Hydrous and anhydrous metal formates – Properties and applications

B. RAAB AND H. PÖLLMANN

Martin-Luther-University Halle-Wittenberg, Mineralogy/Geochemistry, Von-Seckendorff-Platz 3, Germany (bastian.raab@geo.uni-halle.de)

Synthesis and Results

The metal formate hydrates are synthesized by reaction of metalcarbonate, metalhydroxide or metaloxide and formic acid in an aqueous solution. The crystallisation process takes place at a temperature of 20°C.

The characterisation of the crystals was done by X-ray diffraction, thermogravimetry, scanning electron microscopy and Karl-Fischer-titration.

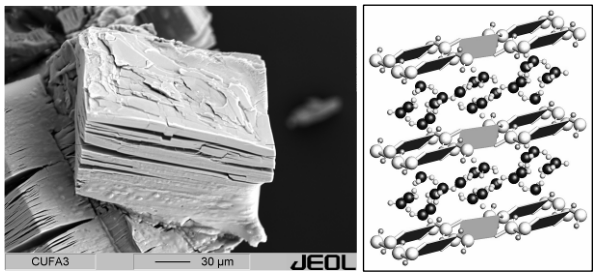

Figure 1: SEM image of $Cu(HCOO)_2$, dehydrated from $Cu(HCOO)_2 \cdot 4H_2O$ at 20°C and the crystal structure

Discussion

It is impotant to investigate the crystallographic properties of the formate and their stability to investigate in further experiments the effect on acceleration and retardation of formates as admixture in Ordinary Portland Cement. In addition, we investigate the dehydration and decomposition of the metal formate to produce particles in nanometer size. The metal carboxylate are suitable because of their low decomposition temperatures.

Conclusion

By using the crystallographic information of hydrous and anhydrous metal formates, theoretical predictions for applications are be obtained.

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Molecular dynamics simulations of fission track annealing in apatite

JEREMY A.L. RABONE[1] AND NORA H. DE LEEUW[2]

[1]School of Crystallography, Birkbeck College, Malet Street, London WC1E 7HX (j.rabone@mail.cryst.bbk.ac.uk)

[2]Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ (n.h.deleeuw@ucl.ac.uk)

Our aim is to use molecular dynamics simulations to elucidate how the composition of apatite minerals $Ca_{10}(PO_4)_6(F,Cl,OH)_2$ affects the annealing rate of the natural fission tracks, which form in the apatites as a result of the spontaneous fission of uranium. Knowledge of the effects that the many species present in natural apatites, particularly fluoride, chloride and hydroxide, have on the annealing rate is invaluable in interpreting accurately the results of fission track data for geothermochronometry.

The fission tracks formed by uranium fission in apatite are typically 14 µm long and 50 Å in diameter. The formation of tracks in apatite can be adequately modelled using a method where atom velocities are altered perpendicular to the track, which model produces tracks which are consistent with those obseved experimentally.

The simulations show that the diameters of tracks formed in two crystal directions are similar for a series of six apatites of different composition. In pure chlorapatite the simulated tracks are somewhat larger in both crystal directions, whereas in fluoride-bearing apatites small clusters of calcium fluoride are consistently formed in the track region.

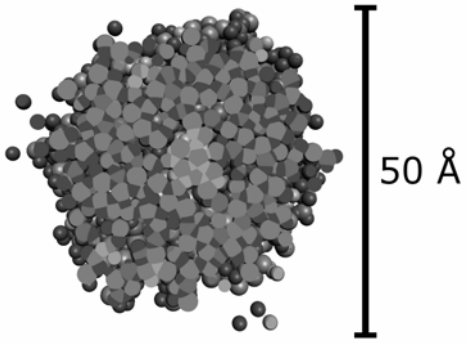

Figure 1: Disrupted atoms looking down a fission track.

Simulating the annealing of fission tracks is a great challenge for molecular dynamics because of the long timescales involved. We are currently developing a method to accelerate annealing by pulling atoms back to their equilibrium positions. The distributions of atomic transition energies from such simulations show some clear trends, in agreement with experiment, which suggest that the rate of annealing can be derived from short molecular dynamics simulations.

The apparent activation energy for biotite dissolution by *in situ* Atomic force microscopy (AFM) observations

K.V. RAGNARSDOTTIR[1], S.J.HAWARD[1,2] AND T.J. MCMASTER[2]

[1]Department of Earth Sciences, University of Bristol, Bristol, UK. (Vala.Ragnarsdottir@bristol.ac.uk)

[2]H.H.Wills Physics Department, University of Bristol, Bristol, UK. (S.J.Haward@bristol.ac.uk, T.McMaster@bristol.ac.uk)

In this study we used *in situ* AFM imaging of biotite (001) surfaces to observe dissolution processes in oxalic acid and hydrochloric acid solutions in real time. In oxalic acid solutions at pH 2 and 1 we observe the combined dissolution processes of slow etch pit formation, followed by relatively fast etch pit growth. The etch pit depth is found to be consistent with the thickness of 1 *tot* layer (~1 nm). Measurements of the fractional surface area covered by etch pits over time provide dissolution rates in the acid solutions. Experiments over a range of temperature, 10°C < T < 35 °C, in the pH 1 solution allow an estimate of the apparent activation energy, E_a= 49 ± 2 kJmol^{-1} using the Arrhenius equation. We find that the average radius of etch pits grows linearly with time for all T, and use these growth rates to obtain a second value of E_a = 53 ± 3 kJmol^{-1}. We also find a linear relationship between the dissolution rate and the density of step edges on the surface for all values of T. However, E_a is found to vary between ~ 40 kJmol^{-1} and >100 kJmol^{-1} at low and high step density, respectively. This variation may reflect the greater energy required for etch pit formation compared with etch pit growth. In an HCl solution of pH 1 we do not observe the formation of discrete etch pits, but a more general degradation over the entire biotite (001) surface. We conclude that etch pit occurrence in the oxalic acid solution proceeds through chelation of aluminium ions in the (001) surface by the oxalate ligand. This may destabilize the silicate structure, leading to the removal of the entire *tot* layer, as observed. In the HCl solution the aluminium cations are less soluble due to the lack of organic ligand so the silicate structure remains intact.

Metal silicate partitioning of Ge, Mo, Ga and P: Constraints on core formation

N. RAI, M.J. WALTER, AND C.J. HAWKESWORTH

Dept. of Earth Sciences, University of Bristol, U.K. BS8 1RJ; (n.rai@bris.ac.uk)

Siderophile element signatures in Earth's mantle are a result of segregation of the iron rich core from the silicate mantle. It is generally argued that during the metal silicate differentiation process these elements were substantially partitioned into the core leaving behind lithophile elements in the silicate mantle. Several core formation models have been proposed to account for the observed abundance of elements in mantle rocks. A recently proposed model [1] suggests that the core formed at the base of a magma ocean which deepened with accretion and in which conditions became more oxidising with time. This also accounts for 5-7% Si in the core.

To test this hypothesis of early reducing magma ocean [1] we are studying the metal silicate partitioning behaviour of selected siderophile and nominally lithophile elements, characterizing the dependence of the metal silicate partition coefficient, D, on oxygen fugacity. We report new experimental results on the partitioning behaviour of Ga, Ge, Mo and P, and these are compared with our previous work on Si, Ta, Nb and V. All these elements can exist in variable and high oxidation states and their partitioning could also be sensitive to silicate melt composition [2]. Experiments were made at 2 GPa and 2000 K, over a range of relative oxygen fugacities from ~IW-2 to IW-6. Silicate melts range from basaltic to peridotitic in composition. The melt compositional parameter, NBO/T, is used as a proxy for silicate melt composition, and has values from 0.7 to 4. Isobaric, isothermal data for each element were regressed using the equation: $\ln D^{met/sil} = a + bfO_2 + c(NBO/T)$. Regressions show that at the experimental conditions Ge has a likely valence state of +2, Ga, Nb and V exist in 3+ valence states, Si shows a valence state of +4, whereas P and Ta appear to exist in a 5+ valence state. Observing the partitioning behaviour of these elements over the redox range investigated, Si exhibits the least siderophile tendency and it appears unlikely for 5-7% Si to sequester into the core under reducing conditions without disturbing the mantle's budget of other siderophile and refractory lithophile elements. Further experiments are in progress to provide more constraints on the influence of fO_2 and melt composition on the metal silicate partitioning of these elements.

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Chemical stratigraphy of UG2, Bushveld Complex, SA: Comparison of analytical methods

D. RAMMLMAIR , B. HARAZIM, H. LORENZ, J. STUMMEYER AND F. KORTE

BGR, Stilleweg 2, 30655 Hannover, Germany; (rammlmair@bgr.de)

The aim of the detailed investigation wais to develop and to validate the EDXRF method as a fast tool to outline zones of interest regarding PGE, Ni and Cu mineralization by using these and other pathfinder elements.

Several methods were applied to obtain geochemical, mineralogical and textural information from UG2-chromitite horizons.

The fastest information was obtained by profiles along half cores using the EDXRF-geoscanner with 250µm steps at 1 to 30 sec/point for major and trace elements. Elemental maps were collected by EDXRF-microscopy in 100µm steps, at 0.5 sec/step for selected areas. Polished thin sections were optically scanned, and investigated by SEM for PGE distribution. Besides these fast methods sub-samples (0.5 to 5 cm) with a more representative sample volume were analyzed by XRF for major and trace elements. The XRF glass beads were digested and analyzed by ICP-MS for REE. Another set of glass beads was produced in graphite containers, embedded in araldite, polished and analyzed for PGE by LA-ICP_MS. For control, the rest of the glass beads was digested in nitric acid and PGE were collected by the telluride precipitation method (Evans *et al*., 2003). Since our observation with SEM confirmed that most of the PGE minerals occur in the interstities of the chromite, selective leaching of the PGE and silicates by nitric acid in the microwave was performed.

Conclusions

A comparison of the methods shows that EDXRF-scanning is a fast and accurate tool to highlight areas of unusual Ni, Cu, PGE pattern. EDXRF mapping provides textural patterns for hand specimen scale and reduces the amount of polished sections needed. Ni, Cu anomalies could easily be verified by other methods (e.g. SEM). PGE distribution patterns have to be treated carefully, since nugget effects might occur or diffraction peaks obliterate the distribution pattern.

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Lithogeochemistry of parautochthonous Variscan metasediments (Northern Portugal). Implications of metamorphism and metassomatism

R. RAMOS AND M. A. RIBEIRO

Centro de Geologia, Departamento de Geologia, Univ. do Porto, Rua do Campo Alegre,687, 4169 - 007 Porto, Portugal (rramos@fc.up.pt; maribeir@fc.up.pt)

The studied metasedimentary rocks, belonging to different lithostratigraphic units, are inserted in the lower Parautochthonous of Galiza Trás-os-Montes Zone (ZGTM), in Northern Portugal Variscan belt. The studied area involve two geographic sectors separated by the Regua-Verin fault. In the western block of the fault the metasedimentry rocks are intruded by abundant pegmatite-aplite bodies and quartz veins and show higher metamorphic conditions: staurolite to biotite zone. In the western block the metamorphic condicion are biotite to chlorite zone.

The metasedimentary lithologies are mainly phyllite and quartz-phyllite rocks in an imbricate structure. Lithogeochemical studies revealed a slow sedimentary sorting and high geochemical maturity in both sectors. The Th/Sc versus Zr ratios indicates, for the two sectors, a geotectonic environment ranging from an Active Continental Margin (ACM) to a Continental Insular Arc (CIA).

The normalization to upper continental crust (UCC) diagrams showed that similar lithologies present geochemical variations according to their proximity to the pegmatite-aplite veins. Next to the veins a deficit in mobile elements in fluid phases are evident, namely in, Rb, U, Th.

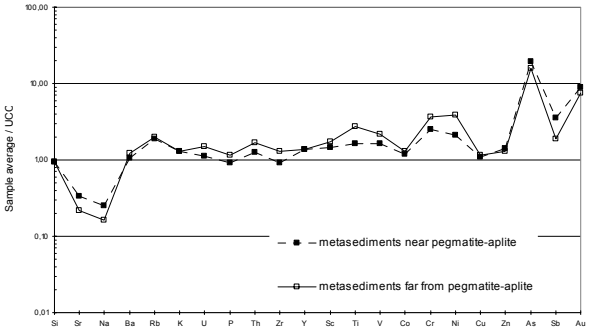

Figure 1: Crustal normalization of samples near and far from pegmatite-aplite veins.

So, the lithologies next to the aplite-pegmatites had been affected by fluid circulation (metassomatic effects) in a high temperature and low pressure (HT-LP) metamorphic conditions, while the lithologies in the both sectors, far from these intrusive bodies, present a isochemical metamorphism.

$\varepsilon_{Nd}(0)$ values of different grain sizes of eolian sand and dust, China

WENBO RAO[1], JUN CHEN[2], JUNFENG JI[2]

[1]Research Academy, Hohai University, China (raowenbo@163.com)
[2]Department of Earth Sciences, Nanjing University, China (Chenjun@nju.edu.cn, Jijunfeng@nju.edu.cn)

Nd isotope is a powerful indicator tracing the provenances of eolian materials [1]. However, Nd isotopic characteristics of different particle sizes of eolian materials are unknown in detail yet. We report here $\varepsilon_{Nd}(0)$ values in different grain sizes of eolian dust in the Duanjiapo section of Chinese Loess Plateau and eolian sand in the Mu Us Desert (Table 1 and Fig.1).

Sample	>45	45-28	<28	<2
Loess	-8.8	-8.5	-9.2	-8.7
Paleosol	-8.5	-8.9	-9	-9.2
Red-clay	-9.1	-8.9	-8.7	-8.6

Table 1 $\varepsilon_{Nd}(0)$ in different grain sizes (μm) of eolian dust

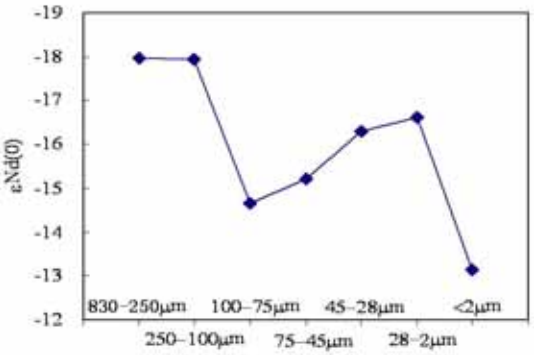

Fig.1 $\varepsilon_{Nd}(0)$ in different grain sizes of eolian sand

Eolian dust in the Duanjiapo section is fine, mostly <75μm, whereas the Mu Us desert sand is coarse, mainly >75μm in diameter. $\varepsilon_{Nd}(0)$ values change little with grain sizes of eolian dust, moreover, are similar among loess, paleosol and red-clay (Table 1), suggesting a uniform source region. But, different grain size fractions of desert sand have obviously different $\varepsilon_{Nd}(0)$ values (Fig.1), implying they have different provenances. In addition, $\varepsilon_{Nd}(0)$ values of different grain-size fractions of desert sand are all more negative than those of eolian dust in the Duanjiapo section, showing the Mu Us desert is not its main source region.

As a result, the Mu Us desert sand is distinct in Nd isotope from eolian dust in the Duanjiapo section, both are probably little related in provenance.

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A new and comprehensive set of bulk distribution coefficients (D's) governing partial melting of hydrous metabasalt

R.P. RAPP[1], G. YAXLEY[2] AND M.D. NORMAN [2]

[1]Research School of Earth Sciences, The Australian National University, Canberra, Australia; (robert.rapp@anu.edu.au)
[2]PRISE, The Australian National University, Australia (greg.yaxley@anu.edu.au; marc.norman@anu.edu.au)

Recycling of hydrous metabasaltic crust into the mantle can occur by a number of different mechanisms, including "normal" subduction, subduction erosion, and delamination of tectonically or magmatically overthickened continental crust. Low-moderate degree partial melting associated with dehydration of this material can produce "adakitic" or "TTG" like magmas with a geochemical fingerprint reflecting a garnet-amphibolite or eclogite "restite". The melt component may coalesce to form granitoid intrusions or may be assimilated in metasomatic reactions with inflowing mantle, while the dense, garnet-rich restite is subsumed by the mantle. However, a reliable and comprehensive set of bulk trace element distribution coefficients (D's) governing this process are lacking. Here we present a new set of bulk D's for Pb, Sr, Y, Ba, Rb, Nb, Ta, Zr, Hf, Ti, Zr, Th, U, Cr, Ni, V, and the REEs, measured at natural abundance levels by laser ablation ICP-MS, for "pristine" adakitic melts in equilibrium with garnet-amphibolite and eclogite restite from the experiments of Rapp and Watson (1995), and for "mantle-hybridized" adakitic melts in equilibrium with pyroxenite reaction residues from new experiments at 1.6-3.0 GPa. Noteworthy observations include D's for Pb which are an order of magnitude lower than previously published experimental values (e.. Klemme *et al*., 2002), and Nb and Ta D's that reinforce the conclusions of Rapp *et al*. (2003) that Nb/Ta ratios of adakite/TTG melts reflect the bulk composition of the source, rather than its mineralogy.

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Coupling crushing and laser ablation in submarine glasses provide new constraints on noble gases composition of Earth's mantle

A. RAQUIN[1], M. MOREIRA[1] AND M.D. KURZ[2]

[1]Equipe de Geochimie et Cosmochimie, Institut de Physique du Globe de Paris, 4 place Jussieu, F75005 Paris, France: (raquin@ipgp.jussieu.fr)

[2]Department of Marine Chemistry and Geochemistry. Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543, United States

Rare gases released with traditional experimental procedures in mantle-derived rocks generally display mixing trends between a mantle and an atmospheric component. The origin of atmospheric contamination is still debated and is interpreted to result from surface contamination or recycling in the mantle.

In order to examine this problem, we analyzed noble gases in single vesicles in submarine glasses, because it gives the possibility to look at the end members. Here, we compare data obtained by crushing and by measurement of in single vesicles using a laser UV ablation system on two samples: 2πD43, considered to be representative of upper mantle volatiles from the northern MAR, and one from the western Galapagos, which appears to sample one of the most primitive mantle noble gas reservoirs.

