

**Geochemical mapping of the
Collahuasi District, N. Chile:
A pilot study for a geochemical atlas
of the Andes**

C.J. OATES¹, S. HART², J.A. PLANT² AND
N. VOULVOULIS²

¹Anglo American plc, London, United Kingdom
(COates@angloamerican.co.uk)

²Department of Earth Science and Engineering, Imperial
College, London, SW7 2BP, UK
(jane.plant@imperial.ac.uk; n.voulvoulis@imperial.ac.uk)

A geochemical baseline survey of the Collahuasi District, N. Chile has been completed based on systematic regional rock and soil sampling. The Collahuasi district hosts 3 major Cu porphyry centres, Rosaria, Ujjina and Quebrada Blanca which are now being mined for Cu and Mo. Approximately 1100 lithochemical whole rock samples were collected on a grid averaging 1-2 sq. kms. over an area of 1500 sq. km and about 250 soil samples were collected over part of the grid, centred on Rosario and covering about 650 sq. km. Approximately 74 chemical elements were determined on whole rock samples by ICPMS and ICPOES and 65 elements on soil samples after aqua regia extraction. All the methods used were those specified by the global geochemical baseline programme for mountainous terrains.

The data are shown to be of value for exploration, lithochemical mapping and understanding the geochemical and metallogenic evolution of the district as well as for environmental purposes. For example high field strength elements can be used to prepare lithological maps in areas where the bedrock geology is poorly known while large ion lithophile elements can be used to map regional hydrothermal alteration. The rock and soil data have been compared to international soil guideline values for chemical elements from N. America and Europe and the ratio of the concentration in soils has been compared to that in rocks for all elements. The results show that even in rock samples away from mineralisation values for several elements exceed all guidelines for part of or the entire district. This observation is critically important in setting guideline values which should more fully take account of bedrock geology.

The results show that a lithochemical atlas of the Andes would define the chemistry of mineralised districts, and the potential for new exploration targets as well as providing an environmental baseline against which to study human health and environmental impacts, including from future mining.

**Constraints on the exhumation
history of the Torres del Paine**

ROLAND OBERHÄNSLI¹, UWE ALTENBERGER¹,
MASAFUMI SUDO¹, LUKAS BAUMGARTNER² AND
BENITA PUTZLITZ²

¹Institute of Geosciences, University of Potsdam, Am Neuen
Palais 10, 14415 Potsdam, Germany

²Institute of Mineralogy and Geochemistry, Université de
Lausanne, Anthropole, 1015 Lausanne, Switzerland

During field investigation on the contact metamorphism and intrusion emplacement on the Torres del Paine laccolith we found samples of suspiciously fresh scoria. These scoria were only found in two distinct steep gullies in the Eastern part of the Torres del Paine laccolith. They occur in the side valleys of Valle Ascencio, Northeast of Monte Almirante in Valle del Mirador as well as North of the Torre del Paine peaks in Valle del Silencio. The two localities relate to each other by a NW-SE running fault system. In Valle del Silencio the scoria is found close to a dike that can be followed from the southern side moraine in the valley running steeply upwards to form a steep cut just north of Torre Monzino. The same holds true for the Valle del Mirador. A dike is running into a notch giving access to the east crest of Monte Almirante. Samples can only be found along the dike gullies above the moraine deposits and below an altitude of 1760 m. At both sampling locations this altitude corresponds roughly to a position in the middle of the intrusion. Since we find scoriae this altitude marks a paleosurface and thus allows using the age constraints by Ar/Ar dating of the scoria in combination with data on age and the depth of intrusion of the Paine laccolith to constrain the exhumation history of the Paine laccolith. The finding of scoria indicates a surface that must be discussed in the light of the glaciation history.

Driekop platinum pipe, Bushveld Complex, South Africa: New insights

T. OBERTHÜR¹, N.S. RUDASHEVSKY²,
V.N. RUDASHEVSKY², L.J. CABRI³, F. MELCHER⁴,
H. KOCKS⁴, J. LODZIAK⁴ AND D. KLOSA⁴

¹BGR, Stilleweg 2, D-30655 Hannover, Germany
(thomas.oberthuer@bgr.de)

²Center for New Technologies (CNT), Grazhdansky Prospect
14, 194220, St.Petersburg, Russia

³CNT Mineral Consulting Inc., 99 Fifth Avenue, Suite 122,
Ottawa, Ontario, Canada K1S 5P5 (lcabri@sympatico.ca)

⁴BGR, Stilleweg 2, D-30655 Hannover, Germany
(f.melcher@bgr.de; h.kocks@bgr.de)

The genesis of the platiniferous pipes of the eastern Bushveld Complex is still enigmatic. Orthomagmatic, metasomatic replacement, and hydrothermal models were proposed (Scoon and Mitchell 2004), however, advance on the understanding of the pipes is hampered by the fact that these orebodies were mined out early in the last century and limited material is available from museum collections only.

Our interest in the pipes was sparked off by investigations of detrital PGM in the Bushveld river systems (Oberthür *et al.* 2004). The present paper reports on a sample from the Driekop Pipe (Wilhelmskopje) collected in 1926 (TU Berlin) and highlights the impact of using novel methods of ore treatment on investigations especially of noble metal ores.

The greenish-greyish, dense sample is a medium-grained dunite with accessory disseminated chromite and has an ore grade of 34.9 ppm Pt. Contents of the other PGE and gold are all <1ppm. Ten polished sections investigated by ore microscopy and SEM yielded a disappointing number of only 5 PGM grains (>50 µm), underlining theoretical data (Ney 1977) on comparable gold ores that, at an average grain size of 100 µm and at a grade of 100 ppm, about 5-10 polished sections are needed to detect one discrete grain of gold.

Therefore, a combination of novel methods was tested on a slab of the sample weighing 676 grams, namely electric pulse disaggregation (EPD), hydrosorption (HS) and preparation of monolayer polished sections (5 size fractions between <63 and >400 µm) for further studies. The results were compelling: At least 500 PGM grains were found in the fractions. Grain sizes range from ~10-330 µm (most common around 100 µm). Many grains are composite. Sperrylite is the dominant PGM (ca. 90%), followed by Pt-Fe alloy and another twelve rarer PGM species. Notably, geversite (c.f. Melcher and Lodziak 2007) is absent. Analytical procedures and new data from our ongoing studies will be presented.

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Testing the hotspot record for evidence of broad melting anomalies

J.M. O'CONNOR¹, P. STOFFERS², J.R. WIJBRANS²,
T.J. WORTHINGTON² AND W. JOKAT³

¹Vrije University Amsterdam, The Netherlands

²Institute for Geosciences, Christian-Albrechts-University,
Kiel, Germany

³Alfred Wegener Institute for Polar and Marine Research,
Bremerhaven, Germany

The notion of a mantle plume has long been that of a mushroom-like 'head' (LIP) and thin 'tail' structure (hotspot chain) rising from a deep thermal boundary layer, generally depicted as the core-mantle boundary. Drifting of tectonic plates over the narrow, presumably fixed, hotspots created by such plume 'tails' has long provided an elegant explanation for time-progressive lines of islands, seamounts and ridges. But a major problem cited for this 'standard' plume model is a lack of evidence in the volcanic record for head-and-tail upwellings.

New evidence from direct dating of the oceanic hotspot record is also suggesting that hotspot melting anomalies might be much broader than commonly inferred from the 'head-tail' plume model and the dimensions of individual seamount chains and aseismic ridges. For example, new age data show that the Galapagos Volcanic Province developed via the progression of broad regions of concurrent dispersed volcanism that we link to a correspondingly broad mantle melting anomaly (O'Connor *et al.*, submitted, 2007). Moreover, recent thermo-chemical numerical modelling is exploring scenarios where upwelling structures are more irregular in shape and behaviour compared to a classic thermal plume 'head-tail' (e.g., Farnetani and Samuel, 2006).

New strategies are therefore needed for investigating the hotspot volcanic record in order to better test the 'fixity' of hotspots and the mantle plume hypothesis. To this end we have recently sampled multiple seamount chains and ridges scattered across a broad region of the southern South Atlantic. Our focus is on investigating multiple hotspot chains stretching across a very broad region of the South Atlantic seafloor as a potentially useful way of testing 1) the new thinking that plume upwellings may differ from the classic 'head-tail' structure and 2) our evolving hypothesis that hotspot melting anomalies are much broader than suggested by regions of active volcanism marking the young ends of individual hotspot trails. A key component of this strategy is our IOPD proposal to drill Walvis Ridge once we have developed a fuller understanding of how Walvis Ridge fits with the predictions of the fixed hotspot and mantle plume hypotheses.

Mineralogical and geochemical study of airborne particulates (PM₁₀) in an urban environment

A. OEHLER¹, R. GIERÉ¹ AND P. STILLE²

¹Universität Freiburg, Germany (anja.oehler@email.de)

²Université de Strasbourg, CNRS-UMR 7517, Strasbourg, France

Airborne particulate matter (PM) is known to affect human health significantly. Especially the fine PM, with sizes <10 µm (PM₁₀), poses a considerable health threat, due to its ability to enter human lungs. Sources of anthropogenic PM₁₀ in the atmosphere include waste incinerators, traffic, and thermal power plants. Coal-fired power plants, for example, emit various distinct phases, including several types of crystalline metal sulphates (Gieré *et al.*, 2006). Knowledge of the identity and composition of individual particles is essential to predict their environmental behaviour.

The study focuses on PM₁₀ collected in the neighbored urban environments of Strasbourg (France) and Kehl (Germany). This urban area, situated on both sides of the river, Rhine is exposed to different PM sources such as a thermal power station, waste incinerators, and a steel plant. Our interest lies in the bulk chemical and mineralogical composition of the overall PM₁₀ in the city centre of Strasbourg and in the specific evolution of these compositions as function of distance from the steel plant. Pb, Sr and Nd isotope ratios of these emissions are already precisely identified and allow to be traced over more than 3km along the prevailing wind pathway (Lahd Geagea *et al.*, 2007). Thus, in this special case study we have a direct control of the origin of the PM₁₀ and can compare the PM₁₀ compositions with those of filter dust from the plant. The bulk chemical composition of PM₁₀ trapped on teflon filters is analyzed by using ICP-MS. Identification and characterisation of the mineral phases is performed using SEM techniques, which allow us to determine morphology and chemical composition of µm-sized individual particles. Preliminary results show that, in addition to soot and various silicate particles, metal sulphates are present in the PM.

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Do fluids flow through or around mineral grains?

ERIC H. OELKERS¹, CHRISTINE V. PUTNIS² AND ANDREW PUTNIS²

¹Géochimie et Biogéochimie Experimentale, LMTG, Université de Toulouse, CNRS, IRD, OMP, 14 ave Edouard Belin, 31400 Toulouse, France (oelkers@lmtg.obs-mip.fr)

²Institut für Mineralogie, Universität Münster, Correnstrasse 24, 48149 Münster, Germany

A large body of evidence demonstrates that mineral transformation commonly occurs through a dissolution/precipitation mechanism where 1) the fluid moves into the parent phase from its original surface and 2) the crystal structure is preserved between the parent and secondary phase (Putnis and Putnis, 2007). The goal of this study is to assess if a similar dissolution/precipitation mechanism can transport fluids through mineral grains where the driving force is either a pressure or a temperature gradient.

