

We measured paired  $^{87}\text{Sr}/^{86}\text{Sr}$ - $\delta^{88/86}\text{Sr}$  ratios of  $\sim 120$  modern and Paleozoic marine brachiopod samples which were screened for diagenetic alteration prior to the measurement. Reproducibility of double spike-derived  $\delta^{88/86}\text{Sr}$  based on an international coral carbonate standard (JCP-1) is  $0.019\%$  (2SD, n=26).

We observe major drops in  $\delta^{88/86}\text{Sr}_{\text{seawater}}$  of  $0.05 - 0.15\%$  at mass extinction events which coincide with a decrease of 10-50% in the number of marine genera [1]. This emphasizes the strong coupling of the carbonate system to  $\delta^{88/86}\text{Sr}$  of seawater. In contrast,  $\delta^{44/40}\text{Ca}_{\text{seawater}}$  changes are much less pronounced at these biotic turnovers. Furthermore, excursions in  $\delta^{13}\text{C}_{\text{carbonate}}$  at strata boundaries are related to changes in the organic carbon production rather than to the carbonate production.

By taking changes in  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{88/86}\text{Sr}$  and Sr/Ca into account we are able to make quantitative statements on the Sr input and output fluxes of the ocean at the major Paleozoic mass extinction events, including the Permian/Triassic boundary.

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## Unconventional matrices prevent novel isotopes turning traditional

F. VON BLANCKENBURG<sup>1</sup>, J. BOUCHEZ<sup>1</sup>,  
M. GUELKE-STELLING<sup>2</sup>, M. OELZE<sup>1</sup>,  
C. OSTERTAG-HENNING<sup>3</sup>, J. SCHUESSLER<sup>1</sup>  
AND G. STEINHOEFEL<sup>1</sup>

<sup>1</sup>Earth Surface Geochemistry at GFZ German Centre for  
Geosciences, Potsdam, Germany (fvb@gfz-potsdam.de)

<sup>2</sup>KIT, Mineralogy and Geochemistry, Karlsruhe, Germany

<sup>3</sup>Bundesanst. Geowiss. Rohstoffe BGR, Hannover, Germany

Do 'non'-traditional isotopes still deserve their prefix? It only takes a look at your preferred stable isotope systems compilation to realise that variations are largest in the biosphere and its geologic derivatives. Hence, to move the field into the next decade, and beyond the Geosciences, we need to develop tools to cater for matrices that are by any geological standard non-traditional. Here we review progress on this effort from our laboratories' past years work.

### Biomedical

Metal isotopes are superb tools to trace the process and timing humans metabolize nutrients. Each human bears a distinct stable Fe isotope signature in its blood, which is identical to that in muscle tissue and that of blood plasma, suggesting that this characteristic ratio is set when Fe is received by the transferrin molecule during intestinal absorption.

### Plant Physiology and human nutrition

Higher plants induce substantial fractionation of Mg, Si, Ca, Fe, and Zn isotopes. Fe isotope fractionation has been shown to differ between grasses and non-grasses, where the former are enriched in light Fe through reduction in soils, and the latter take up unfractionated complexed Fe(III). Plants induce similar fractionation as metals are being moved through their tissue.

### Crude oil

First results of various types of crude oil yielded surprisingly heavy Fe isotope compositions, tracing bacterial iron oxidation/reduction processes during oil biodegradation in the reservoirs.

### Weathering at the micrometer scale

The large diversity of weathering and biotic products in soils requires detection of their isotope variability at the micro-scale. We have now developed a second-generation UV-femtosecond laser ablation system, and measure novel stable isotopes in bulk soil (as fused glass beads or powder pellets), at the mineral scale in thin sections, individual phytoliths, and by ablating fluids after element separation and evaporation.

The challenge to all these cases is to (1) develop tailor-made matrix-suited methods; (2) demonstrate that the analyses are free of artefacts, requiring reference materials; (3) understand the underlying processes - the ultimate aim.