Helium isotopic ratios in single vesicles are constant for both MORB and OIB sample with a mean values of 90,500±3,500 and 32,000±1,000, respectively.

The systematic Ne-Ar in single vesicles of sample 2πD43 indicates that there is only one population of vesicles, with a mantle composition (the mean value of $^{40}Ar/^{36}Ar$ is 25,000±4,000 and is associated to a $^{20}Ne/^{22}Ne$ of 11.5±0.6). This lower $^{20}Ne/^{22}Ne$ ratio compared to those measured by crushing can be explained with a small contribution of gases, with an air-like composition, dissolved in the matrix. We conclude that isotope variations observed by crushing are due to superficial contamination.

In contrast, analyses from individual vesicles of the Galapagos sample show heterogeneities on the scale of individual vesicles ($^{40}Ar/^{36}Ar$ ratio vary from 3,000±500 up to 7,500±300 and being associated to a $^{20}Ne/^{22}Ne$ from 10.3±0.5 to 11.9±0.3). Such high $^{40}Ar/^{36}Ar$ values are not observed during crushing.

Application of statistical methods in geochemical anomalies identification, Baidjan area, North of IRAN

IRAJ RASA[1], SOMAYE BOKHARAEI[2] AND MOHAMMAD HADI NEZAMPOUR[3]

[1]Earth Sciences Faculty, Shahid Beheshti University, Tehran, Iran. (i-rasa@sbu.ac.ir)

[2]Sciences Faculti, North Tehran Azad University, Tehran, Iran.(S_bojarai@yahoo.com)

[3]Earth Sciences Faculty, Shahid Beheshti University, Tehran, Hadi.(nezampour@gmail.com)

Methods

Baidjan Exploration Area is situated in the South of Amol, North of Iran, Whose total surface area is 140 km^2. A total of 264 samples of the fine grained fraction of active stream sediments were collected and were analysed by ICP-MS method. Chemical variable after replaced censored data and normalized on the base of upper stream rock unit processed and mapped by means of R_mode factor, K¬_Means Cluster and Scatter plat methods.

Discussion and result

In these ways were determined three anomaly area in north, centre and west of exploration area. In the north and most important promise point, anomalies at the local scale were identified for Au (up to 37 ppb) and As (95.4 ppm). In this anomaly area, the correlation between these threshold values and silisified carbonate or carbonate hosted sislisic veins is clearly shown. The second anomaly point, in central of exploration area, anomalies at a local scale were identified for Ag (up to 3 ppm), Sb (up to 5.6 ppm), Bi (up to 2.2 ppm), Zn (up to 231 ppm) and Cu (up to 72.8 ppm). This anomaly reflected mainly a local distribution of the outcropping rock type, mainly silisified andesit and basalt that malachite and azurite in the silisic zone or veins clearly shown. The west anomaly shown threshold obtained for REE, especially Ce (up to 541 ppm) and La (up to 104 ppm) and Cu (up to 70 ppm). This anomaly was correlated to altered Eocene tuffite.

Conclusion

The high grade of Ce, La and relatively Au, Cu and Zn and association with favourable geological phenomena, ambient needing further validation, gave some indicative references to the economic potential of this area for these elements mineralization.

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Detection of hydrocarbon micro-seepage using geo-microbiological method: A case study from Deccan Syncline, Maharashtra, India

M.A. RASHEED, D.J .PATIL AND A.M. DAYAL

Stable Isotope and Surface Geochemical Prospecting Lab. National Geophysical Research Institute, Hyderabad, India. (rasheedmicro@rediffmail.com)

Geo-microbial method for hydrocarbon exploration is the search for surface microseeps as clue to the presence of an active petroleum system and / or to the location of possible oil and gas accumulation. It is a surface prospecting technique used to detect the anomalous population of hydrocarbon oxidizing bacteria in the surface soils, which indicate the presence of subsurface oil and gas accumulations. This method is based on vertical seepage of light hydrocarbon gases (C_1 - C_4) from the oil and gas pools to the shallow surface, and are utilized by hydrocarbon oxidizing bacteria. These bacteria utilize hydrocarbon gases as their only food source and are found enriched in the near surface soils above the hydrocarbon bearing structures. These hydrocarbon-oxidizing bacteria used as indicators of invisible hydrocarbon microseepage, and are used to evaluate subsurface hydrocarbon potential. Microbial activity profiles have indicated a good contrast between oil producing and non-oil producing areas.

This paper presents geo-microbial study carried out in Deccan Syncline areas of Maharashtra. In the present study, propane-oxidizing bacteria were considered as indicator microbes as propane gas originates from petroleum pools only. Sub-surface soil samples were collected aseptically in an interval of 5 x 5 km, and analyzed for propane oxidizing bacterial concentration. The propane oxidizing bacterial count in the soil samples of the studied area ranged from 1 x 10^2 to 6.7 x 10^5cfu/gm of soil sample. Two microbial blooms of high concentration of propane oxidizing bacteria were identified and mapped in the study area. Microbial prospecting method has emerged as an important tool for hydrocarbon prospecting and integration of microbial data along with geological, geophysical, and geochemical data, can lead to the successful grading of exploration leads and prospects. The success rate of Microbial Prospecting for Oil and Gas is upto 90% (Wagner *et al*., 2002). The paper presents the details of microbial prospecting methodology developed at National Geophysical Research Institute and its importance in hydrocarbon exploration.

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Evidence for the collapse of upper water masses during ice-rafting events: a multi-species planktonic foraminiferal $\delta^{18}O$ approach

H. RASHID, S. LODESTRO, B FLOWER AND T. QUINN

(hrashid@marine.usf.edu)

We have measured $\delta^{18}O$ in three planktonic foraminiferal taxa *Neogloboquadrina pachyderma* (s), *Globigerina bulloides, Globigerinoides ruber* and benthic foraminifera *Cibicidoides wuellerstorfi* from IODP Site U1313. Concentration of the ice-rafted debris (IRD) and benthic foraminiferal assemblages were also counted. We found similar $\delta^{18}O$ values from mixed-layer and thermocline-dwelling planktonic foraminifera during the large amplitude IRD-events suggesting the collapse of upper water masses. This data suggests that the planktonic foraminifera taxa calcified their shells at similar temperatures in a homogenized upper water column. Similar collapse can be seen from the northern margin of the IRD-belt, implying that this homogenization of water masses were widespread in the region. We suggest that an increase in storminess during large IRD event intensifies vertical mixing of meltwater from ice-rafting in the upper ocean. Lighter $\delta^{13}C$ values correspond to those large IRD-events suggesting coupled perturbation of both surface and deep waters at the subtropical latitude.

Trace elements fractionation in Ca-rich and Ca-poor alkaline-ultrabasic series

I.T. RASS

Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Sciences, Moscow, Russia (rass@igem.ru)

Two separate coexisting series, high-Ca melilite-bearing rocks and more common melilite-free alkaline-ultrabasic rocks, compose the alkaline-ultrabasic association in carbonatite massifs of Maimecha-Kotui Province, NW Siberian Platform [1]. Two analogous series are now known also in other complexes.

The trace element distributions (XRF and ICP data) in the above rocks, comparable in differential degree, from the different massifs, are clearly different. Their logarithmic relations in the sequential derivatives of the series, resulted due to fractionation according to the Rayleigh model, with different partition coefficients; then quite different rock-forming and trace element contents and their zoning patterns in coexisting minerals (EPMA data), dependent on their affiliation to the above series; as well as recent results of melt inclusion investigation in olivine of melilite-bearing rocks from the Guli and Kaiserstuhl complexes, suggest that two parent primary magmas do exist. The separate primitive magma, essentially richer in Ca, was preliminary carbonatised and enriched in Sr, REE, and Nb. Ca-poor magma can fractionate during its ascent from great depths. In turn, primary magma with higher Ca, parent for melilite-bearing rocks, fractionates only at shallower depths where CO_2 activity is lower and oxygen fugacity during crystallization of the melilite-bearing rocks is higher, as compared with conditions during differentiation of Ca-poor magma.

Acknowledgement

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Orbital Forcing, Timescales, and the Pacing of Global Glaciations

MAUREEN E. RAYMO[1], LORRAINE LISIECKI[1], KENJI KAWAMURA[2] AND BEN COSTANZA[1]

[1]Dept. of Earth Sciences, Boston U., 685 Commonwealth Ave., Boston, MA 02215 USA (raymo@bu.edu, lisiecki@bu.edu, costanza@bu.edu)

[2]National Inst. of Polar Research, 1-9-10 Kaga, Itabashi-ku, Tokyo 173-8515, JAPAN (kawamura@nipr.ac.jp)

Not long after Hays *et al.* (1976) proved that orbital variations control climate, the technique of using orbital pacing inherent in climate proxy records to improve geologic time scales was developed. Orbital-tuning of marine or terrestrial records requires assumptions about what specific component of insolation is forcing (usually indirectly) the climate proxy, as well as the magnitude of the lag between this forcing and the climate proxy. Despite these uncertainties, the time scales developed resulted in a significant improvement over paleomagnetic time scales and even led to a reassessment of the errors inherent in radiometric dating techniques. Recently, the orbital tuning of the O_2/N_2 ratio of trapped air in Antarctic ice cores (e.g. Kawamura *et al.,* submitted) is based on a direct physical link between local summer solstice radiation and ice metamorphism; this new method may prove to be a gold standard for orbital tuning as well as make the essential point that not all orbital tuning is equally uncertain.

The extension of ice core records into the early Pleistocene, combined with O_2/N_2 time scales, should allow assessment of one of the major drawbacks of the marine $\delta^{18}O$ record; namely, that it does not speak to where, geographically, the ice volume component of climate variance originates. Since the development of the $\delta^{18}O$ proxy the general assumption has been that the ice volume signal of the last 3 Ma originated almost entirely in the Northern Hemisphere with little variance contributed by the Southern Hemisphere. By contrast, we have recently proposed (Raymo *et al.,* 2006) that from ~3 to 1 Ma a terrestrial ice margin sensitive to local summer insolation may have characterized much of the East Antarctic ice sheet. Because Earth's orbital precession is out of phase between hemispheres while obliquity is in phase, 23 kyr changes in ice volume in each hemisphere would cancel in globally integrated proxies such as ocean $\delta^{18}O$ or sea level leaving the in-phase obliquity (41-kyr) component of insolation to dominate the record. To test this idea for the origin of the *41-kyr world*, well-dated proxy records sensitive to local climate and the lateral movement of ice margins (in both the NH and SH) are needed. Would such records show precessional *and* obliquity pacing?

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^{238}U- and ^{232}Th-decay series constraints on the timescales of generation and degassing for phonolite erupted in 2004 near Tristan da Cunha

M.K. REAGAN[1], S. TURNER[2], M. LEGG[1], K.W.W. SIMS,[3] AND V. L. HARDS[4]

[1]U. Iowa, Iowa City, IA, USA, (mark-reagan@uiowa.edu)
[2]GEMOC, Macquarie U., Australia., (sturner@els.mq.edu.au)
[3]WHOI, Woods Hole, MA, USA, (ksims@whoi.edu)
[4]British Geological Survey, UK, (vicky@mvo.ms)

Phonolite pumice found floating offshore of Tristan da Cunha following intense seismic activity 20 to 30 km southeast of the island July 29-30, 2004 was analyzed for ^{238}U- and ^{232}Th-series nuclides including ^{230}Th, ^{226}Ra, ^{210}Pb, ^{210}Po, and ^{228}Th. The initial (^{210}Po/^{210}Pb) value of 0.16 for the phonolite shows that, like most subaerial lavas, this subaqueous tephra degassed most of its ^{210}Po upon eruption. The (^{230}Th/^{232}Th) and (^{238}U/^{232}Th) values for the phonolite are similar to those of more mafic magmas from Tristan da Cunha. However, in contrast with trachyandesites erupted in 1961 from Tristan da Cunha (Oversby and Gast, 1968), the activities of ^{210}Pb and ^{230}Th are both strongly enriched with respect to ^{226}Ra in the phonolite, which is likely due to ^{226}Ra partitioning into feldspars and hornblende in the decades leading to eruption. Moreover, the initial (^{228}Th)/(^{232}Th) value was 0.94±0.03 (1σ), suggesting that Ra was being fractionated from Th until just before eruption. These disequilibria were modeled to have resulted from continuous crystal fractionation for about 2 centuries assuming that the fractionation began with a 1961-like trachyandesite and involved hornblende, anothoclase, apatite, and sphene. The implied fractionation rates are 2-3x10^{-3}y^{-1}, which are one to several orders of magnitude faster than has been calculated for most other magmas. Nevertheless, these rates are similar to those calculated for the relatively low volume (0.1 km^3) trachyte erupted from Fogo in 1563 (Snyder *et al*., 2007). These data imply that the 2004 magma was not the differentiated cap of a much larger magma body that remained at depth. Instead, it was likely the residue of a relatively small magma body that migrated rapidly through the crust southeast of Tristan da Cunha and underwent extensive and rapid crystal fractionation.

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Carbon isotopes vs temperature: Contact metamorphism in graphitic metapelites at western Venezuela

K. REATEGUI, M. MARTÍNEZ, W. MELÉNDEZ AND S. MARRERO

Centro de Geoquímica, Instituto de Ciencias de la Tierra, Facultad de Ciencias, Universidad Central deVenezuela. Apartado Postal 3895, Caracas 1010 A (katya_reategui@ciens.ucv.ve)

Isotopic characterization of graphitic materials associated with the metamorphic aureole of the La Soledad Granite and the non-carbonatic phyllites of Cerro Azul Association, at western Venezuela, was used to evaluate the correlation between the variations in δ^{13}C with the progress of the metamorphic process.

Raman spectroscopy was used to evaluate the graphite cristalinity and the maximum metamorphic temperature reached. Aditionally, petrographic determination was also applied in this work. The mineralogical assemblage and the presence of andalusite mineral indicated an intermediate methamorphism.

The intrusion process produced, at the contact zone, an increase of δ^{13}C (from -28.3 to -27.5‰) which could be linked with the temperature gradient and hydrothermal fluid action. Isotopic signals showed greater dispersion in zones closer were higher hydrothermal activity was present. However, isotopic data cannot be employed in the evaluation of the metamorphic grade of the rock, because no correlation was found with the calculated temperature derived from spectroscopic parameters (528 to 510 ± 16 °C). Just a weak correlation with %C (0.4 – 2 %C) in the bulk rock was observed, demonstrating that other aditional factors than kinetic ones could be involved.

Several parameters are affecting %C and δ^{13}C in the studied zone, these are: a) temperature; b) composition of hydrothermal fluids and c) the reactions between hydrothermal fluid with the mineral assemblege present in the the rock, as well as with graphite. Results allow us to infer that, for this type of geological environment, isotopic signature of graphite must not be employed as geothermometer.

Dissolution of biogenic silica in the sediments of the Scheldt continuum

L. REBREANU, C. DE BODT, G. CLIP AND L. CHOU

Laboratoire d'Océanographie Chimique et Géochimie des Eaux (LOCGE), Université Libre de Bruxelles, B-1050 Brussels, Belgium (laura.rebreanu@ulb.ac.be, cdebodt@ulb.ac.be, lei.chou@ulb.ac.be)

The riverine fluxes of N and P have been significantly increased by human activities, while the anthropogenic input of Si to the Scheldt estuary is considered to be negligible. This excess delivery of N and P compared to Si has affected the phytoplankton speciation and succession in the Belgian coastal zone. The regeneration and retention of Si in the estuary, and particularly in the sedimentary column, is still poorly known. During the year of 2004, surface sediments and cores were collected along the Scheldt continuum. Dissolution kinetics of biogenic silica (BSi) was carried out in batch reactors for several months on sediments from different locations and depths, and the effect of salinity on the dissolution rate was investigated. Preliminary results show that the salinity effect is stronger for low salinity values, but becomes negligible for higher values. Our results also exhibit high BSi dissolution rates in the second centimetre of the sediments cores, with lower values in the first centimetre but also at depth. These results are coherent with the BSi profiles, as well as the microscopic observations of the sediments that showed a higher abundance of biogenic opal debris in the second centimetre with respect to the first centimetre. A model taking into account a two-phase dissolution was used to fit the experimental data, the two phases considered corresponding to biogenic and lithogenic silica, respectively. Overall, the dissolution rates are low and the amporphous silica saturation concentration is never reached, suggesting that the recycling of the biogenic material in the sedimentary column is very low. Part of the opal reaching the sediments probably dissolves at the surface, while the rest is rapidly incorporated within the sedimentary column where dissolution continues along with other diagenetic reactions.

Controlling and predicting subsurface calcium carbonate precipitation for capture of inorganic contaminants

G. REDDEN[1], Y. FUJITA[1], YI-LIN FANG[2], T.D. SCHEIBE[2], A.M. TARTAKOVSKY[2], M. BEIG[3] AND R.W. SMITH[3]

[1]Idaho National Laboratory
[2]Pacific Northwest National Laboratory
[3]University of Idaho at Idaho Falls

In situ manipulation of biogeochemical conditions to induce the formation of mineral phases is one approach for immobilizing metal contaminants in subsurface environments. Examples include U and Tc bioreduction, engineered precipitation of U phosphate minerals, and microbially facilitated coprecipitation of ^{90}Sr in calcite. Strategies for controlling the formation and distribution of precipitated minerals usually require introduction of soluble chemical amendments to the subsurface. The challenges involve not only controlling the distribution of amendments and resulting reactions, but also predicting how permeability and flowpaths evolve as solid phases are deposited (including biomass). The changing flowpaths and geochemical environment will impact the propagation of solid phases and contaminant mobility. Computational models that can account for the scale-dependent coupling between physical, chemical and biological processes over a range of spatial and temporal scales are not well developed.