Calculations were performed using dissolution rates (c.f. Gislason *et al.*, 1997; Oelkers, 2001), aqueous diffusion coefficients (Oelkers and Helgeson, 1988), and mineral solubilities calculated using SUPCRT92 (Johnson *et al.*, 1992) as a function of temperature and pressure assuming that precipitation rates are consistent with Transition State Theory and the law of detailed balancing. Results show that the degree to which fluid 'flows' through minerals depends on the identity of the mineral. For example the calculated logarithm of water permeability (in Darcy) through quartz, assuming fluid flow is driven by an isothermal pressure gradient, is -10 at 200° C, increasing to -5 at 600-700° C. In contrast, the corresponding log permeability through enstatite is far higher increasing from -6 to -3 over this temperature range. Note at elevated temperatures these latter values are comparable to that of sandstones in sedimentary basins. Moreover, temperature gradients are, in general, more effective at provoking fluid flow due to the relatively stronger effect of temperature on solubility.

These calculations suggest that large quantities of fluid flow can occur through mineral grains at elevated temperatures due to either pressure or temperature gradients. The consequences of this fluid flow in terms of 1) isotopic reequilibration and 2) stability of fluid inclusions will be detailed.

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Accretion of terrestrial planets from oligarchs in a turbulent disk

M. OGIHARA¹, S. IDA¹ AND A. MORBIDELLI²

¹Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Japan (ogihara@geo.titech.ac.jp; ida@geo.titech.ac.jp)

²Observatoire de la Côte d'Azur, France (alessandro.morbidelli@obs-nice.fr)

Introduction

We have investigated the final accretion stage of terrestrial planets from Mars-mass protoplanets that formed through oligarchic growth in a disk comparable to the minimum mass solar nebula (MMSN), through N-body simulation including random torques exerted by disk turbulence due to Magneto-Rotational-Instability. For the torques, we used the semi-analytical formula developed by Laughlin *et al.* (2004). The damping of orbital eccentricities (in all runs) and type-I migration (in some runs) due to the tidal interactions with disk gas are also included.

Without any effect of disk gas, Earth-mass planets are formed in terrestrial planet regions in a disk comparable to MMSN but with too large orbital eccentricities to be consistent with the present eccentricities of Earth and Venus in our Solar system. With the eccentricity damping caused by the tidal interaction with a remnant gas disk, Earth-mass planets with eccentricities consistent with those of Earth and Venus are formed in a limited range of disk gas surface density ($\sim 10^{-4}$ times MMSN). However, in this case, on average, too many planets remain in terrestrial planet regions, because the damping leads to isolation between the planets.

Results

We have carried out a series of N-body simulations including the random torques with different disk surface density and strength of turbulence.

We found that the orbital eccentricities pumped up by the turbulent torques and associated random walks in semimajor axes tend to delay isolation of planets, resulting in more coagulation of planets. The eccentricities are still damped after planets become isolated. As a result, the number of final planets decreases with increase in strength of the turbulence, while Earth-mass planets with small eccentricities are still formed. In the case of relatively strong turbulence, the number of final planets are 4-5 at 0.5-2AU, which is more consistent with Solar system, for relatively wide range of disk surface density ($\sim 10^{-4}$ - 10^{-2} times MMSN).

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Distribution of mercury and methylmercury in deep-sea surficial sediments of the Mediterranean Sea

N. OGRINC^{1*}, J. KOTNIK¹, V. FAJON¹, D. KOČMAN¹, S. ŽIŽEK¹, M. HORVAT¹ AND N. PIRRONE²

¹Dept. of Environ. Sci., "J. Stefan" Institute, Jamova 39, 1000 Ljubljana, Slovenia (nives.ogrinc@ijs.si)

²CNR Iia, Institute for Atmospheric Pollution, 87036 Rende, Italy (n.pirrone@cs.ii.cnr.it)

This communication presents the results of the investigation of the distribution, speciation and methylation of mercury in sediments of the Mediterranean Sea. The samples were collected at different locations in the Western and Eastern Basin of the Mediterranean during the cruise of the Italian research vessel Urania in summer 2003 as part of MERCYMS project. Total mercury (Hg_T) and methylmercury (MeHg) in pore water and sediments were determined down the sediment profile and coupled with other biogeochemical parameters, including organic carbon content. The diffusive fluxes of Hg_T and MeHg were calculated to estimate the importance of sediment-water exchange as potential sources of Hg_T and MeHg. In addition, the radioactive isotope ^{197}Hg was used to determine the methylation potentials. The concentrations of Hg_T in sediments ranged between 0.06 and 2.23 nmol g^{-1} and vary irregularly with depth, which may reflect changes or redistribution during diagenetic processes. No correlation between Hg_T and organic carbon content was found, but a relatively high proportion of MeHg to Hg_T of approx. 2.0% was observed. The integrated flux of Hg_T was estimated to be 109 kmol $year^{-1}$ and agrees well with the mass balance calculation performed for total underwater emissions of Hg_T in the Mediterranean Sea of 80 kmol $year^{-1}$ by Rajar *et al.*, 2007. The emissions of MeHg were estimated to be 14 kmol $year^{-1}$ and indicate that deep-sea sediments could be an important source of the MeHg content in marine biota. It was found that accumulation of MeHg in surficial sediments of the Mediterranean is not directly related to the potential rates of bacterial Hg methylation. Much of the MeHg produced in the sediments is lost to the overlying water. Our results suggest that MeHg production depends on partitioning of Hg(II) influenced by the organic carbon content in the sediment. Reduction of organic carbon in sediment could increase pore water Hg(II) and enhance bacterial production of MeHg.

These are the main results of a first study performed on Hg speciation, partitioning and methylation potential in deep sea sediments, giving a new insight into deep sea Hg biogeochemical cycling.

Contrasting surface chemistry of adsorbed ions in iron oxyhydroxide coatings on feldspar grains in soils deposited over mineralized and unaltered granite in the Big Creek Mining District, Idaho, USA (ToF-SIMS analysis)

PATRICK F. O'HARA¹, DAVID H. KRINSLEY², GREGORY T. HILL³ AND STEPHEN GOLLEDGE⁴

¹Kaaterskill Exploration, 3260 Tower Rd, Suite E, Prescott, Arizona, USA, 86305

²Dept. of Geological Sciences, University of Oregon, Eugene, Oregon, USA, 97403-1272

³785 Andrew Lane, Reno, NV 89521

⁴CAMCOR, University of Oregon, Eugene, Oregon, USA, 97403

An existing hypothesis in applied geochemistry suggests that a variety of ions are absorbed on pre-existing iron and manganese oxyhydroxide coatings formed on mineral grains in soils, and that these ions move upward and laterally by vadose zone, vapour transport, electrochemical and biogeochemical processes to these depositional sites. Desorbants are used to selectively extract these ions from the grain coatings and the analytical results are used in conjunction with geospatial techniques to identify areas of potential mineralization. Feldspar grains from both samples were used to eliminate potential effects of confounding variables that may be associated with other minerals and surface coatings on those minerals. Elemental maps created by ToF-SIMS analysis indicate that hydrothermal trace elements associated with mineralization concentrate in iron oxyhydroxide coatings on feldspar grains in b-horizon soil developed over gold-silver mineralized and altered granite. Weathered pyrite is the probable source of iron oxyhydroxide mineral coatings in this soil. Elemental maps of arsenic, antimony, lead, and copper are variably present in coatings along flat grain surfaces, and are strongly enhanced in surface coatings located on grain corners. These elements are below detection in iron oxyhydroxide coatings on feldspar grains in b-horizon soils developed over an unmineralized granite outcrop located several kilometres from known geochemical anomalies or mineralized sites. Iron oxyhydroxide coatings on soil grains at the unmineralized site are related to weathering of biotite. These observations suggest that the depositional chemistry portion of the hypothesis is valid.

Catalytic potential of silicate, oxide and sulfide minerals for the abiotic polymerization of glycine under high pressure and temperature conditions

SHOHEI OHARA¹, TAKESHI KAKEGAWA¹ AND HIROMOTO NAKAZAWA²

¹Department of Earth and Planetary Materials Science, Graduate School of Science, Tohoku University, Sendai, Japan (ohara@ganko.tohoku.ac.jp)

²National Institute for Materials Science, Tsukuba, Japan

Polymerization of amino acids is the essential step for the origin of life. It is still uncertain if minerals had a progressive role for polymerization of amino acids in any ancient geological environments. Polymerization experiments of glycine, catalyzed by minerals, were performed under 150°C and 100 MPa for 8 days, using a test-tube type autoclave. Various sulfides (millerite, troilite, pyrite and sphalerite), magnetite and montmorillonite were mixed with glycine monomers in order to test if these minerals behave as the catalyzer to promote peptide formation. HPLC and LCMS analyses of the products showed that: (1) glycine in all the experimental runs polymerized from 2-mer to 11-mer; (2) the highest yield of oligopeptides was found in the sphalerite experiment; (3) cyclic anhydride was more abundant in the montmorillonite experiment; and (4) other minerals behaved intermediately between sphalerite and montmorillonite.

In order to examine surface processes, adsorption experiments were also performed by NH₃- and CO₂-TPD (temperature-programmed desorption) methods. The TPD analyses indicated that sphalerite has high adsorption capabilities both of NH₃ and CO₂. These results imply that sphalerite has high adsorption capabilities of amino and carboxyl groups affecting the elongation of peptides. On the other hand, montmorillonite only has the capability to adsorb NH₃, thus amino group. This type of adsorption may only result in cyclization of amino acids preventing elongation of oligopeptides.

Application of compound-specific radiocarbon dating for studying West Antarctic Ice Sheet during the Late Quaternary

N. OHKOUCHI¹, T.I. EGLINTON², M. TOYODA^{1,3},
Y. CHIKARAISHI¹, H. TOKUYAMA³, H. MIURA⁴ AND
Y. YOKOYAMA⁵

¹IFREE/JAMSTEC, Yokosuka 237-0061, Japan

²Woods Hole Oceanogr Inst, Wods Hole MA 02543, USA

³Ocean Res Inst, Univ Tokyo 164-8639, Japan

⁴National Inst Polar Res, Tokyo 173-8515, Japan

⁵Dept Earth Planet Sci, Univ Tokyo, Tokyo 113-0033, Japan

Compound-specific radiocarbon dating is a powerful tool for reconstructing chronologies in high-latitude sediments. Since high-latitude sediments generally lack carbonate, total organic matter has been used to establish sediment chronologies. However, the "contamination" of reworked sediments eroded from the Antarctic Continent leads to anomalously old core-top ages or to age reversals down-core (Ohkouchi and Eglinton, 2006).