## The <sup>10</sup>Be(meteoric)/<sup>9</sup>Be ratio as a tracer of weathering and erosion

F. VON BLANCKENBURG\*, H. WITTMANN  
AND N. DANNHAUS

Earth Surface Geochemistry at GFZ German Centre for  
Geosciences, Potsdam, Germany

(\*correspondence: fvb@gfz-potsdam.de)

We provide a systematic framework to derive weathering and erosion rates from the ratio of the meteoric cosmogenic nuclide <sup>10</sup>Be to stable <sup>9</sup>Be, suggested to serve as proxy for weathering and erosion over the late Cenozoic [1].

In a weathering zone some of the <sup>9</sup>Be, present in silicate minerals, is released and partitioned between a reactive phase (adsorbed to clay and hydroxide surfaces), given the high partition coefficients at intermediate pH, and to a minor degree into the dissolved phase in pore waters. The combined mass flux of both phases is defined by the soil formation rate times a mineral dissolution rate – and is hence proportional to the chemical weathering rate. The surface of the weathering zone is continuously exposed to fallout of meteoric <sup>10</sup>Be. This <sup>10</sup>Be percolates into the weathering zone where it mixes with dissolved <sup>9</sup>Be. Both isotopes may exchange with the adsorbed Be, given that equilibration rates of Be are fast relative to soil residence times. Hence a <sup>10</sup>Be/<sup>9</sup>Be (reactive) ratio results from which the <sup>9</sup>Be weathering flux can be calculated given that the delivery rate of <sup>10</sup>Be is now often known. If the loss of <sup>10</sup>Be into the dissolved phase is furthermore small, the ratio of <sup>10</sup>Be (reactive) to that of the residual mineral-bound <sup>9</sup>Be provides a physical erosion rate.

We have tested this approach in sediment of the Amazon and Orinoco basin, and compared it to dissolved Be isotope data [2]. The reactive Be was extracted from sediment by combined hydroxylamine and HCl leaches. In the Amazon trunk stream, the Orinoco, Apure, and La Tigra river <sup>10</sup>Be/<sup>9</sup>Be (dissolved) agrees well with <sup>10</sup>Be/<sup>9</sup>Be (reactive), showing that in most rivers these two phases also equilibrate. <sup>10</sup>Be/<sup>9</sup>Be ratios range from  $5 \times 10^{-9}$  for the Brazilian shield rivers to  $2 \times 10^{-10}$  for the Beni river draining the Andes, corresponding to denudation rates of 0.01mm/yr for the shields and 0.5mm/yr for the Andes, compatible with denudation rates from *in situ*-produced cosmogenic <sup>10</sup>Be [3]. 10-50% of the <sup>9</sup>Be was mobilised from bedrock.

Once delivered to the ocean, this riverine Be, be it dissolved or reactive, will eventually drive <sup>10</sup>Be/<sup>9</sup>Be ratios of ocean water and disclose global weathering rates.

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## Apatite composition of Southern Germany volcanoes: Clues to origin and magmatic evolution

A. VON DER HANDT<sup>1</sup> AND M.K. RAHN<sup>2</sup>

<sup>1</sup>Geowissenschaftliches Institut, University of Freiburg 79104 Freiburg, Germany

<sup>2</sup>Swiss Federal Nuclear Safety Inspectorate (ENSI), 5200 Brugg, Switzerland

Volcanic activity in SW Germany has focussed along the Upper Rhine graben (with volcanic centres at Kaiserstuhl and Odin's Forest). In addition, eruptive centres are also found far away from known tectonic lines in the Urach and Hegau areas. Dating of these rocks reveals an extended period of activity along the Upper Rhine graben (60-15 Ma [1]), while activity in isolated centres was relatively short (Kaiserstuhl: 16-19 Ma [1, 2], Hegau: 15-7 Ma [3, 4], Urach: 17-? Ma [5]).