Experiments in 2- and 3-dimensional packed-sand media have been conducted where calcium carbonate precipitation and co-precipitation of Sr^{2+} is induced by one of two mechanisms. The first is by propagating calcium carbonate precipitates within the fluid-fluid mixing zone between two solutions that flow in parallel. The second approach involves *in situ* generation of carbonate, in the presence of dissolved calcium, by enzyme catalysed hydrolysis of urea. This is an analog for a natural biological process. In both cases, within the reaction zone, a wide range of saturation indices and ion ratios can be established at the pore scale depending on the relative rates of solute transport, mixing, and precipitation. Multiple precipitation modes (e.g., homogeneous and heterogeneous nucleation and growth), different carbonate phases, and varying morphologies can occur in close proximity. The thermodynamic, kinetic and physical control of precipitate deposition influences Sr partitioning in the porous media, as well as permeability and flow paths in the porous media.

We have simulated solute mixing and flow modifications at the pore scale using the Smoothed Particle Hydrodynamics (SPH) method. Continuum-scale simulations of the experimental results were also conducted using grid-based methods. A goal is to use SPH simulations as the basis for parameterization of macroscopic finite-element multi-component reactive transport models, correlating results from the two model scales with our experimental results.

Rapid hydrogen isotopic exchange between aqueous hydrocarbons and water under hydrothermal conditions

E. REEVES[1], J. S. SEEWALD[2], S. SYLVA[3]

[1]MIT/WHOI Joint Program, Woods Hole Oceanographic Institution, Woods Hole, MA (ereeves@whoi.edu)
[2, 3]Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution

Numerous experimental studies have investigated D/^{1}H isotopic exchange between sedimentary organic matter (*e.g.* kerogen/oil) and ambient water during thermal maturation (Schimmelmann *et al.*, 2006). However, isotopic exchange involving low molecular weight hydrocarbons and water has received relatively little attention. Due to its high activation energy for exchange, alkyl-bound hydrogen (H) is widely considered to be isotopically conservative and incorporation of water-derived H is assumed to be limited to cracking reactions during catagenesis.

We conducted experiments to investigate D/^{1}H exchange between aqueous *n*-alkanes and water using a Au-TiO_2 flexible cell hydrothermal apparatus. C_1–C_5 *n*-alkanes were heated at 325ºC and 350 bar in aqueous solutions of varying initial D/^{1}H ratio (δD) in the presence of a pyrite-pyrrhotite-magnetite (PPM) mineral redox buffer. Extensive incorporation of water-derived H into C_2–C_5 *n*-alkanes was observed on timescales of months. In contrast, relatively minor incorporation was observed for CH_4. Isotopic exchange appears to be facilitated by reversible equilibration of *n*-alkanes and their corresponding alkenes by the reaction:

$$C_nH_{2n+2(aq)} = C_nH_{2n(aq)} + H_{2(aq)} \quad (1)$$

Where $H_{2(aq)}$ is derived from water. The lack of substantial *n*-alkane decomposition on the timescale of observation, combined with an approach to steady-state isotopic composition, suggests that *n*-alkane δD values may reflect an approach to isotopic equilibrium rather than kinetically-controlled fractionation effects associated with degradation reactions. Substantially lower amounts of exchange were observed for ethane relative to C_3–C_5 *n*-alkanes, suggesting that alkene isomerization may enhance incorporation of water-derived H in these compounds. Thus, in reducing aqueous environments, reaction mechanisms exist that allow rapid D/^{1}H exchange of alkyl-H with water at elevated temperatures and pressures on timescales much shorter than previously assumed.

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Nickel isotope anomalies in iron and chondritic meteorites

MARCEL REGELOUS[1,2], TIM ELLIOTT[2] AND CHRISTOPHER D. COATH[2]

[1]Department of Geology, Royal Holloway University of London, Egham, Surrey, U.K.
[2]Bristol Isotope Group, Department of Earth Sciences, University of Bristol, Bristol, U.K.

^{60}Fe decays to ^{60}Ni with a half-life of 1.49 Ma, and can be used to obtain relative ages for meteorites and processes that occurred within the first ~10 Ma of the formation of the Solar System. Radiogenic ^{60}Ni variations of <50 ppm are expected in iron meteorites, given ^{182}W core formation ages of asteroids and an initial ^{60}Fe/^{56}Fe ratio of 4 x 10^{-7}. However, previous studies have not been able to resolve the predicted variations in ^{60}Ni between magmatic iron groups having different Fe/Ni.

We have developed methods for high-precision Ni isotope analysis of metal and silicate samples. Ni is separated using a 3-stage ion exchange procedure, which includes dimethylglyoxime to yield a Ni fraction free of impurities, in particular Fe, Ti, Sn that potentially form interferences on Ni masses. Ni isotope ratios are measured using a Finnigan Neptune MC-ICPMS in medium resolution mode in order to resolve ^{40}Ar^{16}O from ^{56}Fe and correct for ^{58}Fe on ^{58}Ni (<5 ppm). ^{58}Ni signals of 900pA are measured on a Faraday detector equipped with a 10^{10} Ω resistor. Each sample was analysed a minimum of 4 times. Using this procedure we obtain a reproducibility of ~5 ppm on the ^{60}Ni/^{61}Ni ratio. Terrestrial samples (JP-1, BHVO-2, NIST 361 steel) have Ni isotope compositions that are identical within error of the SRM 986 standard.

Our results show that magmatic iron meteorites have variable ^{60}Ni/^{61}Ni, ranging from a terrestrial value in high Fe/Ni group IIAB, to ~15 ppm deficits of ^{60}Ni in low Fe/Ni group IVB samples. Although a positive Fe/Ni-^{60}Ni/^{61}Ni correlation is consistent with ^{60}Fe decay, we find that ^{60}Ni/^{61}Ni ratios are inversely correlated with variations in ^{62}Ni/^{61}Ni, which are likely to be of nucleosynthetic origin. Moreover, ordinary chondrites (LL) and volatile poor (CV) carbonaceous chondrites cover the same range in Ni isotopic composition as seen in the magmatic iron meteorites. These combined observations show that Ni isotopic heterogeneity within bulk planetary samples is widespread, but do not yield clear evidence of live ^{60}Fe during planetesimal core formation. Bizzarro *et al*. (2006) have previously noted variable ^{62}Ni/^{61}Ni in bulk meteoritic material but our different sample set illustrates several contrasting systematics. In particular, we find that iron meteorites have ^{62}Ni/^{61}Ni both higher and lower than terrestrial values. We suggest that Ni isotopes may provide a valuable means to link iron and chondrite groups, with IVB samples apparently derived from a CV-like parent body and IIAB from LL chondrite. Interestingly, the only meteorite group we have found to have Ni isotopic systematics identical to Earth are the enstatite chondrites.

Influence of model aggregation on the parameterization of biogeochemical reaction kinetics in ecosystem models

P. REGNIER[1], S. ARNDT[1] , G. LACROIX[2], N. GYPENS[3] AND C. LANCELOT[3]

[1]Utrecht University, Utrecht, The Netherlands, (regnier@geo.uu.nl, arndt@geo.uu.nl)
[2]UGMM, Bruxelles, Belgium, (G.Lacroix@mumm.ac.be)
[3]Université Libre de Bruxelles, Bruxelles, Belgium, (ngypens@ulb.ac.be, lancelot@ulb.ac.be)

Marine biogeochemical models focusing on organic matter production and consumption are compared to study the effects of complexity on model results. The various models differ in their level of spatial and biogeochemical detail. Reduction of biogeochemical complexity is performed by aggregating the highly detailed, physiologically based, MIRO model (Lancelot *et al*., 2005). In particular, we investigate the relevance of biogeochemical rate constants, determined in situ or through lab experiments, for ecosystem modeling. Results show that models characterized by distinct levels of spatial resolution provide different quantitative estimates of the biogeochemical rates, especially those strongly influenced by the system's heterogenity. An aggregation of different functional groups or the microbial loop also requires an adaptation of reaction rate constants. The rate constants of the aggregated model have to account implicitely for the processes, which are no longer explicitely included. A direct transfer of rate constants determined experimentaly or by the calibration of other models is thus strongly dependent on the respective model formulation.

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Contrasting evolutionary trends in magnetite from carbonatites and alkaline silicate rocks

E. REGUIR[1], N. HALDEN[1], A. CHAKHMOURADIAN[1], P. YANG[1] AND A.N. ZAITSEV[2]

[1]Department of Geological Sciences, University of Manitoba, Winnipeg, Canada (umreguir@cc.umanitoba.ca)
[2]The Natural History Museum, London, United Kingdom (a.zaytsev@nhm.ac.uk)

Magnetite (Mgt) is a common accessory mineral in carbonatites and associated alkaline rocks, and a sensitive petrogenetic indicator. We examined the chemical evolution of Mgt in calciocarbonatite (MCrb) and ijolite (MIj) from Kerimasi, Tanzania. MCrb is characteristically enriched in Mg (0.18-0.32 apfu), Mn (0.05-0.14 apfu) and Al (0.01-0.26 apfu), but depleted in Ti (0.04-0.11 apfu) with respect to MIj (< 0.08 apfu Mg, 0.03 apfu Mn, 0.04 apfu Al, and > 0.21 apfu Ti). MCrb has much lower levels of Cr, V, Co, Ni and, to some extent, Nb (≤ 16, 1210, 120, 100 and 17 ppm, respectively), but noticeably higher Zn (1310-2770 ppm) than MIj (up to 1880 ppm Cr, 1800 ppm V, 190 ppm Co, 210 ppm Ni, 46 ppm Nb and 1150 ppm Zn). The two samples are virtually identical in terms of their Ga, Zr, Hf and Ta contents. MCrb shows a trend of decreasing Ti and increasing Mn (at nearly constant Mg) from the earliest generation to crystallize (macrocryst cores) toward the latest (rims and small groundmass grains). The early generation of MCrb is also distinguished by its higher V, Nb and Nb/Zr values. In ijolite, we distinguished two varieties of magnetite differing in their Mg, Ti, V, Ga, Nb, Ta, Co and Hf contents. The two types are also characterized by very different Zr/Hf and Co/Nb ratios. Both varieties show a trend of increasing Mg, V, Zr, Nb, Hf and decreasing Ti and Ga from the earliest generation (subhedral crystals) to the later-crystallized interstitial grains. There is also a trend of increasing Ta in variety-one magnetite, whereas variety-two is Ta-free. The significant differences in major- and trace-element chemistry of the studied carbonatite and ijolite indicate that these rocks did not originate from a single magma, but are products of two distinct magmas characterized by different distribution coefficients of trace elements with respect to magnetite.

Characterizing Fe-rich dunite xenoliths as cumulates of Phanerozoic and Archaean flood basalt magmatism

TATJANA REHFELDT[1], STEPHEN F. FOLEY[1], DORRIT E. JACOB[1], RICHARD W. CARLSON[2]

[1]Johannes-Gutenberg Universität Mainz, Intitut für Geowissenschaften, Becherweg 21, 55099 Mainz, Germany; (rehfeldt@uni-mainz.de)
[2]Carnegie Institution of Washington, Department of Terrestrial Magnetism, Washington, DC 20015, USA

Fe-rich dunite xenoliths occur amongst a large abundance of mantle xenoliths, in the kimberlites of the Kimberley cluster, but their origin has been unclear. On the basis of texture, major and trace elements, as well as Re-Os isotope characteristics, we interpret these dunites as cumulates of flood basalt magmatism related to the ~183 Ma Karoo and the ~2.7 Ga Ventersdorp events in southern Africa.

The Fe-rich dunites mainly comprise olivine neoblasts with subordinate olivine porphyroclasts and parallel-oriented needles of ilmenite, which enclose spinel in some samples. Olivines have lower forsterite and NiO contents than mantle peridotite xenoliths (Fo87-89 versus Fo93-95 and 1300-2800 ppm versus 2200-3900 ppm, respectively), which rules out a restitic origin. Cr-rich spinels are remnants of the original cumulate mineralogy that survived a late stage metasomatic overprint related to the production of the host kimberlite, producing ilmenite and phlogopite in some samples. Olivine porphyroclasts and neoblasts have different trace element compositions, the latter having higher Ti, V, Cr and Ni and lower Zn, Zr and Nb contents, indicating contrasting origins for neoblasts and porphyroclasts. The dunites have high $^{187}Os/^{188}Os$ ratios (0.11-0.15) indicating young (Phanerozoic) model ages for most samples, whereas three samples show isotopic mixtures between Phanerozoic neoblasts and ancient porphyroclastic material. Most Fe-rich dunite xenoliths can be interpreted as cumulates of fractional crystallization of Karoo flood basalt magmatism, whereas the porphyroclasts are interpreted to be remnants from the much earlier Archaean Ventersdorp magmatic episode.

The calculated parental magma for olivine neoblasts in Fe-rich dunites corresponds to low-Ti Karoo basalts, whereas olivine porphyroclasts had a parental magma with higher MgO contents similar to Archaean high-Mg and komatiitic rocks. Modelling the crystal fractionation of the parental magmas with pMELTS yields element fractionation trends that mirror the element variation of primitive low-Ti Karoo basalts and the basal section of the Ventersdorp Klivriviersberg Group.

Volcanic Outgassing and the Tl Isotope Composition of the Oceans

M. REHKÄMPER[1,2], R.G.A. BAKER[1,2], S.G. NIELSEN[3], T.K. HINKLEY[4] AND J.P. TOUTAIN[5]

[1]Department of Earth Science and Engineering, Imperial College, London SW7 2AZ, UK
[2]Department of Mineralogy, The Natural History Museum, Cromwell Road, London, SW7 5BD, UK
[3]Department of Earth Science, Parks Road, Oxford OX1 4BH
[4]US National Ice Core Laboratory, USGS, Denver CO 80225
[5]LMTG, Université de Toulouse, CNRS, IRD, OMP, 14 Av. E. Belin, F-31400 Toulouse, France

Thallium is a conservative element in seawater with a marine residence time of ~20 kyr [1]. It is thus unsurprising that the present oceans have a nearly constant Tl isotope composition of $\varepsilon^{205}Tl = -6 \pm 1$ [2-4]. This uniformity is also expressed in the recent growth surfaces of hydrogenetic ferromanganese (Fe-Mn) crusts, which incorporate seawater-derived Tl by adsorption and display $\varepsilon^{205}Tl = +13 \pm 1$ [2]. Time-series analyses of six Fe-Mn crusts from the Atlantic, Indian and Pacific Oceans revealed nearly constant Tl isotope compositions over the last 30 Myr. In contrast, it was also shown that the $\varepsilon^{205}Tl$-values of Fe-Mn crusts changed dramatically from about +6 at 60 Ma to +13 at about 30 Ma [5]. This change has been confirmed by a recent high-resolution time-series study of the Pacific Fe-Mn crust CD29-2 [6].

Given these systematics, it is not unreasonable to assume that the time-series data reflect a change in the Tl isotope composition of seawater. Of particular interest is the possibility that the trend was generated by larger fluxes of Tl derived from subaerial volcanism in the early Cenozoic. This interpretation is in accord with observations that (i) volcanic emissions presently provide ~30% of the global input flux of Tl into the oceans [1], and (ii) such emissions may display low $\varepsilon^{205}Tl$ due to isotope fractionation by partial degassing. The increase of $\varepsilon^{205}Tl$ from 60 to 30 Ma may furthermore be essentially synchronous with the decrease of atmospheric CO_2, as inferred from B isotope data [7], and a 5‰ shift in the S isotope composition of seawater sulfate [8]. It has been proposed that both of these changes could reflect decreasing rates of volcanic outgassing during the early Cenozoic [7, 8].

Preliminary Tl isotope data show that volcanic gases have $\varepsilon^{205}Tl$-values as low as -8, and this demonstrates that changes in volcanic inputs may indeed alter the Tl isotope composition of the oceans. To further investigate this possibility, we will acquire Tl isotope data for a larger suite of volcanic emanations from Etna, Kilauea, Merapi, Vulcano and White Island.

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Heavy isotope fractionation in the solar system – A volatile perspective

M REHKÄMPER[1,2], M SCHÖNBÄCHLER[1,2], F WOMBACHER[3], RGA BAKER[1,2], SG NIELSEN[4] AND HM WILLIAMS[4]

[1]Impact and Astromaterials Research Centre (IARC), Imperial College, London SW7 2AZ, UK
[2]The Natural History Museum, London SW7 5BD, UK
[3]Institut für Geologische Wissenschaften, FU Berlin, 12249 Berlin, Germany
[4]Dept. of Earth Science, Parks Road, Oxford OX1 3PR, UK

It is well recognized that most solar system bodies are significantly depleted in volatile constituents relative to primitive CI chondrites but the origin of this signature is only poorly understood. Stable isotope studies of volatile elements in meteorites are well suited for addressing this fundamental question. This conclusion is underlined by the observation that for chondritic meteorites, heavier but more volatile elements (such as Cd) typically display larger isotopic effects than lighter and less volatile constituents (e.g., Zn). This suggests that partial vaporization and condensation play an important role in generating stable isotope variations [1-3].

The isotope data acquired for a number of volatile elements indicates that stable isotope effects are generally much larger for ordinary than for carbonaceous chondrites. The large isotope variations determined for ordinary chondrites (e.g., ~25‰ for $^{114}Cd/^{110}Cd$) are thought to reflect redistribution of volatile constituents by thermal metamorphism on the meteorite parent bodies [1,2]. In contrast, most carbonaceous chondrites display only small or no resolvable isotope effects of ≤0.15‰/amu for Ag, Zn, Cd, and Tl [1-5]. This demonstrates that the variable volatile abundances of carbonaceous chondrites reflect either partial equilibrium condensation/evaporation or mixing processes.

Refractory (CAI- & chondrule-rich) separates from Allende display light Cd and Zn isotope compositions (of about -1‰/amu) relative to the bulk meteorite [2,3]. These signatures cannot reflect Rayleigh evaporation but are most readily explained by the interaction of refractory materials with a volatile-rich nebular gas. Such processes may also be responsible for the lack of nucleosynthetic isotope anomalies of volatile elements in CAI's.

The short-lived ^{107}Pd-^{107}Ag and ^{205}Pb-^{205}Tl decay systems are well suited for studying the time scales of volatile loss in the early solar system. Such studies must be carried out with care, as Ag and Tl have only two isotopes, such that radiogenic and stable isotope effects may not be readily discernable. One example are the troilite inclusions of IAB irons, which appear to have Ag and Tl isotope compositions that were fractionated (~1‰/amu) by diffusion [6,7].