Ohkouchi *et al.* (2003) first reported that the radiocarbon dating of solvent-extractable, short-chain (C₁₄, C₁₆, and C₁₈) fatty acids isolated from surface sediments of the Ross Sea, Antarctica, indicated them to be consistent with the modern DIC reservoir age (Pre-bomb: $\Delta^{14}\text{C} \approx -150\text{‰}$, Post-bomb: $\Delta^{14}\text{C} \approx -100\text{‰}$). Furthermore, the radiocarbon ages of these fatty acids at five down-core intervals progressively increase with the core depth. These results clearly show a utility of the compound-specific radiocarbon dating for developing sediment chronologies in Antarctic margin sediments (Ohkouchi and Eglinton, submitted).

In this study, we determined radiocarbon ages of the fatty acids from a core recovered in the NW Ross Sea to reconstruct sediment chronologies. Furthermore, we determined hydrogen isotopic compositions of sedimentary biomarkers in the core. Around 7, 6, 4.5, and 2.5 kyr ago, the reconstructed δD values of paleo-seawater were -200‰ or lower, suggesting a large amount of meltwater influx to the Ross Sea. We propose that recurrent massive melting of WAIS could have occurred at least four times in the Holocene.

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Mobility and transport of Nd isotopes during weathering of till in a boreal forest

BJÖRN ÖHLANDER¹, MAGNUS LAND² AND JOHAN INGRI¹

¹Division of Applied Geology, Luleå University of Technology, Sweden

²Department of Geology and Geochemistry, Stockholm University, Sweden

It has been suggested that the Nd transported in the large, pristine Kalix River in northern Sweden originates from organic bound REE from the uppermost soil horizons (Öhlander *et al.*, 2000; Andersson *et al.* 2001). Here we present new data of the distribution of Nd isotopes in a spodosol profile developed in a till which was deposited 8700 years ago. In addition, Nd isotopes were analysed in soil water, groundwater and stream water in a small catchment situated within the Kalix River drainage basin.

The results indicate that a large part of the Nd released by weathering in the E-horizon is trapped in the B-horizon, and that the major part of the dissolved Nd exported from the studied catchment via stream water is derived from weathering in the shallow groundwater zone within the till rather than in the top soil. Due to the very low weathering rate at that depth, there is still a relatively little altered pool of reactive minerals containing Nd. It will take a very long time ($\gg 8700$ years) before the Nd leaving the catchment will have an isotopic composition different from today.

The export of Nd from a large boreal drainage basin, in this case to the Bothnian Bay, is, to a large extent, controlled by selective weathering and reactions with organic matter in the upper soil horizons, and by Nd released by slow weathering in the groundwater zone.

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Formation of probable lateritic soils ~3.43 Ga in the Pilbara Craton, Western Australia

H. OHMOTO¹, Y. WATANABE¹, A. ALLWOOD²,
I.W. BURCH³, L.P. KNAUTH⁴, K.E. YAMAGUCHI⁵,
I. JOHNSON¹ AND E. ALTINOK¹

¹Astrobiology Research Center & Dept. of Geosciences, Penn State Univ., University Park, PA, 16802 USA
(ohmoto@geosc.psu.edu; yumiko@geosc.psu.edu;
ijohnson@geosc.psu.edu; ealtinok@geosc.psu.edu)

²NASA Jet Propulsion Laboratory, Pasadena, CA 91109, USA
(aallwood@jpl.nasa.gov)

³Dept. of Earth and Planetary Sciences, Macquarie Univ.,
North Ryde, NSW2109, Australia

⁴School of Earth and Space Exploration, Arizona State
University, Tempe, AZ 85287, USA (Knauth@asu.edu)

⁵IFREE, JAMSTEC, Yokosuka, Kanagawa 237-0061, Japan
(kosei@jamstec.go.jp)

An alteration zone (~20-80 m thick), characterized by the abundance of pyrophyllite (aluminum-rich clay) and the depletion of iron and most elements, is widely developed in pre-3.4 Ga submarine basalts that occur beneath the oldest-known (~3.4 Ga) erosional unconformity (i.e., oldest land surface) in the North Pole Dome region of the northern Pilbara Craton, Western Australia. Some previous researchers suggested this alteration zone as a product of hydrothermal activity ~3.4 Ga.

We have recently discovered more than 100 iron pods (each ~1 to ~6 m thick and ~1 to ~50 m long) within the iron-depleted pyrophyllite-rich zone at seven sites over a ~30 km expanse in the studied area. They typically occur as clusters at 0 - 30 m below and generally parallel to the ~3.4 Ga unconformity, rather than being parallel to the modern groundwater tables. These iron are mostly composed of well-crystalline hematite (~30 to ~90 wt% Fe₂O₃) and pyrophyllite.

The geometrical, geological, mineralogical, and geochemical characteristics of iron pods and alteration zone in the studied area (e.g., the rarity of quartz-sulfide veins; sizes and crystallinity of hematite; trends of Al/Ti, Mg/Ti, Fe/Ti, Ca/Ti, Na/Ti, and K/Ti ratios; trends of trace element ratios; REE behaviors) resemble those of "groundwater-type" laterites of the Phanerozoic and Proterozoic ages (e.g., the ~2.2 Ga Hekpoort and Hokkalampi paleolaterites). Groundwater-type laterites require the following conditions for formation: (i) distinct wet/dry seasons; (ii) the development of microbial mats/vegetation on/in soils during wet seasons, which produce abundant organic acids that leach both ferric and ferrous irons from the soils and create ferrous-rich groundwater; and (iii) an abundance of oxygen molecules supplied from the atmosphere to the soils and groundwater, mostly during dry seasons, to precipitate the aqueous ferrous iron as ferric (hydr)oxides. Therefore, if the North Pole Dome ironstones are indeed ~3.43 Ga laterites, they suggest the very early developments of the terrestrial biosphere and an oxygen-rich atmosphere.

Mass dependent isotopic fractionation of Ce and Nd in geochemical samples

TAKESHI OHNO AND TAKAFUMI HIRATA

Department of Earth and Planetary Sciences, Tokyo Institute
of Technology, Japan (ohno.t.ab@m.titech.ac.jp;
hrt1@geo.titech.ac.jp)

The study of naturally occurring mass dependent isotopic fractionation of rare earth elements (REEs) has a potentially significant influence in geochemical research fields. Isotopic fractionation of REEs with their chemical similarities and gradual changes of ionic radius may provide new insights about chemical weathering processes. One of the most attractiveness of REEs is anomalous behavior of Ce mainly due to the existence in not only the trivalent state but also the tetravalent state. Since the valence of Ce depends on the redox conditions, differences of isotopic fractionation between Ce and the other REEs could provide information about the redox conditions of depositional environment. Among the other REEs, Nd could play an important role in the stable isotope geochemistry of REEs as a reference compared to Ce. Moreover, radiogenic growth of ¹⁴³Nd can also provide chronological constraints on a sample formation process.

In this study, we have developed a new chemical and mass spectrometric procedure for the investigation of mass dependent isotopic fractionation of Ce and Nd in geochemical samples. In order to detect the small isotopic fractionation, mass discrimination effects on Ce and Nd isotopes were externally corrected by Sm and Eu, respectively. The resulting analytical precisions for $\delta^{142/140}\text{Ce}$ and $\delta^{146/144}\text{Nd}$ were better than 0.01% (2SD). Isobaric interferences were eliminated by an extraction chromatography using a Ln spec. resin. We examined isotopic fractionation of Ce and Nd during the separation procedure. The result of the test demonstrated that the cumulative isotopic value of the eluent showed no detectable isotopic fractionation through a few percent loss during the chromatographic separation.

Cerium and Nd isotopic compositions of GSJ geochemical reference samples (Basalt, JB-1a; Andesite, JA-2; Manganese Nodule, JMn-1; Chert, JCh-1; Dolomite, JDo-1) have been measured in order to examine the possible isotopic fractionation of Ce and Nd. The isotopic data of Ce and Nd for the samples revealed $\delta^{142/140}\text{Ce}$ and $\delta^{146/144}\text{Nd}$ data for JDo-1 were different from that of the igneous rock samples. Moreover, there was positive correlation between the resulting $\delta^{142/140}\text{Ce}$ and $\delta^{146/144}\text{Nd}$, implying that the isotopic variation of Ce and Nd observed in JDo-1 might be caused by non-redox reactions such as preferential precipitation or dissolution processes, rather than the redox reaction. In this presentation, Ce and Nd isotopic data on several geochemical materials and possible mechanism of isotopic fractionation will be discussed.

Interactions of heavy elements with microorganisms

T. OHNUKI¹, T. YOSHIDA^{1,2}, T. OZAKI¹, F. SAKAMOTO¹,
N. KOZAI¹, T. NANKAWA¹, Y. SUZUKI¹ AND
A.J. FRANCIS²

¹Japan Atomic Energy Agency, Tokai, Ibaraki, 319-1195
Japan

²Central Research Institute of Electronic Power Industry,
Komae, Tokyo 201-8511 Japan

³Brookhaven National Laboratory, Upton, NW, 11973, USA

Introduction

The high capacity of microbial surfaces to bind actinides may affect the migration of actinides in the environment. However, we have only limited knowledge of the role of microorganisms in the migration of actinides in the environment. We have been conducting basic scientific research on microbial interactions with actinides in order to elucidate the environmental behavior of actinides under relevant microbial process conditions.

Pu(IV) sorption and reduction

Adsorption of Pu(IV)-desferrioxamine B (DFO) on bacteria indicate that Pu(IV) is dissociated by contact with cells, after which Pu(IV) is adsorbed, and that pH dependence of adsorption density of Pu(IV) on cells is dominated by the stability of Pu(IV)-DFO complexes. Study on reduction of Pu(IV) in the presence of citric acid at pH 7.0 suggested that Pu(IV) is reduced to Pu(III) by the activity of sulphate reducing bacteria.

U(VI) mineralization

Uranium mineralization by the yeast *Saccharomyces cerevisiae* was examined by batch experiment at pH 3.2. Analysis of the U(VI)-bearing precipitates by FESEM-EDS, TEM, and visible diffuse reflectance spectrometry demonstrated the presence of H-autunite, $\text{HUO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ and thermodynamic calculations suggest that the chemical compositions of the solutions were undersaturated with respect to H-autunite, but were supersaturated with ten-times more U(VI) and P than were actually observed. These findings indicate that the yeast's cell surfaces, rather than the bulk solution, offer the specific conditions for this geochemical process.

A combined terrestrial and marine geochemical mapping project in Japan

A. OHTA, N. IMAI, S. TERASHIMA, Y. TACHIBANA,
T. OKAI, M. UJIE-MIKOSHIBA AND R. KUBOTA

Geological Survey of Japan, AIST, Tsukuba 305-8567, Japan;
a.ohta@aist.go.jp

Spatial distribution patterns of elemental concentrations on land, geochemical maps, are effective for mineral exploration and environmental assessment. In Japan, the Geological Survey of Japan, AIST conducted a nationwide geochemical mapping program at 1:2,000,000 scale using fine stream sediments for these purpose (Imai *et al.*, 2004). Japan is, however surrounded by a vast expanse of sea, so that examination of geochemical baseline in coastal-open sea is also essential for environmental assessment. Approximately 3000 surface marine sediments around Japan were collected for this purpose and analyzed for 51 elements including heavy metals (e.g. Cu, Zn, Cd, Hg, and Pb). This project is intended: 1) to elucidate background of elemental abundance in terrestrial and marine areas of young island arc; 2) to find mass transport from land to sea; and 3) to estimate diffusion processes of pollutants.