Apatite is a common mineral in many of the eruptive products, which are mostly of mafic to ultramafic as well as carbonatitic composition. Previous studies on these apatites (e.g. Rahn and Selbekk 2008) have shown that their composition is variable with respect to Si and S (replacing P) as well as OH and Cl (replacing F). Thus the question arises whether apatite could be used as an indicator of magmatic evolution and whether there are clear differences to be found, which allow a distinction between the Kaiserstuhl, Hegau and Urach eruptive centres on the basis of apatite composition.

In order to evaluate the compositional evolution, apatites from the Kaiserstuhl and Hegau were dated using the fission track technique. Dated samples were analysed by means of EPMA and SIMS to obtain major and trace element data and check for sample internal variation. Both, Kaiserstuhl and Hegau volcanics show a large compositional range from F-rich to OH-rich chemistry, with Cl-endmember lower than 5%. Apatites close to OH endmember are restricted to samples from the Hegau. A clear distinction of sources is possible on the basis of Sr, Zr and REE element contents. Hegau apatites show a wider spread in magmatic REE fractionation, together with flatter chondrite REE patterns. Combination of age and compositional data allows to clearly attribute distant tuff layers to the Hegau, while no such layers show Kaiserstuhl characteristics. Erupted material from the Hegau has faced up to 80 km of westward air transportation.

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## Chemical speciation of Fe-rich colloids and nanoparticles in the Southern Ocean

B.P. VON DER HEYDEN<sup>1\*</sup>, A.N. ROYCHOUDHURY<sup>1</sup> AND S.C.B. MYNENI<sup>2</sup>

<sup>1</sup>Dept. of Earth Sciences, Stellenbosch University, Stellenbosch 7602, South Africa  
(\*correspondence: bvon@sun.ac.za)

<sup>2</sup>Dept. of Geosciences, Princeton University, Princeton, NJ 08544, USA

Iron is an important nutrient and limits the productivity in the Southern Ocean. Previous biogeochemical studies largely focused on the size-dependent Fe-pools in ocean water with little attention to the chemical speciation of iron. As a result, molecular level factors affecting the bioavailability of particle-bound iron are largely unexplained.

Using clean techniques, samples were collected along two transects between Cape Town, Antarctica and the South Georgia Islands. Iron particles were trapped on 0.2µm filters and subsequently analyzed in their pristine state using *in situ* L-edge XANES spectroscopy and high-resolution scanning transmission X-ray microscopy. Chemical speciation of the discreet, quasi-spherical particles was accomplished through a combination of the spectral shape analysis and the quantitative parameterization of the L<sub>3</sub>-edge splitting.

From these spectroscopic analyses, particles in Southern Ocean could be classified into five broad categories including ferric oxides, magnetite, other mixed valence species and at least two ferrous species. A distinct spatial variation in iron speciation was also evident with ferric species predominating in the mid-latitudes (32°S- 55°S) and ferrous-rich species more common in the high latitudes. A number of mixed-valence species, including magnetite, made up a significant proportion of the particles found to the north of the Polar Front. Proximal to the African- and South Georgian shelves, Al-substitution, a solubility-depressing effect, was observed to occur in the ferric species. The substituted Al in iron oxides displayed a gibbsite-like structure.

We are currently evaluating the cause of this spatial and chemical variability, which may be attributed to the particle source, and to a range of processes including photochemical response and biological interactions. However, it is clear that such variability in speciation will have a profound impact on Fe solubility and iron-ligand interaction, thereby influencing the Fe-pool that is bioavailable.

## Clay mineralogy and chemical environment of an Aptian lacustrine succession in North-Eastern Brazil

W. VORTISCH<sup>1\*</sup>, V.H. NEUMANN<sup>2</sup>, R. GRATZER<sup>1</sup>  
AND D. ROCHA<sup>2</sup>

<sup>1</sup>Montanuniversität Leoben, 8700 Leoben, Austria

(\*correspondence: Walter.Vortisch@unileoben.ac.at,  
gratzer@unileoben.ac.at)

<sup>2</sup>Universidade Federal de Pernambuco, Dep. de Geologia,  
Recife, Brazil (neumann@ufpe.br, dunaldson@msn.com)

The studied core was drilled in the Jatobá Basin, which is underlain and surrounded by the crystalline basement of the Borborema Province (NE Brazil).