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High-resolution geochemistry and lithology of laminated sediment in the Weddell Sea, Antarctica

L. REICHELT[1], M. E. WEBER[2], G. KUHN[3] AND W. RICKEN[4]

[1]Institute for Geology and Mineralogy, University of Cologne, Germany (LReichelt@gmx.de)
[2]Institute for Geology and Mineralogy, University of Cologne, Germany (michael.weber@uni-koeln.de)
[3]Alfred-Wegener-Institute, Bremerhaven, Germany (gerhard.kuhn@awi.de)
[4]Institute for Geology and Mineralogy, University of Cologne, Germany (wricken@uni-koeln.de)

Methods

Sediment sites PS1789 and PS1791 from the southeastern Weddell Sea (Antarctica), were investigated for geochemical and lithological variability. We used several non-destructive means to obtain information at ultrahigh resolution (mm to sub-mm scale). An x-ray-flourescence core scanner should reveal relative chemical composition of some selected elements. Magnetic susceptibility records were compared to counts of ice-rafted debris (IRD). We determined sediment color using both a photospectrometer, RGB readouts from a line scanner, and gray-scale images from x-radiographs. Stratigraphy relies on previously published AMS^{14}C dates.

Results

The glacial sediment sections reveal mostly laminated sediments and rarely intercalated fine-grained turbitdites. Bioturbated section occur at the top and are linked to Holocene or late-glacial times. Geochemical composition is relatively stable during the glacial; only bioturbated sediment shows elevated Fe and diminished Al and Si contents, whereas turbidites reveal the opposite.

In order to reveal wether or not the lamination is a result of an interannual (seasonal) variability, we developed tools for semi-automated layer counting of the gray-scale scans. First results indicate that the lamination is most likely an innerannual process, e.g., site PS1789 contains 4860 visually detectable layer between 199 and 1211 cm core depth, where AMS^{14}C dates indicate an age difference of 2430 years, i.e., more than 90 % of the expected layers encountered.

Future Work

More sites will have to be investigaed to corroborate the preliminary stratigraphic results. Geochemical investigation will focus on the differentation between the seasonal layers, i.e., is there a compositional difference between the darker and lighter layers documented in the gray-scale images or is the alteration caused by grain-size changes only.

In step with time: *In situ* geochronology meets microscale records of geologic processes

MARY R. REID

Department of Geology, Northern Arizona University, Flagstaff, AZ 86011; mary.reid@nau.edu

The profound record of geologic phenomena at sub-millimeter scales can be revealed by in situ geochronology and geochemistry in the context of key textural relationships. Complementary in situ geochemical and isotopic analyses reveal, for example, fluid evolution during cementation, the evolution of low as well as high grade metamorphism, subduction and exhumation, and the nature and duration of crustal growth. The improved accuracy and precision of U-Pb dating at <50 μm by LA-ICP-MS is increasing use of this method for in situ dating, especially for provenance studies and reconnaissance geochronology. Efforts to develop more matrix-matched reference materials will continue to improve the accuracy of *in situ* dating and geochemistry.

Dating of igneous and environmental samples by $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ disequilibria is also possible at a spatial resolution of <100 μm on. Vazquez and Reid (2004) coupled in situ U-series geochronology with crystal-scale allanite chemistry to reveal a t-T-X record for heterogeneous accumulation of the voluminous Toba rhyolite. The advent of the Ti-in-zircon geothermometer (Watson and Harrison, 2005) will ensure further crystal-scale insights into magmatic processes. In situ ^{235}U-^{231}Pa zircon ages may augment ^{238}U-^{230}Th geochronology (Schmitt, 2006). For environmental samples that contain ≥1 ppm U, dating by LA-ICP-MS affords high-resolution reconnaissance studies that can cope with open systems like bones, teeth, and possibly molluscs without chemical preparation (e.g., Eggins *et al*., 2005). Fluctuations in initial ($^{234}U/^{238}U$) and trace element concentrations, such as those found in 2-200 μm thick opal layers in soils, can be linked to glacial-interglacial transitions by ionprobe $^{230}Th/^{238}U$ dating (Maher *et al*., in prep.).

Finally, extension of in situ laser analyses to (U–Th)/He geochronology enables dating of 25 μm domains for provenance and unroofing studies (Boyce *et al*., 2006).

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Continental scale geochemical mapping and the geochemical background

C. REIMANN

Geological Survey of Norway, 7491 Trondheim, Norway, (Clemens.Reimann@ngu.no)

Since 1995, large domains in Northern Europe have been mapped at ever decreasing sample densities: 1 site/300 km^2 in the Kola Project, 1 site/1000 km^2 in the Barents Project and 1 site/2500 km^2 in the Baltic Soil Survey. The geochemical atlas of Europe, based on a sample density of 1 site/5000 km^2, was published in 2005 (see www.gtk.fi/publ/foregsatlas). Results demonstrate that such low-density geochemical mapping allows for the construction of robust geochemical maps of large areas at reasonable cost. The maps contain important new information and politically vital reference data about the varying levels of chemical elements in the surface environment at the continental scale.

The data demonstrate that there exist a number of natural processes that influence the regional distributrion of chemical elements in the surface environment at a variety of scales. Many of the displayed large-scale patterns are surprising and unpredictable based on geological reasoning alone. The distribution of chemical elements at the earth surface has an important impact on animal and human health. Continental scale geochemical maps of a variety of sample media, reflecting different compartments of the ecosystem, are thus urgently needed.

The anthropogenic impact on the natural environment cannot be reliably judged and interpreted without continental-scale geochemical maps and sound knowledge and documentation of the geochemical background. The observed natural variation of element concentrations in all sample materials collected so far covers several orders of magnitude. The statistical definition of a geochemical background or action levels for, for example, metals in soils of Europe, is thus fraught with problems. Obviously there is no single "natural" background value that is valid for a large area. Rather background will change from area to area within a region and between regions. The inherent connections between scale and background variation are key features for understanding environmental processes.

EXAFS analysis of reactive nanoscale iron oxidation in water

B.C. REINSCH[1], G.V. LOWRY[2] AND C.S. KIM[1]

[1]Department of Chemistry, Chapman University, Orange, CA USA, (reins100@chapman.edu)
[2]Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA USA, (glowry@cmu.edu)

Nanoscale zerovalent iron particles rapidly degrade chlorinated solvent groundwater contaminants into non-toxic products *in situ*. The efficacy of this approach is partially dependent on the reactivity and longevity of the zerovalent iron, which is readily oxidized in groundwater. Oxidation on the surface of the nanoscale iron particle can passivate the particle, potentially resulting in lowered reactivity toward target contaminants. A fundamental understanding of the chemical and structural changes that occur as a result of oxidation at the nanoiron surface in aqueous systems is necessary to assess the related impacts on reactivity and to determine the ultimate utility of the particles towards remediative goals.

Nanoscale zerovalent iron particles (initially 70% Fe^0/30% Fe_3O_4 core/shell particles) were allowed to oxidize in anaerobic water for various times ranging from a few days up to 1 year. The resulting iron particles with varying degrees of oxidation were studied using high intensity synchrotron radiation methods at Stanford Synchrotron Radiation Laboratory, beamline 11-2. Iron K-edge extended X-ray absorption fine structure (EXAFS) spectra provided element-specific information regarding the short-range structural order around iron in the nanoparticles. Fitting of the iron EXAFS spectra using model phase and amplitude functions allowed quantification of the direct relationship between oxidation time and relative amount of oxygen present in the atomic structure. Specifically, over the range of samples analyzed the average Fe-Fe coordination number declined from 8.2 ± 0.4 to 2.5 ± 0.3 while the average Fe-O coordination number increased from 1.2 ± 0.8 to 3.1 ± 0.9. The Fe-O and Fe-Fe interatomic distances and coordination numbers determined from the EXAFS fitting process were then compared to those of known crystalline iron oxides/oxyhydroxide phases in order to characterize the progressive structural transformation of the nanoparticles during their oxidation in water.

Metals from agriculture in oxic fluvial sediments: A case study in Western Iberia

A. R. REIS [1], A. PARKER [2] AND A. ALENCOÃO [1]

[1]Department of Geology, University of Trás-os-Montes and Alto Douro, Vila Real, Portugal, and Centre for Geophysics, University of Coimbra, Coimbra, Portugal, (anarreis@utad.pt, alencoao@utad.pt)
[2]Department of Soil Science, University of Reading, Reading, UK, (a.parker@reading.ac.uk)

The transport of fine fluvial sediments and associated pollutants in mountainous rivers is very dynamic, in response to precipitation episodes. The present study highlights the impact of human activities, mainly farming, in a "natural" mountainous catchment in Northern Portugal, underlain by crystalline rocks, in a temperate climate. Some inferences regarding Cu, Pb, Zn and Ca concentrations, their spatial and temporal variability, and potential bioavailability in oxic fluvial sediment samples are presented.

The study was performed on the <63μm sediment fractions. The modified BCR sequential extraction procedure (Rauret *et al.*, 1999) was used to assess metal contents in geochemical phases. The residual phase was decomposed by *aqua regia*. The element concentrations were obtained by ICP-AES.

The studied metals had contents in the ranges (ppm) Cu (1-99), Pb (5-154), Zn (29-448) and Ca (362-40860), showing higher contents in sampling stations located at those points draining areas with intense agriculture. These elements are common components of fertilizers, pesticides and animal manures (cow, horse, rabbit), the last widely used in the studied area. In these sites, the metals' relative contents present in the soluble, oxidisable, and organic fractions are considerably higher. However, differences in the distribution of the potential bioavailable fraction are observed, with marked increases in different phases: Cu in the organics, Zn in the soluble and oxidisable, and Pb in the oxidisable.

Calcium was also considered in this study. Although ubiquitous in natural water systems, its concentrations in the sediment samples are relatively high, considering the local geology (granites and schists). Calcium is a major component in the chemical fertilizers used in the studied area. Calcium is low in the residual fraction, owing to its geochemical behaviour, but is present in considerable amounts in the soluble fraction. The correlations between Ca and Cu, Pb and Zn are highest at the end of the dry period. The first autumn rain leads to increased transport of these elements, either by runoff or leaching of agricultural lands.

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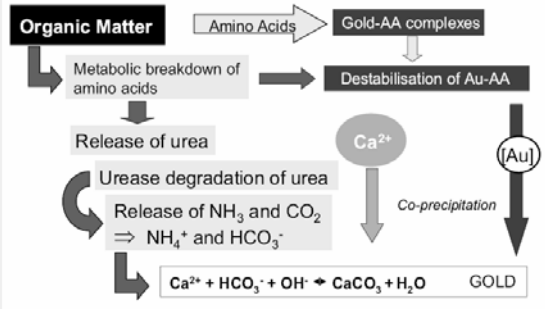
Microbially mediated formation of gold in calcrete anomalies in Australia

F.REITH[1], A. SCHMIDT MUMM[2]

[1]The University of Adelaide, Geol. & Geophys., Adelaide, Australia (Frank.Reith@csiro.au)
[2]The University of Adelaide,. Geol. & Geophys., Adelaide, Australia (andreas.schmidtmumm@adelaide.edu.au)

Regolith carbonates (calcrete) are widely used in Au exploration in Australia, because Au, which is often finely dispersed in calcrete, and Ca are highly correlated suggesting co-precipitation. The genesis of carbonates in pedogenic environments is dominantly ascribed to microbial processes, in particular to microbially mediated carbonate precipitation via ureolysis. Contrary to a genesis model recently published by Lintern *et al.* (2006), Schmidt Mumm and Reith (2007) proposed a comprehensive coupled model that includes a microbial component, which may control Au and Ca co-precipitation (Fig. 1).

Figure 1: Model for the microbially mediated formation of gold in calcrete anomalies (Schmidt Mumm and Reith, 2007).



Using microcosms and microbial enrichment culture experiments to assess the ureolytic capacity of the bacterial community combined with molecular profiling (shotgun cloning and DGGE of 16S rDNA), showed that *Bacilli* spp. resident in calcareous materials at the Barns anomaly are capable of producing Au anomalous Ca-carbonates. Within 96 to 240 h from the start of the incubation the urea was turned over to NH_4^+, the pH in solution rose by approximately 1 unit to pH 9 and Ca^{2+}_{aq} was precipitated as Ca-carbonate crystals; in sterile the controls no carbonates were precipitated. Gold (been added as Au-aspartic acid complexes to the growth medium) was co-precipitated with Ca and uniformly dispersed in the dominantly vaterite crystals, as shown by laser ablation ICP-MS and SEM. These results suggest that microorganisms play an important role in the formation of Au anomalies in calcrete in Australia.

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Origin of brines in the northern Gulf of Mexico

A. REITZ[1], M. HAECKEL[1], K. WALLMANN[1], C. HENSEN[1], AND K. HEESCHEN[2]

[1]Leibniz-Institute of Marine Sciences, IFM-GEOMAR, Kiel, Germany (areitz@ifm-geomar.de; mhaeckel@ifm-geomar.de; kwallmann@ifm-geomar.de; chensen@ifm-geomar.de)
[2]National Oceaography Centre, Southampton, U.K. (kyh@noc.soton.ac.uk)

Brines from the the northern Gulf of Mexico show distinct differences with respect to element concentrations and oxygen, hydrogen, and strontium isotope signatures. Three sites at different water depth were investigated; Bush Hill, GC415 East, and GC415 West at water depths of 540, 950 and 1050 m, respectively. All three locations accommodate near-surface gas hydrates and chemosynthetic communities at the sediment surface. They are characterized by a distinct increase in salinity with depth, however, the origin of this increasing salinity is different for the GC415 sites and Bush Hill and the depth source of the brines is considerably different for all sites. The more saline brines of the GC415 sites result from the dissolution of halite (Fig. 1) by formation water. The brine of GC415 East has most likely a deeper origin and experienced elevated temperatures leading to intensive mineral/water reactions. This process is expressed by the heavier oxygen isotope values and distinct Li, Sr, and Ca enrichments. The brine of GC415 West has a shallower origin which is expressed by a smaller enrichment in Li, Sr, and Ca and lighter oxygen isotopes (Fig.1). The brine from Bush Hill is less saline and its fluid signature indicates intensive water/mineral interaction. Oxygen (Fig. 1) and hydrogen isotope values as well as Na/Cl and Br/Cl molar ratios indicates that the salt enrichment could have been caused by phase separation under sub-critical conditions. A simple heat flow model simulation suggests sub-critical phase separation at a depth of ~1650 m at ~350°C.

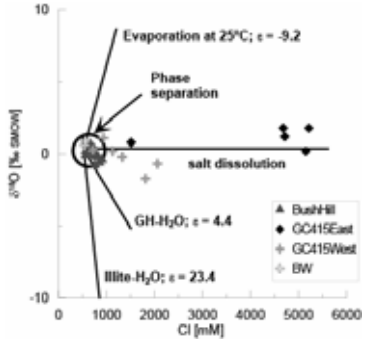

Fig. 1: Cl vs. $\delta^{18}O$ plot. Solid lines show the evaluation path of Cl vs. $\delta^{18}O$ values for (i) evaporation at ~25°C, (ii) gas hydrate (GH) formation, (iii) illite formation, and (v) dissolution of halite; the field expected for phase separation (no fractionation) is indicated by the solid circle.

The effects of sodium and chlorine on the solubility of molybdenum in aqueous vapour

K.U. REMPEL, A.E. WILLIAMS-JONES AND A.A. MIGDISOV

McGill University, Earth & Planetary Sciences, Canada (kirstenr@eps.mcgill.ca; willyj@eps.mcgill.ca; artas@eps.mcgill.ca)

There is growing evidence that the solubility of Mo in water vapour may be high enough for metal transport in the vapour phase to be an important mechanism in the formation of porphyry Mo deposits (Rempel *et al*., 2006). Molybdenum is typically considered to be transported as a hydrated oxide, but research on Mo speciation in H_2O-free vapour suggests that the formation of Mo oxychlorides and sodium molybdates may be important (Hultgren and Brewer, 1956; Choudary *et al*., 1975). This study reports the results of experiments designed to investigate the effects of Na and Cl on Mo solubility in high-temperature water vapour.

The experiments were conducted in NaCl- and HCl-bearing aqueous vapour at 350°C and 60-160 bars. At fHCl<0.5 bars, Mo concentration appears to be independent of fHCl. However, at fugacities of HCl typical of volcanic gases (fHCl from 0.5 to 5 bars), the sum of the fugacity of Mo species increases with increasing fHCl in a ratio of ~1:2. At all fugacities of HCl, ΣfMo species increases with increasing f_{H_2O} in a ratio of 1:2. These observations suggest that the predominant Mo species in the HCl-H_2O system is a hydrated chloride or oxychloride. In the case of the former, the stoichiometry would likely be $MoCl_2 \cdot 2H_2O$, whereas the latter could be $MoO_2Cl_2 \cdot 2H_2O$, a species that has been reported to occur in HCl gas (Hultgren and Brewer, 1956). The sum of fugacities of Mo species in NaCl-bearing vapour rises linearly with increasing ΣfNa species in a ratio of 3:4. Furthermore, ΣfNa species is about two orders of magnitude higher than predicted for the partitioning of NaCl between H_2O liquid and vapour (Bischoff 1991), indicating that the dominant Na species in the vapour is not NaCl. Values of ΣfMo also increase linearly with f_{H_2O} (in a ratio of 1:3), suggesting the formation of hydrated Na molybdates. The ratio of ΣfMo to ΣfNa of 3:4 implies the formation of two or more hydrated Na molybdates, e.g. $Na_2MoO_4 \cdot 3H_2O$ or $NaHMoO_4 \cdot 3H_2O$.

The results of this study, in conjunction with the known elevated concentrations of Na and Cl in magmatic vapours, suggest that such vapours are more than capable of dissolving the concentrations of Mo required to form porphyry Mo deposits.