The elemental concentrations of marine sediments are determined primarily by grain size. Most elemental concentrations increase with decreasing grain size and eventually become constant. Overall, marine sediments and stream sediments show similar elemental abundance patterns, but marine sediments have lower elemental abundance than stream sediments because of dilution effects imparted by calcareous sediments and organic materials. These results suggest that marine sediments in coastal seas originate mainly from terrestrial materials. However, a few examples of direct mass transport from terrestrial area to marine environment are apparent. The spatial distribution patterns of K and Cr concentrations, which are good examples of mass transport, suggest two types of high-concentration area extending continuously from land to sea: high concentration area proximal to a river mouth (20-30km) and high concentration area extending over 60 km offshore along a deep-valley. These results suggest that sediments deposit by fanning out near shore and a part of them are further conveyed along the deep-valley by gravity movement. Diffusion of heavy metals such as Cu, Zn, Cd, Sn, Pb, and Bi is observed in coastal bays surrounded by urban and industrial areas, from which the stream sediments are extremely abundant in those elements. It is noteworthy that the materials with heavy metals seem to remain in the bay without diffusing to the outer sea. The sediments with heavy metals might not diffuse readily to the outer sea because of a strong bottom current (estuary circulation) that flows from outer sea to the inner part of the bay.

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The effect of iron spin transition on electrical conductivity of perovskite and magnesiowüstite

KENJI OHTA¹, SUZUE ONODA², KEI HIROSE¹ AND
KATSUYA SHIMIZU²

¹Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Meguro, Tokyo, Japan

(k-ohta@geo.titech.ac.jp; kei@geo.titech.ac.jp)

²Center for Quantum Science and Technology under Extreme Conditions, Osaka University, Toyonaka, Osaka, Japan

(onoda@djebel.mp.es.osaka-u.ac.jp;

shimizu@cqst.osaka-u.ac.jp)

The electrical conductivity is one of the observable physical properties of the Earth's mantle. The pyrolitic lower mantle mainly consists of Al-bearing (Mg,Fe)SiO₃ perovskite and (Mg,Fe)O magnesiowüstite, and the electrical conduction occurs through these two iron-bearing phases. The electrical conductivity profile in the lower mantle has been estimated by extrapolating the data from 40 GPa [Shankland *et al.*, 1993]. Recently, Badro *et al.* [2003, 2004] discovered a pressure-induced electronic spin transition of iron in both magnesiowüstite and perovskite. The spin transition of iron may have significant effect on electrical conductivity, but it has not been examined yet.

Here we measured the electrical conductivity of Mg_{0.81}Fe_{0.19}O magnesiowüstite and Mg_{0.91}Fe_{0.09}SiO₃ perovskite at high pressures up to 135 GPa and 300 K in a diamond-anvil cell (DAC). The results demonstrate that the electrical conductivity of magnesiowüstite increases with increasing pressure to about 60 GPa and exhibits anomalous behavior at higher pressures; it conversely decreases to around 80 GPa and again increases very mildly with pressure to 130 GPa. Perovskite shows similar profile to that of magnesiowüstite; it increases to 60-70 GPa and decreases to 80 GPa, then again increases mildly with pressure up to 135 GPa.

This observed reduction in electrical conductivity may be explained by the high-spin to low-spin transition of iron in magnesiowüstite and perovskite. A smaller pressure effect on the electrical conductivity of magnesiowüstite above 80 GPa suggests that a dominant conduction mechanism changes by the electronic spin transition. The electrical conductivity of perovskite becomes higher than that of magnesiowüstite above 90 GPa. Therefore, perovskite can be a main conductor, at least in the deep lower mantle. The electrical conductivity below 2000-km depth in the mantle may be much smaller than previous estimates due to the effect of electronic iron spin transition.

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Geochemistry and TEM observation of graphite in 3.8 Ga metasedimentary rocks in Isua Supracrustal Belt

Y. OHTOMO AND T. KAKEGAWA

Institute of Mineralogy, Petrology, and Economic Geology, Graduate School of Science, Tohoku University, Sendai, Japan (otomoyou@ganko.tohoku.ac.jp)

The remnant of oldest life was reported only from one outcrop at the 3.8Ga Isua Supracrustal Belt (ISB), West Greenland [1], although graphite-bearing rocks are located at several spots in the Isua area. New outcrops of graphitic schist, which graphitic contents are up to 8.8 wt %, were found through the course of this study. The graphitic schist is interbedded with banded iron formation and extended for approximately 500m from NW to SE. Major and trace element were determined on graphitic schist samples. Carbon isotope compositions of graphite were determined using the laser micro probe system. TEM analyses were also performed on the extracted graphite samples.

CI chondrite-normalized REE patterns of the new graphitic schist are similar to other Archean shales or banded iron formation. Therefore, new graphitic schist has characteristics of marine clastic to chemical sediments.

Carbon isotope compositions of graphite were determined on 50 samples. Their compositions range from -22.4 per mil to -13.2 per mil. The carbon isotope compositions change systematically, correlated to geological occurrence. Lightest carbon isotope composition was found in the most western area where complicated nano-scale textures of graphite were observed by TEM. The heaviest carbon isotope composition was found in the most eastern area. This carbon isotope shift is probably due to the more metasomatic effect compared to the western samples. Considering those all geochemical data, graphite in new graphitic schist also gives another evidence of 3.8Ga marine biota.

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Wilhemine copper mine, Spessart, Bavaria: A Kupferschiefer-related, hydrothermal mineralization

MARTIN OKRUSCH¹, JOACHIM LORENZ² AND STEFAN WEYER³

¹Mineralogisches Institut, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany (okrusch@uni-wuerzburg.de)

²Joachim A. Lorenz, Graslitzer Str. 5, D-63791, Karlstein am Main, Germany (Jo.Lorenz.Karlstein@t-online.de)

³Institut für Petrologie, Geochemie und Lagerstättenkunde, Universität Frankfurt am Main, Senckenberganlage 28, D-60325 Frankfurt am Main, Germany (stefan.weyer@em.uni-frankfurt.de)

The vein-type copper mineralization in the abandoned Wilhelmine copper mine at Sommerkahl is hosted by orthogneisses of the Spessart Crystalline Complex. These are covered by sedimentary rocks of Permo-Triassic age, including the stratabound base-metal mineralization of the Kupferschiefer. Ore textures in the sulfide veins testify to three stages of mineralization:

(i) An early stage is characterized by colloform textures, documented by spherical, garland-shaped or cockade-like aggregates of tennantite I, enargite I, pyrite I, chalcopyrite I, bornite I and digenite I.

(ii) During a subsequent recrystallization stage, these were overgrown by, or enclosed in, tennantite II, enargite II, bornite II, digenite II, pyrite II and chalcopyrite II. Fine-grained to submicroscopic digenite-bornite intergrowths, exsolved from an initial 1a-solid solution, contain up to 55 mole-% of bornite, indicating a minimum temperature of 175°C for this stage.

(iii) A late alteration stage led to the replacement of primary sulfides by yarrowite, spioncoppite and rare covellite, together with goethite.

The close spatial association of the vein-type Cu mineralization with the overlying Kupferschiefer suggests a genetic relationship. In situ sulfur isotope analyses of sulfide minerals yielded negative $\delta^{34}\text{S}$ values of -12.8 to -23.9 ‰ indicating a derivation from the Kupferschiefer, presumably by hydrothermal leaching. By contrast, we assume that the metals were derived from deep-seated sources, transported upwards by hydrothermal fluids and precipitated by thermochemical sulfate reduction, due to interaction with the Kupferschiefer. Formation of the sulfide ore veins is related to a hydrothermal activity in Middle Jurassic to Early Cretaceous times.

Micro-Raman and cathodoluminescence characterization of shocked quartz from impact craters

T. OKUMURA¹, A. GUCSIK², H. NISHIDO¹, K. NINAGAWA³ AND M. SAKAMOTO⁴

¹Research Institute of Natural Sciences, Okayama University of Science, Okayama, Japan (okumura@rins.ous.ac.jp, nishido@rins.ous.ac.jp)

²Max Planck Institute for Chemistry, Department of Geochemistry, Mainz, Germany (gucsik@mpch-mainz.mpg.de)

³Department of Applied Physics, Okayama University of Science, Okayama, Japan (ninagawa@dap.ous.ac.jp)

⁴Shimohisakata Elementary School, Nagano, Japan

Introduction

Evidence of shock metamorphism can be sufficiently proved by the existence of planar deformation features (PDFs) found in quartz. However, visual identification of the planar features under optical microscope should be unambiguous for clarifying PDFs. To characterize shock-induced planar microstructures such as PDFs in quartz from various impact craters, we used a combination of cathodoluminescence (CL) and micro-Raman spectroscopy with high sensitivity and high spatial resolution.

Samples and Methods

Quartz grains from Ries Crater, Barringer Meteor Crater, and Oikeyama Crater are employed for Raman and CL measurements. They were prepared as polished thin sections. PDFs are observed in several quartz grains under a petrographic microscope. Raman spectra were acquired with a confocal micro-Raman spectrometer at 20 mW using a Nd:YAG laser (532 nm) excitation system. CL imaging and spectral measurements were carried out on a SEM-CL (scanning electron microscope combined with a grating monochromator) with an accelerating voltage of 15 kV.

Results and Discussion

SEM-CL imaging of quartz grains from each crater shows non-luminescent or CL-dark lines related to PDFs, which can be clearly observed under polarized microscope. Raman spectra of shocked quartz from the Ries Crater exhibit a pronounced peak at around 459 cm^{-1} , which can be assigned to Si-O-Si stretching vibration, whereas unshocked quartz has a sharp and intense peak at 464 cm^{-1} . This frequency shift may arise by a distortion of the structural configuration (i.e., formation of high density silica) caused by shock-metamorphism. The Raman imaging of shocked quartz from each impact crater shows a stripe pattern suggesting layers comprised of high and low crystalline parts corresponding to the optical image of PDFs. Our results show that shock-induced amorphization might effect an alteration of electronic transition processes in defect centers that are correlated to CL emission.

Hydrogen isotope geochemistry of basalts from Samoa

J.A. O'LEARY¹, E.H. HAURI¹, S.R. HART² AND H. STAUDIGEL³

¹Department of Terrestrial Magnetism, Carnegie Institution of Washington, Washington DC, 20015 U.S.A.