113 samples were analysed by X-ray diffractometry, 17 of which were selected for clay mineral analysis. Sandstones were also studied by polarising microscopy and scanning electron microscopy.

Petrographically, 5 lithotypes can be defined: (1) generally silty grey shales, (2) grey marly shales to shaly marls, (3) generally fine-grained, argillaceous sandstones (4) micritic limestones, occasionally with a minor content of dolomite, (5) dolostone (dolomite > calcite).

In many of the shales, expandable clay minerals are dominant among the clay mineral suite (predominantly illite-smectite), followed by illite, kaolinite and chlorite.

In contrast to the shales, sandstones can contain considerable amounts of smectite, besides illite and minor proportions of kaolinite and chlorite. Quartz and feldspars are usually main components. Calcite is sometimes present. Some of the sandstones show high contents of unweathered biotite, often marking sedimentary structures like ripple crossbedding as dark layers.

The presence of chlorite and biotite as clastic components, indicate mild regional weathering, and/or fast erosion and transport to the lacustrine basin. Smectite occurring in the sandstones indicates volcanic activity.

The occurrence of dolomite is uncommon for lacustrine freshwater environments. Freshwater conditions are indicated by oxygen isotopes [1] and ostracods. The occurrence of dolomite together with high organic matter content and intensive bacterial activity may explain lacustrine dolomite formation without evaporitic conditions.

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## Constraining subannual variability in river chemistry and hydrology with <sup>87</sup>Sr/<sup>86</sup>Sr: A case study in the Fraser River basin, Canada

B.M. VOSS<sup>1,2\*</sup>, B. PEUCKER-EHRENBRINK<sup>1</sup>,  
T.I. EGLINTON<sup>1,3</sup>, S.L. GILLIES<sup>4</sup>, S. MARSH<sup>4</sup>,  
A. JANMAAT<sup>4</sup>, B. DOWNEY<sup>4</sup>, J. FANSLAU<sup>4</sup>, H. FRASER<sup>4</sup>  
AND G. MACKLAM-HARRON<sup>4</sup>

<sup>1</sup>WHOI, MS 25, Woods Hole, MA 02543, USA

(\*correspondence: bvoss@whoi.edu)

<sup>2</sup>MIT, Cambridge, MA 02139, USA

<sup>3</sup>ETH, Zürich 8092, Switzerland

<sup>4</sup>UFV, Abbotsford V2S-7M8, Canada

River systems present a significant challenge to quantification of global elemental fluxes among atmospheric, terrestrial, and marine reservoirs, as aquatic passageways exhibit complex processing and storage of material on timescales driven by local and distant climatic and geophysical cycles [1-3]. The Fraser River basin in southwestern Canada has three important features making it ideal for testing geochemical approaches to tackling these issues: 1) its moderate size and temperate climate are neither exceptional nor insignificant among global rivers; 2) a spectacular diversity of bedrock geology and vegetation allow for discrimination of sources of transported material; and 3) its modest industrial footprint allows for assessment of relatively unperturbed processes. Three recent field campaigns at low, medium, and high water flow have generated a broad dataset of informative geochemical parameters. Dissolved <sup>87</sup>Sr/<sup>86</sup>Sr signatures of major tributaries and daily discharge data form the backbone of a preliminary attempt to model the geochemical variability of exported material across the hydrograph. Over one full year of time series sampling near the Fraser mouth has demonstrated that subannual variability in dissolved <sup>87</sup>Sr/<sup>86</sup>Sr is significant and mirrors temporal and spatial changes in the hydrology of the basin. Extending this approach to other elemental fluxes of interest and other river basins will vastly improve global biogeochemical budgets and the potential to predict future changes.