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Molecular identification of the Deuterium-rich carrier in insoluble organic matter in carbonaceous chondrites

L. REMUSAT[1], F. ROBERT[2], S. MOSTEFAOUI[2], A. MEIBOM[2], O. DELPOUX[3], L. BINET[3], D. GOURIER[3] AND S. DERENNE[3].

[1]IPGP / UPMC, 4 place Jussieu, 75005 Paris, France
[2]LEME, MNHN, 61 rue Buffon, 75005 Paris, France, (robert@mnhn.fr)
[3]LCMCP, ENSCP, 11 rue P. et M. Curie, 75005, France

Insoluble organic matter (IOM) in primitive carbonaceous chondrites is known to be enriched in deuterium, with D/H ratios > 350×10^{-6}. It is also characterized by a high degree of isotopic heterogeneity, as demonstrated by the observation of D-rich "hot spots" in NanoSIMS ion microprobe images (Robert *et al*. 2006). Understanding the origin of this heterogeneity represents a fundamental challenge with implications for the origin and distribution of organics in the interstellar medium and in the protoplanetary disk from which our planetary system formed.

We have determined the carrier of the isotopically anomalous hydrogen in IOM isolated from the carbonaceous chondrite Orgueil. Electron Paramagnetic Resonance spectroscopy has shown that hydrogen in the benzylic bond of organic radicals has a deuterium to hydrogen (D/H) ratio of $1.25\pm0.75\times10^{-2}$ in Orgueil IOM, which is the highest solar system D/H ratio ever reported (Delpoux *et al*. 2007).

By combining these data with quantitative image analysis recorded at a high spatial resolution with the NanoSIMS, we are able to prove that the organic radicals can account for the deuterium excess in the IOM D-rich "hot spots". Furthermore, the radicals fall on a well-defined trend between D/H ratio and C-H bond energy (Remusat *et al*. 2006), consistent with a new interpretation of the hydrogen isotopic variations in solar system organics according to which pre-existing organics exchange their D with highly deuterated gaseous molecules, such as H_2D^+ or HD_2^+. The distributions of these deuterated species is now being mapped in protostellar disks (Ceccarelli and Dominik 2005).

This conclusion runs contrary to previous interpretations, according to which the IOM is an interstellar product reprocessed in the protosolar gas and deuterium-rich "hot spot" relics of pristine interstellar organic matter, which escaped solar nebula or parent body processes.

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Status of the impact crater age database

P.R. RENNE[1,2], F. JOURDAN[1,2], W.U. REIMOLD[3]

[1]Berkeley Geochronology Center, USA (fjourdan@bgc.org)
[2]University of California, Berkeley, USA
[3]Museum f. Natural History, Germany

The Earth impact crater database (http://www.unb.ca/passc/ImpactDatabase/) includes a total of 174 confirmed impact structures. Ages listed in the database are based on dates recommended in the most recent published papers. Precise and accurate age constraints are crucial in (1) correlating causes and effects on the bio- and geosphere for these catastrophic processes, (2) better constraining the impactor flux through geological time and evaluation of potential impact periodicity, (3) calibrating the absolute chronostratigraphic time scale, and (4) calibrating the age of within-crater continental sedimentary deposits (e.g., for regional paleo-climatic analysis)..

Of the 174 confirmed impact structures only a few have ages constrained precisely enough (mostly using radio-isotopic techniques, e.g. U/Pb and $^{40}Ar/^{39}Ar$), with 26 ages having a stated precision better than 2% and 15 ages with a precision better than 1%. Yet, even in this very restricted subset of the database the accuracy of some of these ages can be challenged and probably improved based on more detailed and statistically more rigorous interpretations. Although geochronologists are often circumspect and advise caution in accepting calculated ages, these ages tend to propagate into the literature without further critical evaluation and become "robust" and widely accepted ages. A quick review of the age data of the 26 short-listed structures suggest that 11 ages seem accurate, 13 are at best ambiguous, and 2 are not well characterized and should not be reported with any uncertainty. We report examples of misleading ages and/or age uncertainties (e.g., poor stratigraphic constraints, data over-interpretations, ambiguity due to inconsistent results) and highlight the robustness of 11 well defined ages. We also provide some suggestions (see also [1]) based on observations and modeling, in order to obtain better ages. This brief review should be interpreted as a call for drastic qualitative and quantitative improvements of the crater age database in the near future.

[1] Jourdan *et al*., this volume

Arsenic uptake and release on sulfide nanoparticles

D. RENOCK[1], S. UTSUNOMIYA[2], T.J. GALLEGOS[3], K.F. HAYES[3], R.C. EWING[2] AND U. BECKER[2]

[1]Dept. of Geological Sciences, University of Michigan, Ann Arbor, MI., U.S.A. (drenock@umich.edu)
[2]Dept. of Geological Sciences (utu@umich.edu, rodewing@umich.edu, ubecker@umich.edu))
[3]Dept. of Civil and Env. Engineering (tgallegos@umich.edu, ford@umich.edu)

Descriptions of molecular-level processes that control the uptake and release of As on sulfide nanoparticle surfaces were obtained from microbeam, spectroscopic, and quantum mechanical modeling techniques.

The precipitation of As-sulfide phases on nanoparticulate mackinawite (FeS) is identified as a possible mechanism for As(III) immobilization under anoxic conditions (Gallegos *et al*. 2007). A major challenge in identifying As-sulfide growth phases is their nanoscale dimensions. High-angle annular dark field scanning-TEM and energy-dispersive X-ray spectrometry were used to identify amorphous AsS phases precipitating on FeS nanoparticles after As(III) adsorption at pH 5. The oxidation state of As in the surface As-sulfide precipitates was determined to be "realgar-like" from X-ray photoelectron spectroscopy results showing an As 3d binding energy of 43.0 eV.

The reverse process, the oxidative dissolution of realgar (As_4S_4) and orpiment (As_2S_3) nanoparticles, is a mechanism by which As is released back into natural waters. *Ab initio* quantum mechanical methods were employed to describe indirect electronic perturbations (proximity effects) between surface adsorbates on As_4S_4 nanoclusters. Proximity effects between O and $(OH)^-$ ion adsorbed on a single As_4S_4 cluster were determined to be on the order of 1 eV, depending on the O-$(OH)^-$ distance. Calculations also show that adsorption of $(OH)^-$ to As_4S_4 could affect the adsorption energy of O to a neighboring As_4S_4 separated from the former by a van der Waals gap (as is the case in As_4S_4 molecular crystals). The findings suggest that As_4S_4 is more susceptible to oxidative attack with the co-adsorption of $(OH)^-$ ions.

The results of this study can be used to improve adsorption isotherms and surface complexation models that decribe the factors that control As concentrations in natural waters.

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Volcán de Colima, an andesitic volcano fed by a dacitic reservoir. Is that typical of continental arc magmatism?

OLIVIER REUBI AND JON BLUNDY

Dept. of Earth Sciences, University of Bristol, Bristol, BS8 1RJ, UK (olivier.reubi@bristol.ac.uk)

Volcán de Colima, Mexico is the archetype of an andesitic arc stratovolcano and is one of the most active volcanoes in North America. All historically erupted magmas have bulk andesitic compositions, yet the melt inclusion and phenocryst compositions indicate that the melt crystallizing in the subvolcanic system is consistently dacitic in composition. Similar mismatches between whole rock and melt inclusion records are documented for several other andesitic volcanoes, which raises questions about the abundance of true liquids with andesitic composition.

Melt inclusions (MI) in phenocrysts of pyroxenes From Volcán de Colima magmas are distinctively more silicic than whole rock compositions (64-75 and 57-62 wt% SiO_2 respectively). A significant proportion of the melt inclusions have "exotic" compositions thought to be produced by grain boundary melting of co-genetic crystal-clots. The other MI show trends consistent with crystallization of the phenocryst assemblage observed in the magmas. Volatile content of these melt inclusions are distinctively low (≤2.5 wt% H_2O, ≤360 ppm CO_2) and indicate crystallization in a volatile-saturated system between 90 and 0 MPa (<7 km in depth). The magmas contain ubiquitous gabbroic fragments up to few mm in size. The whole-rock compositions of the andesites systematically lie on mixing lines between the gabbroic fragments and the less evolved melt inclusions, indicating that entrainment of these gabbroic fragments is the primary factor controlling the bulk andesitic composition and, importantly, that the melt inclusions effectively record the composition of the crystallizing melt. Overall, this implies that despite the monotonous andesitic composition of the erupted magmas, the magmatic system that feed Volcán de Colima comprise a shallow, variably crystallized dacitic magma reservoir and a pre-existing gabbroic plutonic body. It is therefore bimodal in composition, with no andesitic melt.

A compilation of published melt inclusion data for several other continental arc andesite volcanoes also shows a bimodal distribution with a marked minimum at andesite. This implies that andesitic melts are typically minor compoments of the upper crustal magmatic reservoir feeding arc volcanoes and that the abundance of erupted andesitic magmas reflects in large part effective mixing of these two components within the subvolcanic reservoir and/or on the way to the surface.

The building stones of the Khmer-temple at Angkor/Cambodia: A petrological and geochemical approach towards a conservation oriented characterisation of the inventory

R. REUCHER[1], H. LEISEN[2], E. V. PLEHWE-LEISEN[3] AND R. KLEINSCHRODT[1]

[1]Institut of Geology and Mineralogy, University of Cologne, Zülpicher Str. 49b, 50923 Cologne (research@stone-gate.eu, rkleinsc@uni-koeln.de)

[2]Institut of Restoration and Conservation Sciences, University of Applied Science, Cologne, Ubierring 40, 50678 Cologne, (jaeh.leisen@freenet.de)

[3]Untersuchungslabor für Fragen der Natursteinerhaltung (LPL), Schulze-Delitzsch-Str. 88, 50968 Cologne (jaeh.leisen@freenet.de)

The Angkor Park /Cambodia, as a prominent member of the Unesco world heritage, is one of the outstanding cultural relics on earth. Countless Khmer temples were successively built between 9^{th} –13^{th} century.

During the preparation of interventions in individual temples the building stones were investigated concerning their most important properties in regard to conservation strategies. It turned out that there are considerable differences in weathering behavior between the sandstones used at different temples and that the composition and texture of the building stones are determining factors for the degree and the type of decay. The study presented aims at a detailed geochemical and mineralogical characterisation of the building stones starting with samples from some of the most prominent temples. Together with petrophysical data this shall provide a material oriented database for future conservation conceptions.

The material was characterised petrographically by optical microscopy, the components were analysed by electron microprobe and whole rock chemistry of main and some trace elements that were determined by XRF-analysis. X-ray diffraction was used for determining clay minerals in selected rocks.

On a petrographic base most of the rocks can be classified as feldspathic greywackes (according to Pettijohn *et al*. 1972), in one, the Banteay Srei temple, lithic greywackes were found. Inspite of this similarity the rocks display a distinct variability in regard to their chemical composition and texture. The combinations of the methods show clear accordances in the observed variability of the temples building stones. On the other hand the building stones from the Ta Keo (feldspathic greywackes) and the Banteay Srei temple (lithic greywackes) are distinctly different from the others. They also show no correlation with the samples of the ancient quarries.

Future investigations extend to temples (also smaller ones) and ancient quarries in the wider surrounding of the Angkor Park aiming at the set-up of a database on the variability and historical variations in the building stones used during the five centuries of construction.

Aerogels – A kind of ceramic? Properties and applications

MICHAEL REUß AND SUSANNE LISINSKI

Deutsches Zentrum für Luft- und Raumfahrt (DLR), Institut für Materialphysik im Weltraum, D-51170 Köln, Germany (michael.reuss@dlr.de, susanne.lisinski@dlr.de)

Aerogels are nanostructured materials, containing until 99 wt.-% air. They are manufactured by a sol-gel process [1]. After formation of a 3D network of colloidal particles, the wet gel has to be dried without shrinkage to avoid destruction of the network by cappillary forces. The drying process can be supercritical or subcritical, depending on the kind of aerogel. Because of their very special properties (extremely low density, extremely low thermal conductivity,...), aerogels are very interesting for different applications [2]. Aerogels can be classified into organic and inorganic aerogels.

The first aerogels (inorganic, silica aerogels) were manufactured already in 1931/32 by Kistler [3]. Inorganic aerogels are inert against metal liquids and cannot be wetted by them. We use them as crucible material for solidification of metal alloys. It is possible to watch the solidification process directly or by CCD-camera, because these kinds of aerogels are often transparent in a wide range of 350-2700 nm.

In the past few years, there has been a great deal of interest in the synthesis of hybrid materials with nonlinear optical properties, especially second harmonic generation (SHG). We prepare ferroelectric aerogels, like $LiTaO_3$ and $LiNbO_3$, and silica/titania aerogels loaded with ferroelectric nano -and microparticles, like $BaTiO_3$ or $KNbO_3$ [4]. Whenever an infrared laser light wave (e.g. 1064nm) penetrates these materials, the aerogel generates green light (532nm).

In recent years, organic aerogels were presented as a new, nanostructured material with possible applications like binding material for sand cores and moulds in the foundry industry [5] or in its pyrolized carbon form as a material for supercapacitors. The well investigated Resorcin-Formaldehyde (RF) aerogels [6,7] are typically catalyzed with weak bases like sodiumcabronate. Instead of base catalysis it was recently considered to use acid catalysts, especially organic acids [8].

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Opal records of abrupt changes in the Southern Ocean over Termination II

B.C. REYNOLDS[1], S. MANTOURA[2] AND A. SHEMESH[3]

[1]IGMR, ETH Zürich, Switzerland. reynolds@erdw.ethz.ch
[2]Formally at the Dept. of Earth Sciences, University of Cambridge, UK. (s.mantoura@nature.com)
[3]Dept. of Earth Sciences, The Weizmann Institute of Science, Israel. (aldo.shemesh@weizmann.ac.il)

Diatoms sequester CO_2 and other nutrients into their organic matter, as well as forming biogenic silica (opal), and can account for over half of the world's primary productivity in the surface oceans. Silicon (Si) is an important oceanic nutrient for their growth and primary production in surface waters, especially at high-latitudes. Opal bio-mineralization leads to a mass-dependent Si isotope fractionation, such that the Si isotope composition (expressed as $\delta^{30}Si$) of seawater and biogenic opal reflect the degree of Si utilization in ocean surface waters by siliceous algae, analogous to variation in carbon isotopes, but linked only to diatom productivity.

An unprecedented high temporal-resolution Si-isotope record has been measured from the South Atlantic from ODP site 1094 over the penultimate deglaciation. The qualitative trends observe a very large shift from low glacial values to high interglacial values over Termination II. These large changes are in accordance with a record from the Antarctic zone of the South Atlantic (Core RC13-259, [1]). The high temporal-resolution of this study allows us to ascertain two important features which have hitherto not been demonstrated: firstly, we can compare the time of changes in $\delta^{30}Si_{opal}$ to change in the other stable isotope opal based proxies, namely $\delta^{15}N$ and $\delta^{13}C$ [2], secondly, we can demonstrate that $\delta^{30}Si_{opal}$ changed by 1‰ in less than 2 kyrs.

The changes in diatom productivity estimated from both diatom-bound $\delta^{15}N$ and $\delta^{13}C$ records, actually occur significantly prior to the change in $\delta^{30}Si_{opal}$, (~1 kyr). This also suggests that change in the N utilization do not occur at the same time as change in Si utilization. Overall, the degree of change (1.3‰) is greater than the isotope enrichment factor during the utilization of Si by diatoms (~1.1‰), so cannot be explained as only changes in the degree of utilization (this cannot be more than 100%). Secondly, the rate of change is similar to the mixing time of the oceans (~1500 years) and many times less than the residence time of Si in the oceans (~15 kyrs), so cannot be related to changes in marine inputs to the oceans. The observed shift in $\delta^{30}Si_{opal}$ must be caused by a dramatic switch in provenance of waters coming into the Antarctic Sector of the Southern ocean with distinctly different Si isotope compositions as well as any potential change in diatom productivity.

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The FE-EMPA – Applications for the sub-micron analysis in geosciences

D. RHEDE

GeoForschungsZentrum Potsdam (GFZ), Potsdam, Germany, (rhede@gfz-potsdam.de)

The use of a thermal field-emission cathode in an electron microprobe (JEOL Hyperprobe JXA-8500F) has opened a new window in the analysis of structures in the sub-micron range. Small electron-probe beam size (< 50 nm) with variable probe current (5–200 nA) at low accelarating voltage (5–10 keV) allow a sub-micron spatial resolution for single spot analyses and detailed X-ray mapping of composition contrast in the range of 100 nm. The results are afflicted by reduced intensities of the X-rays (high energy K-lines are not excited, demanding the use of L- and M-lines), peak overlapping, a higher current density, and contamination. The quality of the sample polish and the thickness of the coating layer are essential. New measurement strategies and unconventional approaches are required to overcome these problems.

A selection of examples should demonstrate the improved possibilities of the FE-EMP as a tool between conventional EMP and TEM:

- Measurement of the chemical composition and the internal zoning of exsolution lamellae and symplectite in feldspars.
- Characterization of small reaction rims in natural samples in order to study the transport mechanism for the rutile-titanite transformation via a fluid phase.
- Study of the complex, diffusion-controlled growth of orthopyroxene reaction rims (zonation of Fe and Mg).
- Investigation of inclusions in minerals (unaffected by their host) down to 500 nm size, depending on composition and density.
- "Chemical" age dating of Th–U-containing minerals occurring as microinclusions in other minerals.
- Characterization of complex zoning patterns of small areas in accessory minerals (zircon, monazite, xenotime, etc.).