²Department of Geology & Geophysics, Woods Hole Oceanographic Institution, Woods Hole MA 02543 USA

³Scripps Institution of Oceanography, University of California-San Diego, La Jolla CA 92093 USA

Hydrogen is present at low concentrations (tens to hundreds of ppm H₂O) throughout the upper mantle but exerts a strong influence on the melting behavior and rheologic properties of peridotite. The distribution of hydrogen in the entire mantle is a key constraint on mantle convection that remains unquantified. The D/H ratio of hydrogen in fluids and in silicate materials can be fractionated by tens of per mil under mantle conditions and offer an opportunity to identify and describe hydrogen storage and transport processes within the mantle. To pursue this goal we examined the hydrogen isotope composition of submarine ocean island basalt glasses collected from Malumalu, Vailu'lu, and Ta'u in the Samoan island chain. Lavas from the Samoan islands contain extreme trace element and radiogenic isotope enrichments that define the EM 2 (enriched mantle 2) mantle endmember [1]. The D/H composition of Samoan lavas vary between -79 and -37 per mil, a similar range to what is found in other ocean island basalt localities and in back-arc basin basalts that are influenced by fluids released from subducting ocean crust. The lowest δD values of Samoan glasses (-79 per mil) are close to the mode of values for mid-ocean ridge basalts (-75 per mil) while the highest value is similar to the isotopic composition of serpentine in equilibrium with seawater. This range in hydrogen isotope composition suggests that the mantle source region of Samoan lavas may contain fluid derived from ancient subducted ocean crust that has retained a distinct hydrogen isotopic composition over the timescale of mantle mixing.

Correlations between La, ⁸⁷Sr/⁸⁶Sr, and water content in Samoan lavas are attributed to equilibration of initially water rich subducted materials with the ambient mantle water content [2]. Equilibration is possible due to rapid diffusion of hydrogen in mantle minerals [3]. The preservation of D-rich compositions in the source of Samoan basalts suggests that hydrogen isotope anomalies are not diffusively lost, possibly due to high concentrations of D-rich hydrogen in subducted materials that result in large regions of the mantle with high D/H ratio.

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The model structure of kaolinite in relation to surface complexation

M. OLIN, E. PUHAKKA AND J. LEHIKONEN

VTT Technical Research Centre of Finland, P.O. Box 1000, FI-02044, Finland (markus.olin@vtt.fi)

Methods

Surface complexation modelling using the FITEQL software was applied to explain the surface acidity of kaolinite. In this context, a number of different models and modelling approaches were tested. Further, a density functional method, CASTEP (Accelrys, 2001), was used to investigate the crystal and surface structures of kaolinite, and to calculate surface charge densities.

Results and discussion

To enable the interpretation of adsorption results with surface complexation modelling, an adequate characterization of the surface charging of the adsorbent is needed. In general, titration experiments are capable of providing this information for ionisable interfaces. However, results based on experimental data give only average values of surface charge densities. Therefore, in this study, molecular modelling was used to calculate surface charge densities of likely the most reactive kaolinite crystal faces separately (see Figure 1 for the (010) surface). Based on this information, an attempt will be made to constrain the number of surface sites and magnitude of surface hydrolysis constants, often considered as adjustable parameters devoid of deeper understanding, in surface complexation models.

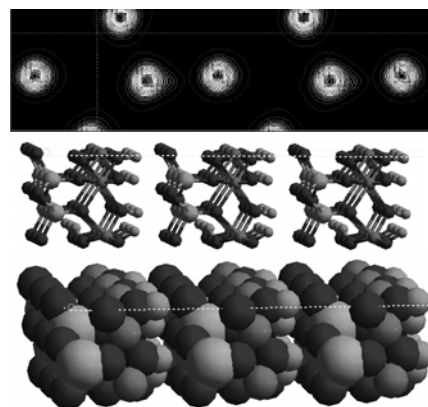


Figure 1: Model (010) surface of kaolinite and its surface charge density.

Conclusions

The molecular-level modelling produced invaluable background information of the kaolinite surface for further development of surface complexation models in terms of the surface charging and the adsorption of metal cations.

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Chemostratigraphy and lead isotopic composition of a sediment core profile from a small pond in a remote equatorial island

S.M.B. DE OLIVEIRA¹, L.C.R. PESSENDA²,
S.E.M. GOUVEIA², M. BABINSKI¹ AND D.I.T. FAVARO³

¹Institute of Geosciences, Un. São Paulo, rua do Lago, 562,
São Paulo, 05508-080 Brazil (soniaoli@usp.br,
babinski@usp.br)

²C Laboratory, CENA, Un. of São Paulo, C.P. 96, Piracicaba,
SP, 13416-000, Brazil, (pessenda@cena.usp.br,
susyeli@cena.usp.br)

³IPEN, C.P. 11049, São Paulo, Brazil, (defavaro@ipen.br)

A 72-cm long core was collected from Lagoa da Viração (LV), a small pond in the Fernando de Noronha island, northern Brazil, in order to study vertical changes in major, trace and Pb isotopes concentrations with depth. Sediments from the lower section of the core (20-70 cm) contains essentially mineral matter, while in the upper section (0-20 cm) mineral matter is mixed with organic matter, which is increasingly more abundant toward the top. Lithogenic conservative elements – Si, Al, Fe, Ti, Co, Cr, Cu, Ga, Hf, Nb, Ni, Y, Zn, Zr and REE – exhibit remarkably constant values along the core, with concentrations similar or moderately higher than those of the bedrock. The vertical distribution of soluble elements – Ca, Mg, Na, K, P and Mn – is also homogeneous, but these elements are systematically depleted in relation to the bedrock. LOI, TOC, Br, Se, Hg and Pb, although showing nearly constant values in the lower section of the core, are significantly enriched in the upper section. Pb isotopic ratios are nearly constant and very similar to those of the bedrock in the lower section of the core, but are increasingly less radiogenic in the upper section. Ti-normalization allowed the separation of natural and anthropogenic Pb, indicating that the latter was restricted to the upper section of the core, and was probably added to the sediments via atmospheric transport. Se and Br appears to be originated from seawater sprays. The source of Hg seems more uncertain, but at least partially it might have been accumulated via atmospheric deposition. Whatever the source of Pb, Br, Se and Hg, their close association with TOC suggests that organic matter has played an important role in their accumulation in the surface sediments.

Molecular markers and trace-metals as proxies of biomass combustion in Central Amazon sediments

T.C.S. OLIVEIRA, A. WAGENER AND A.L. SCOFIELD

Departamento de Química, Pontifícia Universidade Católica do Rio de Janeiro, 22453-900 Rio de Janeiro, Brazil
(terist@rdc.puc-rio.br; angela@rdc.puc-rio.br;
scofield@rdc.puc-rio.br)

Large scale forest fires occur in the region denominated “deforestation arc” circumscribing the southern area of the Amazon Region. Under certain meteorological conditions like in the dry season of 2005 clouds of particulate matter reached Manaus and the Central Amazon. The goal of the present work was to search for indicators of combustion in sediments of the Solimões River and associated lakes. For this sediments were sampled in the wet and dry seasons in 2005 and were analysed for 39 PAHs, molecular markers and trace-metals. Among other approaches, to verify the contribution of biomass combustion to the PAH pool in the sediments the diagnostic ratio Fl/(Fl+Py) was plotted versus $1.7/(1.7+2.6)$ DMPH, which was used as a proxy for combustion sources. The cross evaluation shows PAH in sediments deriving predominantly from mixed combustion sources. Evidently the traffic of ships along the river contributes for the pool of PAH in the sediments. Significant correlation ($p \ll 0.05$) of perilene, the major PAH, with BbFl, BkFl, BaPy and several metals were found. These and additional correlations were confirmed in the factorial analysis in which the correlation coefficients in factor 1 were: 0.79 for Fl, 0.76 for BaA, 0.83 for BbFl, 0.66 for BkFl, 0.82 for BaPy, 0.83 for Cd, 0.77 for Pb, 0.79 for Cu and 0.73 for Zn. The association of perilene with combustion derived PAH and metals, which can also be produced in forest burning, is an indication that combustion is one of the relevant sources of this compound to the sediments. For the dry season samples, strong correlations were found between $1.7/(1.7+2.6)$ DMPH and trace metals (Cu, V, Zn, Pb, Cd) which confirm the contribution of forest fires for the pool of trace metals in sediments, especially in such occasions of intense combustion as in late 2005. The same approach applied to a dated core showed that biomass combustion imprint is present in sediments deposited since the end of the 19th century. In general the high values for the ratio $\sum 3-6$ ring PAH/ $\sum 5$ Alk PAH series sustain the evidence that combustion is a major source of PAH in the examined sediments.

Seasonal variations of physical and chemical erosion: A three-years survey of the Rhône river (France)

P. OLLIVIER, B. HAMELIN AND O. RADAKOVITCH

CEREGE Aix-Marseille Université/ CNRS.

For obvious logistical reasons, most previous studies on the main world rivers were based on wide scale investigations carried out on short timescales. By comparison, much less effort has been devoted at long term monitoring, as a mean to verify the temporal variability of the average characteristics, temporal trends, and representativity of short-term investigations. Here we report the results of a three years survey (November 2000 to December 2003) of the geochemical composition of major and trace elements in dissolved and suspended matter in the lower Rhône River (France), the largest river of the Mediterranean area. Subsurface water samples were collected in Arles, 40 Km upstream of the estuary, twice a month routinely, and at high frequency during flood events.

We show that the annual average SPM flux of the Rhône River to the Mediterranean Sea (7.25×10^6 tons/yr) was largely controlled by the flood events (83% of the solid discharge occurred in less than 12% of the time), and that the precision on the total output flux depends strongly on the precise monitoring of SPM variations during the floods. Chemical budgets have been calculated to discriminate the respective contributions of marine aerosols in rain water, carbonate, silicate and evaporite weathering, as well as anthropogenic inputs.

Our data corroborate previous studies suggesting a strong coupling between chemical and physical erosion fluxes, during the Rhone hydrological seasonal cycle. However, the correlation observed between physical and chemical transport rates is clearly different from that reported on global compilations of annual averages in the largest world rivers.

The steady state model of Gaillardet *et al.* (1995) has been applied to the chemical composition of dissolved and solid products. We show that the Rhône River exports currently much less material than produced at steady-state by weathering in its watershed. The sediment flux inferred from the steady-state calculation (20×10^6 t yr⁻¹) is on the same order as those estimated in the literature for the nineteenth and the beginning of the twentieth centuries. This unbalance may suggest that the Rhône is under a transient erosion regime following climate change (i.e. significant decrease of the floods frequency). On the other hand, the unbalance may also be due to the trapping of alluvion by the numerous dams on the river and its tributaries.

Abiotic hydrolysis of glucose-1-phosphate adsorbed at the water-goethite interface

R. OLSSON¹, R. GIESLER² AND P. PERSSON¹

¹Dep. of Chemistry, Umeå University, 901 87 Umeå, Sweden (rickard.olsson@chem.umu.se)

²Dep. of Ecology and Environmental Science, 901 87 Umeå, Sweden

Phosphorus is essential to organisms. In the environment it occurs mainly as inorganic phosphates or as organophosphates. Due to the high reactivity of the phosphate group, these interact strongly with environmental particles. In order to make the phosphate in organophosphates available for uptake by organisms, hydrolysis is usually required. This process may be mineral-surface-mediated (abiotic) or enzymatic (biotic).