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## Review of geochemical problems and mitigation during the production of geothermal reservoirs

FRANCOIS-D. VUATAZ AND NIELS GIROUD

Laboratory for Geothermics - CREGE, University of Neuchatel, CH-2000 Neuchatel, Switzerland  
(francois.vuataz@unine.ch)

### Introduction

In many geothermal fields worldwide, production and reinjection of hot brines modify the temperature and pressure conditions around the wells. This induces geochemical processes within the reservoir and/or along the well casings and the surface pipelines. Some geothermal fluids are relatively benign even at high temperature, whereas others can cause numerous problems due to either a high salinity or a high content of particular gases or dissolved solids. Permeability decrease, well and pipeline partial plugging or metal corrosion are the main consequences of these chemical processes. If they are not taken seriously into consideration and solved, the outcome can be a production decrease, a high maintenance cost, or even the loss of a well.

### Mineral scaling

Due to the high solubility of silica at high temperature, silica scaling is a frequent problem in geothermal plants. Amorphous silica precipitates after flashing or cooling of the fluid in surface pipelines or reinjection wells. Silica can be removed from the fluid and exploited commercially as a by-product. Carbonate scaling occurs in carbonate reservoirs and CO<sub>2</sub>-rich fluids. Other minerals can form scales, such as anhydrite, sulphides and oxides.

### Metal corrosion

Various types of corrosion are observed on well casings and surface pipelines, due to dissolved H<sub>2</sub>S and CO<sub>2</sub>, high chloride content or gas exsolution. Numerous laboratory experiments on the corrosion processes have been performed, but the results often differ from on-site monitoring experiments of the corrosion processes.

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## Liquid carbonates investigated by First-principles Molecular Dynamics simulations

R. VUILLEUMIER<sup>1\*</sup>, A. SEITSONEN<sup>2</sup>, N. SATOR<sup>3</sup>  
AND B. GUILLOT<sup>3</sup>

<sup>1</sup>Ecole Normale Supérieure, Département de Chimie, UMR 8640 CNRS-ENS-UPMC, 24, rue Lhomond, 75005 Paris, France (\*correspondence: rodolphe.vuilleumier@ens.fr)

<sup>2</sup>Physikalisch Chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland (Ari.P.Seitsonen@iki.fi)

<sup>3</sup>Laboratoire de Physique Théorique de la Matière Condensée, Université Pierre et Marie Curie (Paris 6), UMR CNRS 7600, case courrier 121, 4 place Jussieu, 75252 Paris cedex 05, France (sator@lptmc.jussieu.fr, guillot@lptmc.jussieu.fr)

The Earth mantle is mainly composed of silicates and its carbon contents is very low, of the order of 10 to 500 ppmw [1]. However carbon and its oxidized forms as carbonates and CO<sub>2</sub>, likely play a crucial role in the dynamics and chemical differentiation of the mantle. The onset of partial melting at about 300km deep in the mantle, corresponds to the formation of liquid carbonates or carbonatites. In the asthenosphere, the observed electrical conductivity anomalies [2] could originate from carbonatitic magmas exhibiting a very large conductivity, about 100 to 100 000 times that of olivine. However the physical and chemical properties of carbonatites at mantle conditions are poorly known and some theoretical guidance could be useful in this context.

We present a First-principles Molecular Dynamics simulation study of liquid CaCO<sub>3</sub>. Its structural and transport properties have been investigated in the (T, P) range 1000–2000K and 0–6 GPa. Diffusion constants are found in good agreement with available data on viscosity [3]. Surprisingly CO<sub>3</sub><sup>2-</sup> units diffuse nearly as fast as the Ca<sup>2+</sup> cations. Because of the fast dynamics into the melt it was also possible to estimate the ionic conductivity. For the investigated thermodynamic conditions, we found an ionic conductivity close to 100 S. m<sup>-1</sup>, in agreement with the available experimental data [2]. The local structure around the CO<sub>3</sub><sup>2-</sup> anions has been studied in details and appears to be quite complex, sharing some similarities with the crystalline polymorphs calcite and aragonite. Simulation data on vibrational spectroscopy of liquid CaCO<sub>3</sub> will also be presented.