Preliminary characterization of São Jorge island mantle source (Azores)

L.P. RIBEIRO[1], Z. FRANÇA[2,3], B. RODRIGUES[4] AND V.H. FORJAZ[2,3]

[1]EMEPC – Estrutura de Missão para a Extensão da Plataforma Continental, Portugal, (luisapr@emepc.gov.pt)
[2]Depart. de Geociências da Univ. Açores, Portugal
[3]OVGA – Observatório Vulcanológico e Geotérmico dos Açores, Portugal
[4]Depart. de Geociências da Univ. Aveiro, Portugal

The Azores archipelago, formed by nine islands spread along the Azores Plateau, is situated in a complex tectonic setting, containing the junction of three tectonic plates, the American, Euroasiatic and Nubia plates. East of the MAR is located the central group island where São Jorge island developed (38º46' – 38º33'N and 28º20' – 27º45'W). This is an elongated shape island (WNW-ESE) with aligned volcanic cones and dikes unveiling the importance of the regional tectonic setting during volcanic activity. Stratigraphically, the island developed during three main volcanic phases (Forjaz & Fernandes, 1975), giving place to Topo complex in the SE, Rosais complex in the NW and to Manadas complex that covered the centre of the island.

São Jorge lavas are dominantly alkaline with $Y/Nb \leq 1.0$, and experience some degree of differentiation extending from basanite and tefrite to basaltic trachyandesite composition. The analyses of REE and incompatible elements of the more primitive samples ($Mg\# \geq 0.44$ and $Ni \geq 110$ ppm) can be good indicators of the petrogenesis of the three complexes.

The REE diagram shows LREE enrichment, relative o HREE, as is common in ocean island where garnet is present in the source. We also found, in Topo complex , differences between Caldeira and Cubres sequences as for instance REE ratios [(Tb/Yb)n] and incompatible elements patterns. Primitive lavas from Rosais, when compared with other lavas, are relatively enrich in La, Rb, Ba and Th contrasting with only a small K anomaly and relatively high Ba/Ce ratio. This could be explain if during partial melting Rosais lavas sampled a slightly different compositional source, constituted by a K enriched phase as reported in other Azores islands as Corvo (França *et al*., 2006) and Atlantic islands (Halliday *et al*., 1995, Ribeiro, 2001).

The question is how source composition and partial melting affected magma composition in these continuous lava sequences and the relation with the remaining Azores islands and seamounts in the Azores region.

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Comparative study of geospeedometry methods

D. RICHARD, F. W. V. AULOCK, K.-U. HESS AND D. B. DINGWELL

Department of Environmental and Earth Sciences, Ludwig-Maximilians-Universität, Munich, Germany (richard@min.uni-muenchen.de)

Limitations of classical geospeedometry

The natural cooling rate of natural glasses is an important parameter in the assessment of volcanic hazards because it influences the degassing and flow behavior of lava. Relaxation of enthalpy (ΔH) has been successfully used to estimate cooling rates of natural glasses. This method consists of heating and cooling a glassy sample at various rates and using the Tool-Narayanaswamy model (1971) to obtain a natural cooling rate. It is however challenging to apply this technique to some glasses where the heat capacity (ΔH/ΔT) curves are not reproducible due to possible degassing and/or the ΔH/ΔT peaks are too small to be modelled.

An advanced dilatometric method

A method recently developed by Helo *et al*. (2006) considers the volume relaxation of multiphase samples during heating at a fixed rate, with the advantage of measuring samples containing only small amounts of glass. This method allows us to (1) estimate the calorimetric glass transition temperature (Tg_{cal}) and to (2) measure the dilatometric glass transition temperature (Tg_{dil}), which corresponds to the softening point of the material. A pantellerite from Pantelleria, Italy, was heated through the glass transition. From length changes, we estimated a Tg_{cal} of 521°C, and from enthalpy changes measured with a scanning differential calorimeter, we obtained a Tg_{cal} of 524°C. These temperatures are identical within the precision of the instruments.

An alternative to classical geospeedometry

Moreover, repeated dilatometric heating at 10 K/min and cooling at 15 K/min revealed a gradual exponential increase in the Tg_{dil} from 625°C to 649°C, possibly due to water degassing. The first heating of the sample produced a Tg_{dil} of 611°C, which plotted below the trend produced by the subsequent measurements. We attribute this gap to the natural cooling rate, which we estimate to be about 10 K/min. This is the first time that a geospeedometry method considers changes in material properties to estimate a natural cooling rate. Classical geospeedometry assumes that Tg does not change through a series of cooling and heating treatments. However, we show that for some glasses, another method is required because Tg may change due to a number of processes such as degassing.

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A thermodynamic model of uranium reduction by organic matter in the Proterozoic hydrothermal systems of Oklo (Gabon)

LAURENT RICHARD AND ALEYDA TRAORÉ

G2R, Nancy-Université, BP 239, 54506 Vandoeuvre-lès-Nancy, France (laurent.richard@g2r.uhp-nancy.fr)

Numerous geological, mineralogical, and geochemical studies have been carried out at and around Oklo (southeastern Gabon) over the last four decades, which have contributed to a better understanding of the reactions involved in the formation of these uranium deposits (e.g. Gauthier-Lafaye and Weber, 1989; Nagy *et al*., 1991; Cuney and Mathieu, 2000). The Oklo deposits represent one of the best examples of associations between uranium and organic matter, which raises the question of the role played by hydrocarbons in the reduction of uranium-VI to uraninite. The observation of uraninite crystals entrapped within solid bitumens in the Oklo uranium deposits led Nagy *et al*. (1991) to propose that a liquid, aliphatic-rich bitumen may have acted as a reductant to precipitate uraninite from hydrothermal solutions. Advances in theoretical organic geochemistry have led to the constitution of an extensive set of thermodynamic properties for solid and liquid organic compounds of geochemical interest (Helgeson *et al*., 1998; Richard and Helgeson, 1998), which makes it possible to investigate organic/inorganic interactions in geological processes.

A thermodynamic analysis has been made as a function of temperature, pressure, and oxygen fugacity of the reactions responsible for the formation of the uranium deposits at Oklo (southeastern Gabon). The generation of liquid hydrocarbons at 150°C as a result of the maturation of Proterozoic kerogens in the FB shales has been characterized and quantified with the aid of activity diagrams. Mass transfer calculations have been carried out to describe the alteration of U-bearing monazites and the mobilization of uranium by oxidizing hydrothermal fluids circulating in the FA sandstones, as well as the reduction of aqueous uranyl by the liquid hydrocarbons as a result of the mixing between the hydrothermal fluids and the petroleum. The latter calculations resulted in the simultaneous precipitation of uraninite and pyrobitumen, in agreement with the petrographical observations.

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A reappraisal of the petrology and origins of the Lherz peridotite

A.J.V. RICHES[1], N. W. ROGERS[1], B. L.A. CHARLIER[1] AND J-L BODINIER[2]

[1]The Department of Earth Sciences, The Open University, United Kingdom. (a..j.v.riches@open.ac.uk , n.w.rogers@open.ac.uk , b.l.a.charlier@open.ac.uk)

[2]Laboratoire de Tectonophysique, ISTEEM, Université Montpellier 2, France (Jean.Louis.Bodinier@dstu.univ-montp2.fr)

The massifs of the eastern Pyrenees have been the focus of a number of extensive studies and have made a significant contribution to our understanding of mantle composition and evolution. Specific problems remain, in particular the relationship between adjacent harzburgites and lherzolites, which have been proposed to be either; (1) melt depletion of an original lherzolite [2, 3] or, (2) refertilisation of a primary harzburgite by basaltic melt [1, 4].

Whole rock and clinopyroxene compositions of the peridotites and associated pyroxenites offer a means of resolving the nature of the relationship between harzburgites and lherzolites. Whole rock major and trace element analyses show that the lherzolites have a range of compositions while the harzburgites are relatively uniform. Laser ablation analyses of individual clinopyroxenes indicate some variation of lherzolite sample composition whilst harzburgites alone display marked LREE enrichment.

Whole rock ^{187}Os -^{188}Os values define a broad positive correlation with ^{187}Re-^{188}Os and indices of melt depletion (Al_2O_3 and S). Model ages derived from these correlations range from ~1.4Ga to ~1.5Ga. Re-Os isotope systematics alone define an errorchron corresponding to an age of ~1.7Ga. These model ages are all younger than those reported in the literature [3, 5], which previously suggested a melt depletion event across the Pyrenean suite at 1.9-2.4Ga.

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U(VI) sorption on sandstone: Experiments and modeling

A. RICHTER, C. NEBELUNG AND V. BRENDLER

Forschungszentrum Dresden-Rossendorf e.V., Institute of Radiochemistry, P.O. Box 510119, 01314 Dresden, Germany (Anke.Richter@fzd.de)

Experimental

The sorption of U(VI) on natural and synthetic sandstone was investigated in batch sorption experiments (air atmosphere, 0.1M $NaClO_4$, pH 3-11, [U(VI)] 10^{-9}-10^{-4}M. The synthetic sandstone was a mixture of quartz with muscovite and hematite. The surface area (N_2-BET) of quartz was 0.047 m^2/g, of muscovite 0.88 m^2/g, of hematite 0.89 m^2/g and of natural sandstone (mainly quartz) 0.69 m^2/g.

Results and discussion

The pH dependence shows a maximal sorption between pH 5.5-7.5. The U(VI) sorption varied between 95% (10^{-9}M) and 7% (10^{-4}) on natural sandstone, and between 80% (10^{-9}M) and 2% (10^{-4}M) on synthetic sandstone. Fig. 1 shows the comparison of sandstone with pure components (at similar conditions) quartz, muscovite, and hematite. More U(VI) was adsorbed on natural and on synthetic sandstone, than on quartz. The higher sorption are caused by the other components muscovite and hematite, and by the higher surface area.

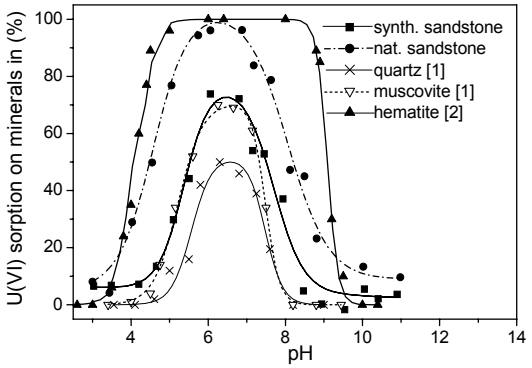

Fig. 1: pH dependence of U(VI) sorption: Comparison of pure components of synthetic sndstone with the miture and with natural sandstone.

The linear Freundlich sorption isotherms indicate one binding type. Sorption predicted by the Diffuse Double Layer Model (using the code FITEQL) agreed with the experimental sorption values within their uncertainty.

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Isotopic fingerprints of mass transport processes

FRANK M. RICHTER

The University of Chicago, Department of the Geophysical Sciences, 5734 Sou8th Ellis Ave. Chicago, IL 60637 (richter@geosci.uchicago.edu)

I will discuss three types of mass transport related isotope fractionations. 1. Isotope fractionation by evaporation of silicate liquids. 2. Isotope fractionation by chemical diffusion in liquids. 3. Isotope fractionation by thermal diffusion in molten basalt.

We (Richter *et al*., 2002 and work in progress) have carried out a large number of experiments on isotope fractionation during evaporation and find that it follows a Rayleigh fractionation law of the form $R_{iJ}/R_{iJo}=f_J^{\alpha-1}$ where R_{iJ} is the ratio of isotopes i and j when a fraction f_J of isotope j remains in the condensed phase and R_{iJo} is the original isotope ratio of the of the condensed phase. The fractionation parameter α is the ratio of the isotopic composition of the evaporation flux to that of the substrate. In the case of magnesium evaporating from silicate liquid at 1400°C, (relevant to the evaporation history of Ca-Al-rich inclusions found in primitive meteorites), we find α=0.9910, which is significantly different from the often assumed value of $\alpha=(24/25)^{1/2}$= 0.9798 for the fractionation of $^{25}Mg/^{24}Mg$ in the evaporation residue.

We (Richter *et al*., 1999, 2003) reported the results of experiments for the isotopic fractionation of Li, Ca, and Ge (used as a Si analogue) during diffusion between molten basalt and rhyolite, and now have new data on the isotopic fractionation of Mg is this system. We have also carried out experiments on the isotopic fractionation of Li, Mg, and Cl during diffusion in water (Richter *et al.*, 2006). The results are reported in terms of the exponent β in $D_i/D_J=(m_J/m_i)^{\beta}$, where the D_k is the self diffusion coefficients of isotope k and m_k is its atomic mass. For molten silicate we found $\beta_{7Li/6Li} \approx 0.215$, $\beta_{44Ca/40Ca} \approx 0.075$, $\beta_{26Mg/24Mg} \approx 0.05$, $\beta_{76Ge/70Ge} \approx 0$. In water $\beta_{7Li/6Li} \approx 0.015$, $\beta_{37Cl/35Cl} \approx 0.025$, $\beta_{26Mg/24Mg} \approx 0$. Note the very much smaller fractionations in water.

Our most recent experiments involve isotopic fractionations by thermal diffusion (often also called Soret diffusion). We are finding surprisingly large isotopic fractionations (~8‰ for $^{26}Mg/^{24}Mg$) associated with a change of only about 150˚C across molten basalt. We are in the process of determining the thermal isotopic fractionation factors of the other major elements in molten basalt.

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Deglacial rearrangement of carbon and nutrients in surface and intermediate depth waters

R.E.M. RICKABY [1] D.J. HARDING [1], G. BAYON[2] AND I. R. HALL[3]

[1]Department of Earth Sciences, Parks Road, Oxford, UK OX1 3PR (Rosalind.Rickaby@earth.ox.ac.uk)

[2]Departement Geosciences Marines, IFREMER, 29280 Plouzane, France

[3]School of Earth, Ocean and Planetary Sciences, Cardiff University, Cardiff, Wales, UK CF10 3YE

Changes in the pattern of conveyor circulation, reconstructed from the combined nutrient proxies Cd/Ca and $\delta^{13}C$, have been implicated in abrupt climatic events of the last deglaciation. But, the assumption that characteristic endmember water mass signatures derived from southern nutrient rich surface waters close to sea ice, and northern nutrient depleted ice free surface waters, have remained invariant in time, has recently been called into question. We contrast new deglacial planktonic and benthic foraminiferal histories from intermediate depths in the high latitude North and Equatorial Atlantic with records from the South Atlantic and Pacific. The timing and amplitude of the deglacial minimum in $\delta^{13}C$ of atmospheric CO_2 from Taylor Dome, is captured by the surface $\delta^{13}C$ records. The surface $\delta^{13}C$

minimum is paralleled at intermediate depths in the high northern latitudes throughout the early deglacial. This may indicate continued northern sourced ventilation with an altered endmember $\delta^{13}C$ signature, which can account for the early deglacial warming documented in the North Atlantic. Globally, intermediate depth signatures converge to the same value at the start of the deglaciation. Our data are consistent with vertical fractionation of carbon and nutrients into a poorly mixed deep reservoir during the last glacial, which is reventilated at the deglaciation and the sequestered carbon mixed via the intermediate waters to the surface and atmosphere. Divergence between the surface and intermediate depth chemical signatures occur only during the Younger Dryas. Our results confirm that endmember water mass signatures change significantly on a glacial-interglacial cycle.

Seasonal variation of oxygen and organic carbon isotopes and skeletal aragonite from *Unionidae* in the Rhine river

WERNER RICKEN[1,], THOMAS STEUBER[2], HEIKO FREITAG[1], MARKUS HIRSCHFELD[1], HELMUT ERLENKEUSER[3], HAINO UWE KASPER[1], AND MICHAEL WEBER[1]

[1]University of Cologne, Department of Geology and Mineralogy, Cologne, Germany (wricken@uni-koeln.de)
[2]The Petroleum Institute, Abu Dhabi, U.A.E. (tsteuber@pi.ac.ae)
[3]Institute of Age Determination and Isotope Research, University of Kiel.

Seasonal variations in the oxygen and carbon isotopic composition of Rhine River water were compared with the isotopic record from recent and historical specimens of freshwater bivalves (*Unionidae*). The purpose of this study was to investigate these aragonitic bivalves as proxies for climate change. Seasonal variations in the river water $\delta^{18}O$ are on the order of 1 to 2 ‰. During the summer, the run-off is dominated by Alpine melt-water, resulting in average values of -10 to -10.5 ‰, whereas the non-Alpine contribution is higher during winter, as indicated by mean $\delta^{18}O$ values of -8.5 to -9 ‰. The $\delta^{18}O$ of growth increments in the prismatic shell layer of *Unio crassus nanus* corresponds perfectly to what is predicted by known fractionation of ^{18}O between water and aragonite. Variations in $\delta^{18}O$ and the river water temperature are faithfully recorded by relatively large growth increments during summer. The isotopic signatures of individual flood events are also recorded in the shells. In summer, snowmelt-related Alpine waters with low DIC contents and heavy $\delta^{13}C$ lake productivity signals (-9 ‰) were observed at Cologne. In winter, however, the components of the non-Alpine Rhine dominate the discharge at Cologne. Waters had light $\delta^{13}C_{DIC}$ signals of –11‰ soil respiration in the non-Alpine zone. Sampling of Lake Constance waters showed the effect of bioproductivity in the summer surface water. Bioproductivity is related to the withdrawal of light organic carbon and has a positive $\delta^{13}C_{DIC}$ increase of 2 ‰ in the surface waters.

Speciation of Cu and Zn in natural hydrothermal boiling systems: Evidence from fluid inclusion studies by X-ray absorption techniques

K. RICKERS[123], J. CAUZID[3], J.-L. HAZEMANN[4], O. PROUX[5] AND V. LÜDERS[2]

[1]DESY, Hamburg, Germany; (karen.rickers@desy.de).
[2]GFZ Potsdam, Germany; (volue@gfz-potsdam.de).
[3]ESRF, Grenoble, France; (jean.cauzid@esrf.fr).
[4]Institut Néél, CNRS UJF, Grenoble, France; (hazemann@grenoble.cnrs.fr).
[5]LGIT, UJF CNRS, Grenoble, France; (olivier.proux@esrf.fr).

Metal speciations in fluids are responsible for the partioning of metals into the liquid and vapour phase during fluid phase separation and can lead to major changes in fluid compositions of hydrothermal systems. Here we present data for the partitioning behaviour of Cu and Zn in coexisting liquid and vapour phase fluid inclusions formed by sub-critical phase separation. Synchrotron-radiation induced micro X-ray fluorescence analysis (SR-XRF) and temperature-dependant X-ray absorption near edge structure (XANES) experiments were performed on individual inclusions. The studied fluid inclusion boiling assemblages are hosted in quartz from miarolic cavities of the Torres del Paine granite complex (Chile). The formation temperatures of hydrothermal quartz in vugs range between 280°C and 340°C.