Glucose phosphate is one of the dominant components of the natural organophosphate pool [1]. The aim of the present work is to study the interactions between glucose-1-phosphate and goethite, with respect to adsorption characteristics and the role of the mineral surface in the abiotic hydrolytic process. The work was done in series of batch experiments, measuring ligand adsorption as a function of pH and time. The concentrations of the hydrolytic products glucose and phosphate were also measured. ATR-FTIR spectroscopy was used to evaluate the surface speciation of glucose-1-phosphate. Kinetic data will be presented which show the pH dependent surface-promoted hydrolysis, and these will be discussed in combination with molecular-level results obtained by ATR-FTIR spectroscopy.

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As(V)-bearing lepidocrocite and green rust reduction by *Shewanella putrefaciens*: Evidence for Fe(II) carbonate hydroxide formation

G. ONA-NGUEMA^{1,2}, G. MORIN¹, Y. WANG¹, F. JUILLOT¹,
F. GUYOT¹, G. CALAS¹ AND G.E. BROWN, JR^{2,3}

¹IMPMC, UMR7590, CNRS, Univ. Paris 6&7, IPGP, France
(calas@impmc.jussieu.fr, guyot@impmc.jussieu.fr,
juillot@impmc.jussieu.fr, morin@impmc.jussieu.fr,
onanguem@impmc.jussieu.fr, yuheng@impmc.jussieu.fr)

²Surface & Aqueous Geochemistry Group, Department of
Geological and Environmental Sciences, Stanford
University, Stanford, California 94305-2115, USA
(onanguem@stanford.edu, gordon@pangea.stanford.edu)

³Stanford Synchrotron Radiation Laboratory, SLAC, 2575
Sand Hill Road, MS 69, Menlo Park, California 94025,
USA

Arsenic is a toxic metalloid involved in important health issues due to the contamination of water resources. High arsenic concentrations typically derive from the breakdown of As-bearing Fe-oxides, particularly under anaerobic conditions. A variety of microorganisms influences arsenic mobility using oxidation, reduction, and methylation reactions that strongly control arsenic speciation in the environment. In the present study, *Shewanella putrefaciens* strain ATCC 12099, an iron-respiring bacterium, was incubated under anaerobic conditions with As(V) ions, As(V)-bearing lepidocrocite, or a lepidocrocite without arsenic. Results show that strain ATCC 12099 is capable of reduction of HAs(V)O_4^{2-} to $\text{H}_3\text{As(III)O}_3$ when the former oxoanion is dissolved in solution (at pH 7.8), or when it is adsorbed onto the surface of lepidocrocite. Cultures in which lepidocrocite was used as the sole electron acceptor led to the formation of biogenic hydroxycarbonate green rust prior to ferrous carbonate hydroxide. In contrast, when the electron acceptor was As(V)-bearing lepidocrocite, XRD analysis revealed ferrous carbonate hydroxide to be the dominant reaction product; no green rust formation was observed in this case. As K-edge XANES spectroscopy indicated that all As(V) (K-edge(max) = 11875eV) was reduced to As(III) (K-edge(max) = 11871.3eV). These results suggest the presence of As(III) either on the surface of ferrous carbonate hydroxide, and/or in another ferrous-solid phase, and they show for the first time bacterial reduction of hydroxycarbonate green rust.

Nd Isotopic Constraints from the 3.8 Ga Nuvvuagittuq Greenstone Belt for the Degree of Depletion of the Early Earth's Mantle

JONATHAN O'NEIL¹, DON FRANCIS¹ AND
ROSS K. STEVENSON²

¹Earth & Planetary Sciences, McGill University, Montreal,
Quebec, Canada, H3A 2A7 (oneil_jo@eps.mcgill.ca;
donf@eps.mcgill.ca)

²GEOTOP-UQAM-McGill, PO Box 8888, St. Centre-ville,
Montreal, Quebec, Canada, H3C 3P8
(stevenson.ross@uqam.ca)

Rare occurrences of Eoarchean mantle-derived crust provide the only compositional and isotopic constraints on the early crust-mantle differentiation of the Earth. There is currently considerable debate about the implications of the Nd isotopic compositions of such early Archean mantle-derived rocks. The relatively high positive initial ϵNd values obtained on Eoarchean rocks (Nulliak Assemblage, Labrador, Canada; Amitsok Gneisses, Akilia and Isua supracrustal assemblages, SW Greenland) are interpreted to indicate derivation from a mantle source already strongly depleted in the Eoarchean, implying that significant volumes of continental crust had formed early in the Earth's evolution. Here we present the Nd isotope data of the newly discovered ca. 3.8 Ga Nuvvuagittuq greenstone belt (Northern Québec, Canada), and discuss their implications for early mantle depletion.

The Nuvvuagittuq greenstone belt contains numerous ultramafic and gabbroic sills. Most of the gabbro and ultramafic samples display positive $\epsilon\text{Nd}_{(3.8\text{Ga})}$ values ranging from -1.8 to +3.9, with an average of $+1.3 \pm 0.2$ in 29 samples. The few samples that yield $\epsilon\text{Nd}_{(3.8\text{Ga})}$ values $> +3$ (up to +3.9) suggest that they may have been derived from a mantle source that had already experienced an extensive trace element depletion well before 3.8 Ga, equivalent to that seen in the present-day MORB source. Such a degree of depletion of the early Archean mantle, however, is not supported by the flat to slightly LREE-depleted profiles of the gabbros. Furthermore, whole rock analyses for a series of samples from an ultramafic sill and a second series of samples from a gabbroic sill fall along ~3.8 Ga isochrons with initial ϵNd values of +1.3 and +2 respectively, values which are similar to the mean of all the individual sample values. This suggests that the few higher $\epsilon\text{Nd}_{(3.8\text{Ga})}$ values are either anomalous or indicate heterogeneity of the mantle source of Nuvvuagittuq's rocks. Nevertheless, the Nd isotopic compositions of these mantle-derived rocks suggest that the degree of depletion of the mantle recorded in the Nuvvuagittuq greenstone belt is not as extreme as that indicated by the Nd isotopic compositions of the 3.8 Ga SW Greenland rocks.

The P/Nd ratio of basalt as an indicator of pyroxenite in its source

HUGH ST.C. O'NEILL AND GUILHERME MALLMANN¹

Research School of Earth Sciences, Australian National University, Canberra, ACT 0200, Australia
(hugh.oneill@anu.edu.au)

In principle, basalt may be produced by low to moderate degrees of melting of mantle peridotite, the usual scenario, but also, possibly, by higher degrees of melting of a source of basaltic or approximately basaltic composition, like eclogite or pyroxenite. Huge amounts of basalt have been recycled into the mantle over geological time, potentially to provide such a source. The question is whether this basaltic material preserves its major-element compositional identity long enough to take part in subsequent melting cycles, or becomes so thoroughly mixed back into peridotite that only its isotopic and trace-element signatures linger. Initial melts from eclogite are silica-rich dacitic liquids that would freeze out on contact with peridotite or its partial melts because of the pyroxene thermal divide, so are unlikely to contribute directly to basalt production [1]. However, Sobolev *et al.* [2, 3] argue that reaction of such silica-rich liquids with peridotite forms an olivine-free pyroxenite source, melt from which may contribute to the distinctive chemistry of ocean-island basalts (OIBs).

This hypothesis is difficult to test using incompatible trace elements, because most of these are held preferentially among crystalline phases in cpx and/or gt, and therefore their concentrations are not sensitive to the ol/opx ratio of the source. An exception is phosphorus, which, unusually among incompatible trace elements, substitutes for Si in silicate minerals, and prefers the isolated SiO₄ tetrahedra of orthosilicates (ol and gt) over the linked tetrahedra of chain silicates such as pyroxenes. We have measured experimentally the partition coefficients (D) for P between melt and ol, opx, cpx and gt in multiply saturated assemblages at 1.5 and 3.0 GPa, and confirmed that values of D_P for ol and gt are 2 to 3 times larger than for pyroxenes. The P/Nd ratio of a basalt should therefore be an indicator of the ol/opx ratio in its source. Interrogation of petrologic databases shows that P/Nd ratios of MORBs and IABs (derived from spinel lherzolite) are remarkably constant at 65±10, as previously pointed out [4-6]. The P/Nd ratios of OIBs are slightly lower at 55±10, consistent not with pyroxenite melting but with a peridotite source, in the garnet facies. The elevated P/Nd ratios expected of pyroxenite sources are uncommon.

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Using δ³⁰Si to follow the soil-plant Si cycling in a weathering sequence of volcanic ash soils, Cameroon

S. OPFERGELT^{1,2}, B. DELVAUX¹, D. CARDINAL² AND L. ANDRÉ²

¹Université catholique de Louvain, Unité Sciences du sol, Croix du Sud 2/10, B 1348 Louvain-la-Neuve
(opfergelt@sols.ucl.ac.be)

²Musée Royal de l'Afrique Centrale, Chaussée de Louvain 13, B 3080 Tervuren

Plants take up Si as silicic acid and form phytoliths, a biogenic opal (BSi). This Si biocycling affects the availability of Si for clay formation, and for Si export through waterstreams. Si stable isotopes measurement provides a tool to quantify present and past impacts of plants on the continental Si cycle.

In order to calibrate this proxy, we report on detailed δ³⁰Si of plants, sand (>50µm), silt (2-50µm) and clay fractions (<2µm), and amorphous Si (ASi) in a weathering sequence of andesitic ash soils from the Mungo area (Cameroon). Plant communities consist of 50 years old banana stands. The soil sequence involves an increasing clay content from young (Y) to old (O) volcanic soils (vs). The δ³⁰Si values were measured by MC-ICP-MS Nu Plasma in medium resolution, operating in dry plasma with Mg doping: δ³⁰Si vs NBS28 ± 0.07‰ (±1σ).

Compared to fresh andesitic ash (-0.39‰), clay fractions displayed a gradient from -1.19‰ in Yvs to -1.62‰ in Ovs, thus confirming the trend of lighter isotopic compositions with increased weathering. The isotopic signatures of silts fractions (-0.44‰ in Ovs, -0.03‰ in Yvs) compared to clay fractions support that δ³⁰Si may reflect the ratio between primary and secondary minerals. ASi fractions (involving phytolith-rich BSi, volcanic glasses, and allophanic constituents) were heavier in surface horizons than at depth (Δ³⁰Si = +0.34‰), in agreement with the surface accumulation of phytoliths. Indeed, banana plant isotopic compositions were +0.10 and +0.55‰ respectively in Yvs and Ovs. Moreover, ASi were lighter in Yvs (-0.38‰) than in other soils (+0.44‰) pointing to a larger effect of phytoliths in ASi of weathered soils, devoid of volcanic glasses. Surrounding river waters in this area were very heavy (+1.20‰).

Our δ³⁰Si data thus support that plants can induce a strong isotopic imprint by rejecting phytoliths to soil surface. Numerous and successive plant cycles leading to phytolith accumulation would gradually produce a heavier signature in dissolved Si export. This plant impact was underestimated until now. It may have considerable implications on the understanding of the Si continental cycle and the quantitative assessment of Si transfer from land to sea and ocean.