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## A low sulphur epithermal gold mineralisation in Kısacık-Ayvacık area (Çanakkale-Turkey)

ALAADDIN VURAL<sup>1</sup>, DOĞAN AYDAL<sup>2</sup>  
AND İBRAHİM AKPINAR<sup>1</sup>

<sup>1</sup>Gumushane University, Engineering Faculty, Geological Engineering Department, Bağlarbasi, 29100, Gumushane, Turkey (\*correspondence: vural@gumushane.edu.tr) (hiakpinar@gumushane.edu.tr)

<sup>2</sup>Ankara University, Engineering Faculty, Geological Engineering Department, 06100, Tandoğan, Ankara, Turkey (aydal@ankara.edu.tr)

Kısacık-Ayvacık area is located in northern part of Küçükkuşu (Çanakkale), town within Biga Peninsula, northwestern Anatolia, Turkey. In general, throughout the area magmatic rocks and ultramafic rocks, sporadically at their contacts, are seen.

The purpose of this work is to investigate the occurrences conditions, types, places of gold enrichment and probing the genetics of gold enrichment in Kısacık-Ayvacık area along with outlining alteration distribution, petrographic and ore mineralogy features of the rocks in the region. In general, Pre-Tertiary rock units of Kazdağı Group and ophiolitic melange, and Tertiary magmatic rocks consisting altered haematitized-silicified andesite, rhyolite, ignimbrite, quartz porphyry and pyroclastic rocks are present. These rocks have subalkaline composition, nevertheless showing a calcalkaline tendency.

The gold mineralizations in Kısacık-Ayvacık area are observed within altered volcanic rocks of dacite, andesite and tuffs. These rocks have galena, pyrite, chalcopyrite, graphite, and haematite minerals and mineralisation of invisible gold enrichment. Gold values in studied volcanic rocks changes between 40 ppb-8500 ppb. Occurrences temperatures of gold mineralizations change between 190 °C and 290 °C, salinity 0-7 % NaCl and S isotope values are mostly near zero. Consequently, these values imply a low-sulphidized epithermal type gold mineralization in the study area.

## Application of experimental mineralogy to the description of new platinum-group minerals

A. VYMAZALOVÁ<sup>1\*</sup>, M. DRÁBEK<sup>1</sup> AND F. ZACCARINI<sup>2</sup>

<sup>1</sup>Czech Geological Survey, Geologická 6, 152 00 Prague 5, Czech Republic

(\*correspondence: anna.vymazalova@geology.cz)

<sup>2</sup>University of Leoben, Peter Tunner Str.5, A8700 Leoben, Austria (federica.zaccarini@unileoben.ac.at)

According to [1] there are more than 500 platinum-group (PG) phases termed as unidentified and require complete or clearer identification to be approved as new mineral species, in particular crystallographic characterization is often missing. One of the significant tools enabling the better characterisation of a natural phase can be an application of a synthetic material. The advantage is that the synthetic PG-phases are prepared in a required amount, under controlled chemical and physical parameters, such as chemical composition and temperature. The synthetic PG-phase can be thus applied as a comparative and descriptive material of a natural analogue. Such approach has been used in case of description of milotaite (PdSbSe) [2] or pašavaite (Pd<sub>3</sub>Pb<sub>2</sub>Te<sub>2</sub>) [3]. The synthetic material should display the identical optical and physical (microhardness and reflectance) properties and chemical identity with natural sample. Significant role plays the structural identity of natural and synthetic material that has to be also proved. Electron back-scattering diffraction (EBSD) study can be applied to support structural identity. Furthermore the Raman spectroscopy, a nondestructive, structurally sensitive technique, suitable for grains of small mineral size (less than 10 microns) such as those of PGM is a sufficient method to prove structural identity.

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