SR-XRF element maps revealed that Cu and Zn show a contrasting partitioning behaviour: while Cu is dominantly detected in vapour-rich inclusions, zinc is more abundant in brine-type inclusions.

XANES experiments were performed at temperatures up to 460°C using a Linkam THMSG-600 heating-stage. Measurements were carried out at ID22 and FAME, ESRF with spot sizes of 4 and 15 µm, respectively. In vapour-rich inclusions, most of the Cu is concentrated in daughter crystals. During heating runs, the daughter crystals dissolve and Cu oxidation state changes between 190°C and 280°C from Cu^{2+} to Cu^{1+}. While Cu^{2+} seems to be coordinated with water ligands forming the complex $Cu[H_2O]_6^{2+}$, Cu^{1+} is coordinated by two chorine ions forming $Cu[Cl_2]^-$. In brine-type inclusions, Cu is contained in the liquid phase. XANES-spectra show that Cu disolved in brines has an oxidation state of 2^+ between 25°C and 460°C. These findings are in accordance with the interpretation that at temperatures of phase separation Cu^{1+} species is more stable and responsible for the concentration of Cu in the vapour phase.

XANES spectra indicate that Zn is most propably complexed as $ZnCl_4^{2+}$ in the temperature range 25 –370° for both, liquid and vapour rich inclusions. This shows that in contrast to Cu, changes in speciation are not responsible for the partitioning of Zn into the liquid and the vapour phase.

Hafnium and neodymium isotopes in Atlantic ocean waters

J. RICKLI[1], M. FRANK[2] AND A.N. HALLIDAY[3]

[1]IGMR, Dept. of Earth Sciences, ETH Zurich, Zurich, Switzerland, (rickli@erdw.ethz.ch)
[2]IfM-GEOMAR, Leibniz Institute for Marine Sciences at the university of Kiel, Germany, (mfrank@ifm-geomar.de)
[3]Department of Earth Sciences, University of Oxford, Oxford, U.K., (alexh@earth.ox.ac.uk)

Numerous studies have documented the sources and behaviour of Nd in the present day ocean providing a background for paleoceanographic interpretations. In contrast, much less information is available on Hf isotopes. As a consequence, there is still an ongoing debate on the sources of Hf in seawater.

We present isotopic compositions for the dissolved Hf and Nd in seawater samples taken on a transect from the Bay of Biscay to Cape Town (RV Polarstern cruise ANXXIII/1 in 2005). Hafnium and Nd were pre-concentrated by iron co-precipitation from 70 to 140 liters of filtered (0.45 μm) seawater. Separation of Hf and Nd followed previously established ion chromatographic procedures. Hafnium and Nd isotopic compositions were measured by MC-ICPMS (Nu Plasma) with a 2σ external reproducibility of 0.65 and 0.3 ε -units, respectively. Sample sizes varied but were typically in the range of 5 to 7 nanograms of Hf.

Surface seawater as well as deep water samples extending to ~5,000 m, plot on the "seawater array" defined previously from measurements of ferromanganese crusts and nodules. Surface seawater isotopic compositions are rather uniform for Hf and Nd at most sampling locations ranging from +0.1 to +1.7 in ε_{Hf} and from -12.1 to -11.5 in ε_{Nd}. Two locations at 22.5°N and 10.5°N show less radiogenic compositions in the subsurface (ε_{Nd} down to -12.9 and ε_{Hf} down to -0.8).

Deep water compositions range from +0.8 to +4.2 ε_{Hf}. The ε_{Hf} variations with depth in the different profiles generally follow the patterns observed for ε_{Nd}. The overall variations in deep water Nd isotopes in our data set is twice as large as that of Hf isotopes (ε_{Nd} between -13.9 and -7.9) but the spread in Hf isotopes of some depth profiles is significantly larger than for Nd.

Particularly unradiogenic Nd signatures are found in the Angola Basin, where ε_{Nd} is as low as -15.4. This may reflect inputs from the Congo River or sediment seawater exchange within the basin. Hafnium isotopes, however, do not show such a shift.

Neodymium isotopes are in general agreement with the results of earlier studies. Antarctic Intermediate Water, however, has been sampled at three locations where it is clearly less radiogenic (ε_{Nd} = -11.1, -13.9 and -11.4) than reported before (ε_{Nd} = -8.9 to -6.2).

Ice migration in the early solar system: From Jupiter to the Earth

HANS RICKMAN[1,] NIKOLAI PISKUNOV, WLADIMIR LYRA, SAMUEL REGANDELL[2] AND GIOVANNI B. VALSECCHI[3]

[1]Space Research Center, Polish Acad. Sci. (hans@astro.uu.se)
[2]Uppsala Astron. Observatory (nikolai.piskunov@astro.uu.se, wlyra@astro.uu.se, samreg@astro.uu.se)
[3]INAF-IASF, Roma (giovanni@iasf-roma.inaf.it

We will report on a project carried out at Uppsala, where we attempt to simulate the dynamical evolution of planetesimals remaining in the region of giant planet accretion after the formation of planetary embryos of substantial masses. The simulation includes the gas drag and gravitational perturbations of the solar nebula. For each orbital period these effects are found by interpolation on a precomputed grid in orbital element space, and close encounters with the embryos are modelled by the Öpik method, thus yielding gravitational kicks that transfer the planetesimals along the routes of the circular restricted three-body problem. We aim to investigate the transfer of icy planetesimals inward across the snow line into the region which is now occupied by the outer parts of the asteroid Main Belt, from where they may have been incorporated into the growing Earth during the late phases of accretion.

Greenhouse gas driven hyperthermals of the Paleogene: How much carbon, how fast?

A. RIDGWELL[1], K. PANCHUK[2] AND L. KUMP[2]

[1]School of Geographical Sciences, University of Bristol, Bristol, UK (andy@seao2.org)
[2]Dept. of Geosciences, Penn State, University Park, PA, USA (kpanchuk@geosc.psu.edu, kump@geosc.psu.edu)

Terrestrial and marine deposits from the early Cenozoic record a 55 million year old transient warming of the Earth's surface, dubbed the 'Paleocene/Eocene Thermal Maximum' (PETM). The occurrence of a prominent carbon isotopic excursion indicates massive release to the ocean and atmosphere of CO_2 and/or CH_4, thought to be similar in magnitude to current fossil fuel reserves. The PETM thus represents a potentially compelling analogue candidate for future greenhouse gas driven global change. In particular, understanding this event could provide us with invaluable insights into key mechanisms of feedback between climate and global carbon cycling as well as what the long-term impacts on calcifying plankton and animals of surface ocean 'acidification' might be. However, the parallels that can be drawn with anthropogenic climate change hinge critically on the magnitude and time-scale of the greenhouse gas forcing of this hyperthermal event.

Here we apply an Earth system model (GENIE-1) to the interpretation of the marine geologic record of the PETM and tackle the question of what the rate and total input of carbon to the ocean and atmosphere might have been.

Surface structural modeling at the solid-solution interface of nanocrystalline anatase

MOIRA K. RIDLEY[1], MICHAEL L. MACHESKY[2], DOUGLAS A. BLOM[3], LAWRENCE F. ALLARD[3] AND VINCENT A. HACKLEY[4]

[1]Texas Tech University, Lubbock, TX (moira.ridley@ttu.edu)
[2]Illinois State Water Survey, Champaign, IL (machesky@uiuc.edu)
[3]Oak Ridge National Laboratory, Oak Ridge, TN (blomda@ornl.gov, allardlfjr@ornl.gov)
[4]National Institute of Standards and Technology, Gaithersburg, MD (vince.hackley@nist.gov)

To begin to assess the effects of particle size on the surface reactivity and charging of metal-oxide nanoparticles in aqueous solutions comprehensive experimental and characterization studies were completed. Commercially available crystalline anatase (TiO_2) particles were used in the study. Particle size ranged from 200 to 3 nm diameter, with corresponding BET surface areas of 10 to 350 m^2/g, respectively. Potentiometric and electrophotetic mobility titrations of the anatase samples were performed in NaCl media at ionic strengths from 0.005 to 0.3 molality, at 25ºC. All samples were characterized extensively; using electron microscopy and aberration corrected electron microscopy (ACEM), neutron and X-ray small-angle scattering, and laser diffraction techniques.

A principle parameter obtained from the surface titration studies was the pH_{znpc} value. The pH_{znpc} of 40 nm diameter anatase particles (pH_{znpc} = 6.22) corresponded closely to previously published values; whereas, the pH_{znpc} value of 3 nm particles was higher (pH_{znpc} = 6.90). Furthermore, the development of positive surface charge was enhanced for larger anatase nanoparticles (>20 nm) over 3 nm diameter particles; in spite of this, the overall development of negative surface charge, relative to the respective pH_{znpc} values, was approximately the same for all particles sizes studied. At high ionic strengths the apparent pH_{znpc} value of the 3 nm particles was offset slightly toward lower pH values, which suggests some specific adsorption of the Na^+ electrolyte ions.

Surface complexation modeling (SCM) was completed to rationalize the bulk surface titration data. The SCM's incorporate all available molecular information (e.g., Ti-O bond lengths), with crystallographic information acquired from the ACEM. ACEM imaging revealed that the [100] face predominates on the 20 nm particles, and edges/facets include [010], [001], and [0-11]. A MUSIC model description of surface protonation permitted rationalization of the decrease in pH_{znpc} values with increasing particle size. Additionally, a Stern-layer representation of the EDL, and inner-sphere adsorption geometry of the electrolyte cation were also accounted for.

Fluid influence on retrograde assemblages in UHP eclogites

ASTRID RIEMANN, ANDREAS MÖLLER AND ROLAND OBERHÄNSLI

Institut für Geowissenschaften, Universität Potsdam, Germany (ariemann@geo.uni-potsdam.de)

This study is a combination of modelling the phase stability, fluid availability and observations in ultra high pressure (UHP) rocks from the Chinese Continental Scientific Drilling (CCSD) project. We investigate the origin of the fluid and its influence on the mineral chemistry and (re-) equilibration processes for a better understanding of the retrograde PT-path. All investigated sample lithologies (eclogites, ortho- and paragneisses and schists) have been influenced by fluids to varying degrees. The main evidence for these fluids are different types of fluid inclusions, healed cracks, pro-and retrograde formation of hydrous minerals and late crosscutting veins. Retrograde assemblages in the eclogites range from UHP to greenschist facies. These form in centimetre wide zones that can be subdivided into a transition zone and a strongly altered inner part. While the fluid inclusion bearing assemblage garnet-omphacite-coesite-phengite-rutile reflects UHP conditions, albite-clinopyroxene symplectites appear in the first stage of retrogression as a response to post peak decompression. Garnet in the transition zone is cracked and rimmed by pargasitic amphibole, signalizing fluid influence in the amphibolite facies. Fluid also triggers the breakdown of garnet and omphacite to an amphibole bearing symplectite and intergrowth of rutile and newly formed ilmenite. Phengite adjacent to omphacite breaks down to biotite, albite and white mica. The inner part of the retrograde zone is a greenschist facies assemblage with a new white mica generation, which contains fluid inclusions. Quartz and calcite veins crosscut the rock in a late stage of retrogression. These different stages of metamorphic reactions influenced by fluids allow new PT estimates for the retrograde path. This evolution indicates the influence of various fluids during the exhumation history that have a significant effect on (re-)equilibration.

Cd/Ca ratios of in situ sampled planktonic foraminifera

S. RIPPERGER[1], M. REHKÄMPER[2], R. SCHIEBEL[3] AND A. N. HALLIDAY[4]

[1]Institute of Isotope Geochemistry and Mineral Resources, ETH Zurich, CH-8092 Zurich, Switzerland, (ripperger@erdw.ethz.ch)

[2]Department of Earth Science and Engineering, Imperial College, London SW7 2AZ, UK, (markrehk@imperial.ac.uk)

[3]School of Ocean & Earth Science, National Oceanography Centre Southampton, Southampton SO14 3ZH, UK, (rxs@soc.soton.ac.uk)

[4]Department of Earth Sciences, University of Oxford, Parks Road, Oxford OX1 3PR, UK, (alex.halliday@earth.ox.ac.uk)

The Cd/Ca ratios of fossil planktonic foraminiferal tests are of particular interest to paleoceaographers as they can be used to reconstruct past surface water nutrient utilization [1]. The reliability of this proxy has hitherto not been comprehensively studied, however. In order to fill this gap, we performed Cd/Ca analyses of planktonic foraminifers (*G. ruber*, *G. sacculifer* and *G. bulloides*) collected from the water column and from surface sediment samples at approximately the same locations. These analyses utilized an isotope dilution technique and a MC-ICPMS instrument equipped with a multiple ion counting system.

The Cd/Ca ratios obtained for *G. ruber* sampled from the natural habitat in the upper 80 m of the water column generally display a correlation with seawater phosphate content. No such trend, however, was observed for *G. sacculifer* and this indicates that vital effects may be responsible for the different Cd/Ca systematics of these species. Moreover, the results reveal differences in Cd/Ca between (i) specimens collected from their habitat (live specimens), (ii) settling shells (deceased specimens) and (iii) tests from surface sediments. Settling tests of *G. ruber* exhibit about 2-5 times lower Cd/Ca values than live specimens. This suggests that Cd is preferentially released during partial dissolution of calcite during settling of the tests through the water column. Fossil shells of *G. ruber* display Cd/Ca ratios that are up to 15 times larger compared to results obtained for settling shells of the same species. This observation is most readily explained, if sedimentary tests are primarily deposited in mass sinking events that are associated with much higher settling velocities in comparison to those experienced by single settling shells. Furthermore, the Cd/Ca ratios of *G. ruber*, *G. sacculifer* and *G. bulloides* from surface sediments are consistently higher than those obtained for live collected specimens from the natural habitat. Post-depositional alteration of the tests is unlikely to be responsible for this discrepancy. A number of alternative explanations are possible but these remain speculative at present.

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Tracing the sources of carbon in the rivers of Lesser Antilles

K. RIVE[1], J. GAILLARDET[2] , P. AGRINIER[1] AND S. RAD[2]

[1]Lab. Géochimie des Isotopes Stables, IPGP,Tr54, 4pl. Jussieu, 75005 Paris, France. (rive@ipgp.jussieu.fr)
[2]Lab. Géochimie et Cosmochimie, IPGP, Tr14, 4pl. Jussieu, 75005 Paris, France.

At long timescales, the continental weathering of volcanic areas is one of the processes that control the atmospheric CO_2 (e.g. Louvat, 1997, Dessert *et al*., 2003). However, the nature of the links between CO_2 cycle and the chemical weathering of volcanic rocks is poorly known.

The CO_2 consumption by chemical weathering can be estimated with the concentration of Dissolved Inorganic Carbon (DIC ≈ HCO_3^-) in the rivers. Nevertheless, some processes are likely to modify the DIC concentration in the river (e.g. equilibration with the atmosphere, precipitation of calcite, photosynthesis, respiration).

The processes governing the CO_2 consumption by chemical weathering were studied in three volcanic islands in Lesser Antilles (Guadeloupe, Martinique and Dominica). The Lesser Antilles are ideal sites for the study of weathering due to their tropical climate and high relieves, inducing high weathering rates (Rad *et al*., 2006). Carbon stable isotopes of DIC and major elements chemistry were studied in streams, springs and soil solutions of these three islands during dry and wet season.

The $\delta^{13}C_{DIC}$ and major elements concentrations, highly variable, allowed us to identify the origin of DIC as a mixing between soil CO_2 (average value of $\delta^{13}C \approx -29.1 \pm 2.0$‰) and volcanic CO_2 ($\delta^{13}C_{DIC} = -3.25 \pm 0.25$‰, Agrinier *et al*., 2002). In addition, we observed an equilibration process of the riverine DIC with the atmospheric CO_2. Finally, as highlighted by Rad *et al*. (2006) for major elements, this isotopic study of the DIC cycling in the river demonstrates the importance of the volcanic fluids on chemical weathering processes.

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Sedimentary ^{232}Th as a tracer of dissolved detrital inputs to the ocean

LAURA F ROBINSON[1], TARYN L NOBLE[1] AND JERRY F MCMANUS[2]

[1]Dept of Marine Chemistry and Geochemistry, Wood Hole Oceanographic Institution, Woods Hole, MA, 02543.
[2]Dept of Geology and Geophysics, Wood Hole Oceanographic Institution, Woods Hole, MA, 02543

This study uses long lived thorium isotopes as a tracer for dissolved detrital inputs to seawater. ^{232}Th is derived exclusively from the partial dissolution of detritus. ^{230}Th is produced at a predictable rate by the decay of uranium, and its subsequent removal by efficient adsorption onto settling particles provides a method to quantify dissolved ^{232}Th fluxes to the seafloor. Ten core-top sediment samples were treated with up to eight leaching techniques and a total digestion to determine the best method for the separating adsorbed from lattice-bound thorium. Adsorbed (and total) ratios giving high dissolved (and total) ^{232}Th fluxes were measured in sediments from locations with high expected detrital inputs. These fluxes are reasonable by comparison to global estimates of detrital inputs to the ocean. The half-lives of both thorium isotopes are long enough to allow us to apply this technique to sediments that span several glacial-interglacial cycles. Coupled with total sedimentary ^{232}Th fluxes this data has the potential to evaluate various proposed linkages between ocean and atmospheric processes in the past. Preliminary downcore results display higher ^{232}Th/^{230}Th ratios that are consistent with enhanced ice-age dust deposition in the central Atlantic, North Pacific and three out of four Southern Ocean sites. However the two- to four-fold glacial increases indicated by the thorium isotope proxy are smaller than the order of magnitude changes recorded in high latitude ice cores.