Influence of acid mine drainage on aquatic life at Sar Cheshmeh copper mine

S. ORANDI¹, A. YAGHUBPUR², H. SAHRAEI AND M. BEHROUZ¹

¹Water and Environment Researchs Department, Sar Cheshmeh Copper Deposit, Kerman, Iran (orsa00@yahoo.com)

²Department of Geology, Tarbiat Moallem University, Tehran, Iran. (ayaghubpur@yahoo.com)

Introduction

Investigations on impact of waste dumps on producing of acid mine drainage at Sarcheshmeh copper mine showed a pH range of 3-5.5, which increase the concentration of some toxic heavy metals (Cu, Zn, Pb, As, Cd, Se, Sb ...) higher than the permitted standard limits (WHO). In such degraded water some of dominant microorganisms are able to survive. The fungi (*Geotrichum* sp. & *Aspergillus* sp.), bacteria (*Pseudomonas* sp. & *Tiobacillus* sp.) and non-bacterial microorganisms (*green algae*) were recognized in some of acidic drainages. A kind of filamentous green algae, tolerant to acid and high dissolved elements observed. The genus of mentioned algae is *Ulothrix* and species is *Gigas*, without antimicrobial and antifungal properties. These algae are present in drainages with high total dissolved solids (TDS≈1800 ppm) and acid conditions to pH 3.

Discussion of results

This research suggest the level of acidity, type of dissolved elements and the secondary minerals formed on substrate, all are important factors in distribution of these algae. Field data show the prolific growth of *Ulothrix* between pH 3 – 4.5. The colloidal conditions, in particular the presence of suspended iron and aluminium, prevent the growth of them. Sampling and Chemical analysis of algae for some heavy metals (Cu, Zn, Pb, As, Sb, Cd, Se, Mo) showed the high absorption of some heavy metals (Cu 3500ppm, As 500ppm...) to manifold in comapre with soil and water samples, against their less tendency to absorption of Cd (10ppm). The bacteria especially *Pseudomonas* may strongly impact environmental conditions in acid mine drainages.

Conclusions

The natural presence of these algae in acid mine drainage is a factor to remove heavy metals in this mine. Further works to determine natural contributions of these algae and bacteria to mitigation of poor water quality is under investigation.

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Nanometric jarosite/alunite in carbonaceous matter rich cherts: Marble bar drill core (#1 ABDP): Indications for acid-sulfate conditions in a hydrothermal system

B. ORBERGER¹, R. WIRTH², N. RIVIDI³, C. WAGNER⁴, A. HOFMANN⁵, J.P. GALLIEN⁶, G. MONTAGNAC⁷ AND E. QUIRICO⁸

¹Université Paris Sud, UMR IDES, 8148, Bât. 509, 91405 Orsay, France beate.orberger@u-psud.fr

²GFZ Potsdam, Telegrafenberg, Potsdam, Germany

³Université Paris 7, IPGP, 2, Place Jussieu, 75251 Paris Cedex, France

⁴Université Paris 6, CNRS-UMR 7160, Lab. PMMP, 4 Place Jussieu, 75251 Paris Cedex 05, France

⁵University of KwaZulu-Natal, 4041 Durban, South Africa.

⁶LPS UMR 9956, CEA Saclay, F-91191 Gif-sur-Yvette,

⁷ENS Lyon, Lab. de Sciences de la Terre, CNRS-UMR 5570, 46 Allée d'Italie, 69364 Lyon Cedex 7, France

⁸Université. J. Fourier, Lab. de Planétologie, CNRS-UMR 5109, BP53, 38041 Grenoble Cedex 9, France

Jarosite/alunite are observed in supergene (sulfate zone of gossans) or in hydrothermal environments [1,2]. These hydroxysulfates, which were also detected on the Martian surface, can be formed abiotically [1,3] or biotically [4]. In the light of this discussion, carbonaceous matter (CM)-rich Archean cherts (0.5wt C_{org.}, 3.5 Ga) from Marble Bar Drill core #1 (~75m depth) were studied. They represent a silt to fine sand-sized volcanoclastic silicified sediments crosscut by micro-quartz veins. CM occurs diffuse or as aggregates in the micro-quartz matrix, in pyrite, associated to Fe-oxides or as patches in quartz veins. The Raman spectra of CM show a crystallinity compatible with a temperature of at least 300°C. The black cherts, S (~3.8 wt.%) and Fe₂O₃ (4.8 wt.%) rich, contain pyrite, but also sphalerite, galena, chalcocopyrite, Ni-Fe-arsenides and Fe-oxides. Large pyrite grains (~100µm) have irregular rims often characterized by nanometric pyrite spherules. When showing euhedral grain boundaries, pyrite is rimmed by muscovite. FIB-TEM investigations show that these pyrites are composed of nano-poly- and single crystals, containing traces of Ni, As, Pb and variable Si contents. A nanofilm of amorphous carbon occurs at the interface between pyrite and muscovite. Muscovites contain N (550 ppm) and C (250 ppm) and are non-stoichiometric. The non stoichiometry is related to the presence of nanometric Fe-(K-Na)-sulfates (jarosite/alunite) indicating local acidic-oxic conditions. A hydrothermal origin and temperatures of about 300° C for these sulfates is favoured as shown by low-angle boundaries at nanoscale in micro-quartz grains and the maturity of CM.

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Hercynian gabbroic intrusions from the Spanish Central System: Constraints on mantle composition under central Spain

D. OREJANA¹, C. VILLASECA¹, J.A. LÓPEZ-GARCÍA²,
C. PÉREZ-SOBA¹ AND K. BILLSTRÖM³

¹Department of Petrology and Geochemistry. Complutense University of Madrid. Spain. (dorejana@geo.ucm.es)

²Department of Crystallography and Mineralogy. Complutense University of Madrid. Spain.

³Swedish Museum of Natural History. Stockholm. Sweden.

Small basic to intermediate intrusions are scarce within the Spanish Central System (SCS), outcropping among abundant coeval peraluminous granitoids. Although mixing with granitic magmas is very common, in this study we only deal with the most primitive basic rocks. They range from norites to olivine gabbro-norites, with some Amph-Phl-rich varieties.

Major and trace element composition suggests a low degree of magma differentiation ($Mg\# = 0.52-0.75$; $Cr = 96-1170$ ppm), though some Cr-Spl + Ol fractionation might have occurred. K_2O content is in the range 0.73-2.82 wt% and a medium-K to high-K calc-alkaline affinity is observed. Their sub-alkaline nature argues against their inclusion in the appinite suite, as previously suggested.

Although two groups of gabbros may be distinguished according to LILE-U-Th concentrations, these rocks show high LREE and LILE concentrations in general, indicative of an enrichment event in the mantle source. Their chondrite and primitive mantle normalised multielement plots show negative Nb, Ta and Ti anomalies and positive Pb anomalies, suggesting involvement of subduction-related fluids or crustal recycling. These patterns resemble those of continental arc-related gabbros, but with lower Ba-Sr contents.

Their Sr-Nd isotopic signatures display a slightly enriched composition close to BSE ($\epsilon Nd = -2.6$ to 0.7 ; $^{87}Sr/^{86}Sr = 0.7045-0.7063$). This is also shown by other SCS gabbroic intrusions (e.g. Bea *et al.*, 1999). The short isotopic compositional range suggests the lack of significant crustal assimilation during emplacement. Pb isotope ratios of gabbros also define a small compositional field, similar to SCS granitic rocks. The presence of two gabbro types might be related to variable mineral modes in the mantle sources.

The late-Hercynian mantle under central Spain has been proved to show an heterogeneous composition (Villaseca *et al.*, 2004). This new dataset reinforces that conclusion and points to the involvement of a recycled crustal component into their mantle sources.

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The ties that bind: Dynamics of syntrophic associations in marine methane seeps

VICTORIA J. ORPHAN¹, ANNELIE PERNTHALER¹,
ANNE DEKAS¹, CRYSTAL GAMMON¹, AND
CHRISTOPHER H. HOUSE²

¹Division of Geological & Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA.
vorphan@gps.caltech.edu

²Department of Geosciences, Pennsylvania State University, University Park, PA, 16802, USA.

The deep-sea methane seep environment supports active and diverse microbial assemblages supported by the anaerobic oxidation of methane (AOM). Unknown to science less than a decade ago, the microorganisms and the molecular mechanisms underlying this enigmatic and globally important biogeochemical process have been the subject of intensive study worldwide. The identification, activity, distribution, and partial metabolic pathway reconstruction of methanotrophic archaea and co-associated sulfate reducing bacteria has been characterized. However fundamental questions still remain regarding the necessity of a physically coupled syntrophic association between sulfate reducing bacteria and methane oxidizing archaea, the underlying biochemistry enabling sulfate-coupled methane oxidation, and the extent of the diversity of microbial assemblages involved in AOM. Using microanalytical stable isotope analyses of whole cells in tandem with genomics enabled molecular methods, we examined the variation in metabolic activity between individual aggregations of microorganisms recovered from methane seep sediments. Significant differences in activity were observed between archaeal-bacterial associations and mono-specific aggregations of putative methanotrophic archaea and sulfate-reducing populations, supporting enhanced metabolism in multi-species aggregates. Application of a new SSU rRNA targeted method for capturing and concentrating specific uncultured microbial populations from methane seep sediments has uncovered novel partnerships and additional insights into the metabolic potential of the methanotrophic archaea and co-associated bacteria.

Breaching the North African watershed: Driver for Mediterranean anoxia?

A. OSBORNE¹, D. VANCE¹ AND E. ROHLING²

¹Department of Earth Science, University of Bristol, UK;
(anne.osborne@bristol.ac.uk; d.vance@bristol.ac.uk)

²National Oceanography Centre, Southampton, UK;
(e.rohling@noc.soton.ac.uk)

Quaternary climate change in North Africa appears to drive periodic changes in the redox chemistry of the Eastern Mediterranean, and such interactions may also be of importance for the interpretation of wider ocean anoxia. Deep Mediterranean anoxia is associated with negative oxygen isotope anomalies and the timing has been linked with northward shifts of the Inter Tropical Convergence Zone (ITCZ) and intensification of the African monsoon during Northern Hemisphere insolation maxima [e.g. 1]. These observations have led to the hypothesis that an increased flux of freshwater to the Eastern Mediterranean was a major contributing factor to the changes in deep ocean chemistry. Nd isotopes have previously been used to support a distinct increase in Nile discharge during the central periods of sapropel S1 (~9-6ka BP) and S5 [2]. However, a Nile source alone cannot account for the entire duration of S1 and S5 (~125 ka BP) deposition. We present new evidence of a wider North African margin source of freshwater at the time of S5 from Nd isotopes in the Western Levantine and from Quaternary lake deposits in Libya.

A large oxygen anomaly of ~ -4‰ is observed across S5 in ODP core 971A from the western Ionian Sea [3]. This anomaly is much greater than that recorded in cores from close to the Nile outflow (~ -2‰) [3]. Our data from 971A show a distinct change in the ϵ_{Nd} of planktonic foraminifera (*G. ruber*) towards more radiogenic values across S5. Analyses of gastropod fossils from Quaternary lake deposits in Libya also give a radiogenic Nd signal ($\epsilon_{Nd} \sim -2$), as expected of waters rising in the range of basaltic mountains comprising the North African watershed at ~ 21°N.

These data support the hypothesis that a northward movement of the ITCZ breached the North African watershed during Northern Hemisphere insolation maxima and contributed freshwater to the Mediterranean basin. Further investigation is needed to determine the importance of this contribution in the development of anoxia, relative to Nile inputs.

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Oligomerization of amino acid on mineral surface under the pH controlled conditions

Y.OTA, T.SATO AND S.TAMAMURA

Graduate School of Engineering Hokkaido University, Japan
(yukieota@eng.hokudai.ac.jp)

The role of mineral surfaces as a catalyst on the oligomerization of the amino acid, glycine, during wetting and drying cycles was investigated. Several types of montmorillonite with different interlayer cations (H, Ca, Na) and silica (quartz type) powder (10mg) were suspended with 10mM amino acid solution (1ml) under pH controlled conditions. The suspensions were dried at 95°C to simulate the drying step, while addition of distilled water represents the wetting step. These wetting and drying steps were performed in several repetitions.

Amino acid oligomerization proceeded more favourably in silica as a catalyst at its point of zero charge (PZC) near pH2.6 (Figure 1). The peptide yield was subsequently reduced under more acidic condition (i.e. pH 2) due to excess positive charges of both silica surface and amino acid ions – exerting an inhibiting effect on amino acid adsorption. At the PZC of montmorillonite and glycine (pH 6.0), the catalytic efficiency of minerals was reduced due to zwitterions forming which has a low reactivity for glycine (Zamaraev *et al.*, 1997). The catalytic influence of minerals on amino acid oligomerization is largely influenced by the surface charge of the minerals.

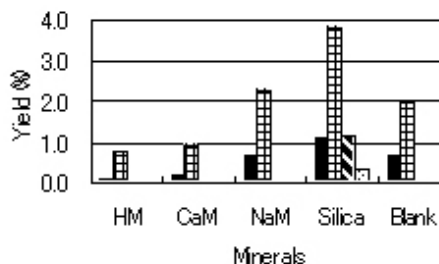


Figure 1: Peptide yield from glycine in different mineral systems at pH 2.6. Glycine anhydride (■), Gly-Gly (▤), Gly-Gly-Gly (▨), Gly-Gly-Gly-Gly (▩)

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Mechanism of Cr⁶⁺ immobilization in different soils

K. OTOMO AND N. SHIKAZONO

Laboratory of Geochemistry, Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Yokohama 223-8522, Japan (k-otomo@dance.ocn.ne.jp; sikazono@aplc.keio.ac.jp)

We carried out experimental studies on the changes of Cr⁶⁺ concentration in the solutions with different pH which were reacted with different soils containing large amount of Cr⁶⁺ (1,000ppm) at room temperature. Soils used for the experiments include Kanto loam (weathered basaltic soil), weathered acidic soil and kaolinite bearing soil derived from weathered granitic rocks. The results obtained from the study indicated that Cr⁶⁺ released within a very short period (three minutes), but it decreased rapidly with time when the Kanto loam soil was used in the experiment and in this case the Cr⁶⁺ concentration in the solution (after 3 minutes) was 0.36 μg mL⁻¹. This decrease may be due to the reduction of Cr⁶⁺ by Fe²⁺ in the soil. Therefore, this study suggests that the basaltic weathered soil (Kanto loam soil) is very useful material for the immobilization of Cr⁶⁺ from the soils and sediments.

Noble gases in Frontier Mountain ureilites

U. OTT¹, L. FRANKE¹, H.-P. LÖHR¹ AND K.C. WELTEN²

¹Max-Planck-Institut für Chemie, Abteilung Geochemie, Joh.-J.-Becher-Weg 27, D-55128 Mainz, Germany (ott@mpch-mainz.mpg.de)

²Space Sciences Laboratory, University of California, Berkeley, CA 94720-7450, USA (kcwelten@berkeley.edu)

Introduction. We report results from noble gas analyses of four ureilites from the Frontier Mountains area, Antarctica. These noble gas data complement cosmogenic radionuclide data obtained by [1] thus shedding light on the cosmic ray exposure history of these meteorites. Of interest are also the trapped noble gases, since ureilites represent a unique class of achondritic meteorites with high abundances of carbon and trapped noble gases.

Cosmogenic noble gases. Results are summarized in Table 1. FRO 90036 and FRO 90054 may be paired, with a common GCR exposure age of ~ 9 Ma. They may belong to an extensive shower as indicated by radionuclides of additional FRO ureilites [1]. FRO 97013 and FRO 01030 are separate falls. While the latter has an exposure age of ~ 4 Ma, the former was irradiated under high shielding and possibly received the bulk of its exposure on the parent body.

meteorite	³ He _c	²¹ Ne _c	³⁸ Ar _c	(²² Ne/ ²¹ Ne) _c
FRO 90036	15.4	2.64	--	1.171
FRO 90054	15.1	2.12	~0.33	1.225
FRO 97013	2.88	0.731	--	1.052
FRO 01030	9.64	1.022	~0.9	1.224

Table 1: Abundances of cosmogenic nuclides (units: 10⁻⁸ cc STP/g) and shielding parameter (²²Ne/²¹Ne)_c.

Trapped noble gases. Trapped Ar, Kr and Xe abundances are listed in Table 2. Most remarkable are the low (compared to other ureilites) abundances in FRO 90054 – in line with its very low reported carbon content [2] - and the very high Ar/Xe and Kr/Xe ratios of FRO 01030, which even exceed those for the previous record holder Goalpara [3].

meteorite	³⁶ Ar	⁸⁴ Kr	¹³² Xe
FRO 90036	190	1.78	0.601
FRO 90054	9.46	0.0415	0.0252
FRO 97013	508	2.65	0.295
FRO 01030	66.8	0.866	0.233

Table 2: Trapped Ar, Kr and Xe (units: 10⁻⁸ cc STP/g).

Acknowledgments. Luigi Folco (U. Siena) provided the FRO 97013 and FRO 01030 samples while FRO 90036 / 90054 were obtained from Euromet.

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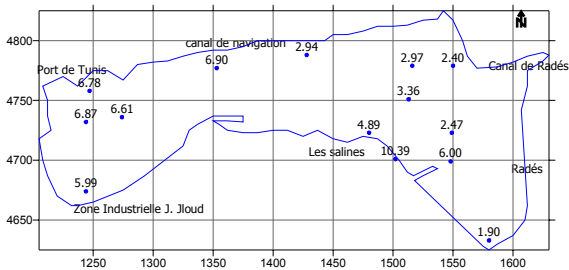
Evolution of anoxic aquatic systems under urban environments : Case of "Lac Sud" Tunisia

N. OUERTANI, R. HAMOUDA AND H. BÉLAYOUNI

Faculté des Sciences de Tunis, Département de Géologie,
Laboratoire de Géochimie organique
(nizarouertani@yahoo.fr)

The "lac sud" of Tunis, is an anoxic confined environment evolving under the direct control of an urban environment that affects him to various degrees (Didyk, B.M., *et al* 1978).

The quantitative and qualitative study of the organic matter contained in surface sediments, by the determination of the total organic carbon (TOC), the free and potential hydrocarbon compounds (S1 and S2), the total hydrocarbons and specially the saturated fraction (analyzed by gas chromatography) permit to distinguish 3 principal zones in the lake characterized by various degree of anoxia.



The western zone is characterised by an advanced and irreversible anoxic state, with an exceptional rate of conservation of organic matter (TOC > 6 %) and an exceptional enrichment in hydrocarbon compounds of biogenic and anthropological origin (HT > 2033 ppm).

The zone situated in the east of salt works is characterized by an anoxic state less accentuated with a rate of organic matter conservation (TOC < 3 %) and a total hydrocarbon content (HT < 820 ppm), less important. Hydrocarbons present are of mixed origin continental and marine (Jaffé *R. et al*, 2001).

Finally, in the central and north-eastern zone the anoxic state is in way of installation, the contents in organic matter and in total hydrocarbons are the weakest.

In addition, the analysis of the lipidic fraction allowed to show that the whole system is under direct influence of the urbanization (Medeiros P.M. and Bicego M.C., 2004):. The development of the anoxia in preferential zones of the lake is

Evolution of aquatic systems in urban environments must be considered with a lot of interest to avoid the risk of controlled by the low reactivity of organic matter of anthropological origin.reaching an irreversible state.

References

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In situ geochemical data from metamorphic rocks in the active Mariana subduction zone

S. PABST¹, T. ZACK¹, I.P. SAVOV², D. ROST³ AND E.P. VICENZI³

¹Mineralogisches Institut, Universität Heidelberg, Germany
(spabst@min.uni-heidelberg.de)

²DTM, Carnegie Institution of Washington DC, USA

³Department of Mineral Sciences, Smithsonian Institution, Washington DC, USA

The active serpentine mud volcanism of the Izu-Bonin-Mariana (IBM) forearc exposes variably serpentinized harzburgites and blueschist-facies mafic fragments to the ocean floor. The latter indicate that some of the fragments are derived from depths corresponding to the slab-mantle interface (20-40 km), i.e. between the actively subducting Pacific oceanic crust and the IBM subarc mantle.

In the past, only a few blueschist-facies mafic fragments (up to several cm in diameter; [1]) were analyzed petrologically in great enough detail. For example [1] estimated that PT-metamorphic conditions for key mineral assemblages (lawsonite + quartz, aragonite, lawsonite + pumpellyite) reveal low temperatures (150-250 °C) at pressures reaching 0.5-0.6 GPa. But to date, no in-situ trace element data exist on mafic blueschist-facies clasts from any serpentine mud volcano.

We will present abundant petrological descriptions of several newly discovered mafic fragments from the South Chamorro Seamount, ODP Leg 195. The mineral assemblages of the blueschist-facies clasts include (a) Na-amphibole + phengite + chlorite ± apatite ± sphene ± spinel ± rutile, (b) Na-amphibole + chlorite + sphene + rutile + epidote + allanite + phengite + spinel ± pumpellyite ± pyroxene (Acm-Di-Jad) ± zircon, (c) chlorite + epidote + allanite + Na-amphibole + sphene + garnet + Fe-oxide ± rutile ± apatite and (d) phengite + Na-amphibole + chlorite ± spinel. Albite and quartz are always absent.

For studying the light elements boron and lithium we used Time-of-Flight SIMS imaging capability with a μm-scale resolution. Our multi-element maps with high spatial resolution show that in the shallow subducted slab Li resides in phengite ≥ chlorite > amphibole and that boron preferentially resides in both phengite and chlorite. SIMS analyses verify the high concentration in B and Li in these phases (with ~35 μg/g B and ~80 μg/g Li in phengite). Interestingly our images also show that boron is strongly enriched in parts of chlorite, possibly due to B remobilization from circulating fluids. Thanks to the high concentration of B in phengite and chlorite, we will measure $\delta^{11}\text{B}$ by SIMS and evaluate existing models of early B-release and subsequent isotope fractionation by forearc slab fluids.

References

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