Crustal contamination of the upper mantle: Evidence from ophiolites

P. T. ROBINSON[1], R. TRUMBULL[1], S. KOSTROWSKI[1], J. ERZINGER[1], A. SCHMITT[2] AND R. EMMERMANN[1]

[1]GeoForschungsZentrum, D-14473 Potsdam, Germany (robinson@gfz-potsdam.de; bobby@gfz-potsdam.de; sankos@gfz-potsdam.de; erz@gfz-potsdam.de; emmermnn@gfz-potsdam.de)

[2]Department of Earth and Space Sciences, UCLA , Los Angeles, California (axel@argon.ess.ucla.edu)

Our studies of podiform chromitites in the Luobusa ophiolite, Tibet and the Semail ophiolite, Oman provide evidence that their mantle sources were contaminated by crustal minerals. The chromitites contain rounded, reworked grains of zircon, corundum, quartz, feldspar, diopside and amphibole(?). These are associated with moissanite (SiC), graphite, PGE minerals, rutile, Fe, Ti and Si alloys and native elements. Careful sample collection and preparation, and duplication of results in several laboratories rule out natural or anthropogenic contamination.

The zircon grains range from 20 to 300 μ across, are typically well rounded and have complex internal zonation. Rare grains are subhedral and have regular, concentric zoning. Some contain inclusions of quartz, rutile, orthoclase, mica, ilmenite or apatite. in situ $^{206}Pb/^{238}U$ dates by SIMS for the Luobusa zircons are very heterogeneous and range from 1657-549 Ma, far older than the ophiolite (~120 Ma), clearly indicating a mixed population of crustal protoliths.

The grains of quartz, corundum, feldspar and diopside range from 0.1 - 0.5 mm and are moderately to well rounded.

The morphology, composition and age of these minerals strongly suggest that they were originally derived from reworked sedimentary or metamorphic material transported into the mantle by subduction and later incorporated into the chromitites. Their occurrence with ultrahigh pressure minerals such as diamond, and coesite in the Luobusa ophiolite suggests derivation from depths of at least 100 km.

Olmec serpentinitic pieces from La Merced: isotopic and geochemical constraints

J. ROBLES-CAMACHO[1], H. KÖHLER[2], P. SCHAAF[3] AND R. SANCHEZ-HERNANDEZ[1]

[1]Instituto Nacional de Antropología e Historia, Mexico (jasinto_robles@yahoo.com, jadeite@hotmail.com)

[2]Institut für Mineralogie, Petrologie und Geochemie. L-M-U München, Germany (hermann-koehler@hotmail.com)

[3]Instituto de Geofísica, UNAM, Mexico (pschaaf@geofisica.unam.mx)

Geoarcheology and petrological methods

The olmec (1,200 B.C. to 400 B.C.) was the first mesoamerican culture, characterized by extensive use of serpentinites (Heizer, 1961; Rodríguez and Ortiz, 2001). To know the geological provenance were performed XRF, ICP-MS, EM-WDS, and thermal ionization MS (Rb-Sr and Sm-Nd isotopic systems) on 17 archeological samples (SAO) from La Merced and 15 geological (GS) from Mexico and Guatemala.

Discussion of results

Mineralogy and geochemical composition (V, Zr, Zn, Cr, Ti; REE series) show a better correlation among SAO and GS from south Mexico. Likewise, Sr isotopic ratios for SAO $^{87}Sr/^{86}Sr$ (0.70567-0.71258) and the Nd isotopic system displays ε-Nd values from -5.4 to +6.6 $_{(today)}$.

Conclusions

Petrological information indicate that only the Sierra de Juárez geological samples have affinities to the SAO objects from La Merced; near Vista Hermosa fault.

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A depleted lithosphere component in the Hawaiian plume: Noble gas evidence from plume-related mantle xenoliths

A. ROCHOLL[1], D. GÜNTHER[2], M. TRIELOFF[3] AND R. WIRTH[4]

[1]Department für Geo- und Umweltwissenschaften, Universität München, 80333 München, Germany, (rocholl@min.uni-muenchen.de)
[2]Laboratory of Inorganic Chemistry, ETH Hönggerberg, 8093 Zürich, Swizerland; (guenther@inorg.chem.ethz.ch)
[3]Mineralogisches Institut, Universität Heidelberg, 69120 Heidelberg, Germany; (trieloff@min.uni-heidelberg.de)
[4]GeoForschungsZentrum Potsdam, 14473 Potsdam, Germany

Garnet pyroxenite (GPX) xenoliths from Salt Lake Crater, Oahu, are interpreted as high-P cumulates (60-90 kms depth) of Hawaiian plume-derived basaltic melts [e.g. 1,2]. Two generations of secondary melt/fluid inclusions document two distinct episodes of metasomatic overprint: (1) Young, immature and irregularily shaped "type-A" inclusions represent nephelinitic host magma, trapped along poorly sealed cracks during eruption some 0.3 Myrs ago. (2) Old, mature and polygonal "type-B" inclusions aligned along well-sealed cracks document pre-eruptive metasomatism of the mantle. LA ICP-MS analyses of "type-B" inclusions indicate high contents in siderophile and chalcophile trace elements including the PGEs. TEM and spectroscopic evidence shows that, after trapping, a highly reducing C-O-H-S-Cl-rich melt differentiated into a CO_2-rich gas phase, "basaltic" glass and nm-sized "exotic" minerals including nano-diamond, native Fe and Cu, PGE minerals, and corundum [3]. Combined step-heating, TEM and isotope data reveal a distinct degassing behaviour of both inclusion types. Highly "depleted" [e.g. 4] noble gas signatures of type-B inclusions ($^{40}Ar/^{36}Ar \approx 12000$, $^{3}He/^{4}He \approx 7$ R/Ra, $^{21}Ne/^{22}Ne \approx 0.05$, $^{20}Ne/^{22}Ne \approx 12$) indicate generation of the trapped melts within a depleted MORB-type mantle and are compatible with the presence of old, recycled, depleted lithosphere intrinsic to the Hawaiian plume, as also suggested by the Hf-Nd-Sr isotope systematics of the GPX host [1] which the melts infiltrated. Alternatively, the melts may have originated from upper mantle material incorporated into (or enveloping) the Hawaiian plume.

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Interaction of gypsum and $As(V)_{aq}$ at different pH ranges

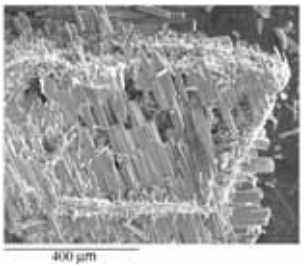
J.D. RODRÍGUEZ-BLANCO[1], A. JIMÉNEZ[1], S. GARCÍA-GRANDA[2], AND M. PRIETO[1]

[1]Facultad de Geología. Universidad de Oviedo. C/ Jesús Árias de Velasco, s/n. 33005 Oviedo. (juandiego@geol.uniovi.es)
[2]Facultad de Química. Universidad de Oviedo. C/ Julián Clavería, 8. 33006 Oviedo. (sgg@fq.uniovi.es)

This research is focused on the study of As(V)-gypsum interactions in aqueous solution within different ranges of pH and concentration. The main goals of this study are: 1) to evaluate the capacity of gypsum to remove arsenic from aqueous solutions; 2) to understand the nature of the processes by which the removal takes place and, 3) to characterize the solid phases derived from these interactions. Although the mobility and toxicity of arsenic in the environment has been abundantly studied, the crystal-chemistry, thermodynamic properties and solubility products of arsenates continue to be poorly known. This lack of data is an important handicap because an in-depth study of arsenate mobility in natural systems requires a precise knowledge of the solid phases that may or may not precipitate, as well as their crystal-chemistry, and their solubility.

The study has been carried out at different pH ranges using batch experiments. The aqueous solutions were characterized by AAS, ionic chromatography, and ICP-AES. The solids were characterized using SEM-EDS, powder, grazing incidence, and single-crystal XRD.

Figure 1: pharmacolite ($CaHAsO_4 \cdot 2H_2O$) overgrowth on gypsum.



The results show that at high pH (>10.5) there is a virtually complete removal of As(V) due to the surface precipitation of amorphous $Ca_3(AsO4)_2 \cdot nH_2O$ and crystalline $NaCaAsO_4 \cdot 7.5H_2O$. In contrast, the effectiveness of the uptake process is very low at lower pHs, as it involves the surface precipitation of different calcium arsenates (guerinite, sainfeldite, pharmacolite, ferrarisite). The study included determinations of solubility products, growth morphologies, and epitaxial relationships. In addition, structural characterization by single crystal XRD has been carried out for $NaCa_2H(AsO_4)_2 \cdot 6H_2O$ and $NaCaAsO_4 \cdot 7.5H_2O$.

Modelling transfer of elements from the continent to the ocean at the large watershed scale in a tropical environment

C. ROELANDT,[1] Y. GODDERIS[1] M.-P. BONNET[1] AND F. SEYLER[1]

[1]LMTG, CNRS-IRD, Observatoire Midi-Pyrénées, Toulouse, France, (godderis@lmtg.obs-mip.fr)

Continental weathering of silicate rocks has been recognized as a major driver of climatic changes at the geological timescale. New evidences and preliminary modelling works [1] show that the impact of continental weathering on the geochemical cycles and climate might be non negligible at shorter time scales, from 10^2 to 10^4 years, with for instance an increase in total continental weathering by 12% from the LGM towards the present day [2].

Continental weathering at large scale (10^6 km^2) is generally described through parametric laws (see for instance [3]), linking weathering rates to mean annual air temperature and continental runoff. These laws are masking numerous other parameters, implicitly included, such as the role of vegetation and physical erosion. These laws generally overestimate weathering rates in tropical area, because of high local temperature and runoff. It was indeed stressed by Edmond *et al*. and others [4] that chemical weathering in tropical environment might be extremely low due to the development of thick soils undergoing weak physical erosion.

A coupled model of biospheric and weathering processes has been developped to estimate the transfer of elements to the ocean originating from tropical watersheds. The BERNI model is the result of the coupling of LPJ – dynamic global vegetation model [5] with the WITCH model [6] that estimates dissolution/precipitation of minerals in the soil environment from kinetic laboratory laws.

Here we present results obtained for the Orinoco watershed. Output of the coupled model includes major ion concentrations that are compared to available data, and CO_2 consumption through weathering for a tropical environment. We emphasize the need for the development of mechanistic numerical models of weathering processes working at the continental scale.

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Microbial leaching of iron from magnetite under aerobic and anaerobic environments

YUL ROH[1], JONGMIN OH[1], YONGJAE SUH[2], AND HEE DONG JANG[2]

[1]Chonnam National University, Gwangju, South Korea (rohy@chonnam.ac.kr)
[2]Korea Institute of Geoscience and Mineral Resources, Daejeon, South Korea

It is in its infancy to use bacteria as a novel biotechnology for leaching precious and heavy metals from raw materials. The objective of this study was to investigate biogeochemical processes of iron leaching from magnetite reduction by iron-reducing bacteria isolated from intertidal flat sediments, southwestern part of Korea. Microbial leaching experiments were performed using both Aldrich magnetite and magnetite ore, in well-defined media with and without bacteria under aerobic and anaerobic environments. Water soluble Fe production was determined by Inductively Coupled Plasma Spectroscopy (ICP) analysis of bioleached samples in comparison to uninoculated controls, and the resulting precipitated solids were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

The pH typically decreased from 7.3 to 5.5 during 4-week incubations. The Eh of the initial medium decreased from ~ 40 mV to -550 mV under anaerobic environments upon incubation with the metal reducing microorganisms. Measured pH and Eh are consistent with the thermodynamic stability of ferrous iron formation. The decrease in pH is due to glucose fermentation producing organic acids and CO_2. The extent of iron leaching from magnetite in the aerobic conditions (Fe = 107 ppm) was higher than that in the anaerobic environments (Fe = 94 ppm). In the anaerobic conditions, Fe(III) in the magnetite was also reduced to Fe(II), but no secondary mineral phases were observed. Amorphous iron oxides formed in the medium under aerobic conditions where there was sufficient supply of oxygen from the atmosphere. This study suggests that the reduction processes involve dissolution-precipitation mechanisms as opposed to solid state conversion of magnetite to amorphous iron oxides. The ability of bacteria to leach soluble iron and precipitate amorphous iron oxides from crystalline magnetite could have significant implications for biogeochemical processes in sediments where Fe(III) in magnetite plays an important role in the largest pool of electron acceptor as well as the tool as a novel biotechnology for leaching precious and heavy metals from raw materials.

Provenance of Lower Cretaceous sediments from Svalbard and NE Greenland: A detrital zircon study

T.S. RØHR [1], T. ANDERSEN[2] AND H. DYPVIK [3]

[1]Department of Geosciences, University of Oslo, P.O. Box 1047 Blindern, 0316 Oslo, Norway (t.s.rohr@geo.uio.no)
[2](tom.andersen@geo.uio.no)
[3](henning.dypvik@geo.uio.no)

Upper Jurassic – Lower Cretaceous sedimentary successions in the Wandel Sea Basin of North Greenland have previously been shown to correlate stratigraphically with similar aged formations on Svalbard, including the mainly fluvial Helvetiafjellet Fm (Dypvik *et al*., 2002). Detrital zircons from Lower Cretaceous sedimentary formations from the Wandel Sea Basin (Kilen and Peary Land) and Svalbard (the Helvetiafjellet Fm.) have been dated by U-Pb and analysed for Lu-Hf isotopes by laser ablation plasma source mass spectrometry (LAM-ICPMS). Samples from all three areas display a similar range of U/Pb ages, with significant zircon populations at 1.0 – 1.2, 1.8 – 2.0 and 2.6 – 2.8 Ga. Major hiati occur between 2.1 and 2.4 and from 0.48 to 0.91 Ga. Low initial $^{176}Hf/^{177}Hf$ ratios indicative of recycled older crust are predominant in Caledonian-aged zircons, in the Palaeoproterozoic 1.8 – 2.0 Ga populations, and among late Archean zircons. Other U/Pb age populations in the studied samples are dominated by zircons with positive ε_{Hf} values, indicating a significant contribution of mantle-derived material. There is commonly a narrow range of ε_{Hf} values seen within the various U/Pb age population, and the values seen in the different samples are in general correlated with the different age populations. One exception is the 1.8 – 2.0 Ga population where variations suggest variable sources for this age group. The U/Pb data indicate that Greenland could be the sole source of the studied sandstones, which to a large extent is supported by Lu/Hf data. However, concordant ages in the range 1.0 – 1.1 Ga are generally infrequent in the published record from Greenland, and no large terrane of this age have as yet been discovered in Greenland. This mismatch suggests the presence of a source outside the Greenland subcontinent.

The sedimentological link between Mesozoic sediments on Svalbard and North Greenland has been known for some time. This work demonstrates that the two areas most likely had the same areas of provenance, documented by near identical U/Pb age and Lu/Hf isotope signatures of detrital zircons.

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Metal saturation in the upper mantle

A. ROHRBACH[1,2], C. BALLHAUS[1], U. GOLLA–SCHINDLER[2], P. ULMER[3] AND D. SCHÖNBOHM[1]

[1]Mineralogisch–Petrologisches Institut, Universität Bonn, Germany (rohrbaa@uni–muenster.de)
[2]Institut für Mineralogie, Universität Münster, Germany
[3]Institut für Mineralogie und Petrographie, ETH Zürich, Switzerland

The uppermost mantle represented by samples and partial melts appears to be quite oxidized at oxygen fugacities (fO_2) around the FMQ equilibrium. However, whether the oxidation states found in shallow mantle regions are representative for the entire upper mantle remains unclear. There is evidence for reduction with depth. Thermodynamic model calculations and analyses of natural garnet peridotite samples indicate that fO_2 in the upper mantle decreases with increasing pressure [1]. In addition, experiments have shown that phases stable in the transition zone (400 to 670 km) and the lower mantle (670 to 2900 km) can incorporate so much Fe^{3+} that an Fe–rich metal phase is likely to be stable [2,3].

To simulate redox controls in the upper mantle experimentally, we have equilibrated Fe_2O_3–free synthetic fertile mantle material in metallic Fe capsules between 1 and 14 GPa and 1220 to 1650°C. fO_2 at run conditions, approximated from the FeO content of the silicates, are IW – 0.5 to –1.2. Analyses of pyroxene and garnet with Electron Energy Loss Spectroscopy (EELS) show that above 7 GPa, subcalcic pyroxenes and majoritic garnets incorporate so much ferric iron that a mantle composition with 8 wt.% FeO and 2000 ppm Fe_2O_3 will be within metal saturation. Hence, the earth's upper mantle at > 250 km depth is likely to be saturated with an (Fe,Ni) metal phase.

It was proposed [3] that the high ferric iron concentrations noted in experimental transition zone and lower mantle phases may be derived by disproportionation of ferrous iron components in silicates, according to $3FeO = Fe° + Fe_2O_3$. If this was the case for the upper mantle, the $Fe°–Fe_{1-x}O–Fe_3O_4$ triple point in the Fe–O system (at ~ 570°C at 10^5 Pa) should be shifted to higher temperature with increasing depth. An in–situ determination of the wuestite–magnetite phase transition between 0.5 and 5 GPa in the presence of metallic Fe in the MAX80 high pressure device, using white synchrotron radiation, shows that the disproportionation reaction has a negative slope in P–T space. Therefore, to relate the high ferric iron concentrations in upper mantle pyroxene and garnet to pressure–induced FeO disproportionation alone seems a simplistic view.

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Oxygen isotopic composition in deep-sea coral, *Lophelia pertusa*

C. ROLLION-BARD [1], D. BLAMART[2], J.-P. CUIF[3], A. MEIBOM[4], A. JUILLET-LECLERC[2] AND Y. DAUPHIN[3]

[1]CRPG-CNRS, Nancy, France (rollion@crpg.cnrs-nancy.fr)
[2]LSCE, CEA-CNRS, Gif-sur-Yvette, France
[3]Univ. Paris XI, Orsay, France
[4]Museum National d'Histoire Naturelle, Paris, France

The deep-sea coral *Lophelia pertusa* is a scleractinian coral (azooxanthellate) found mainly in Atlantic Ocean. The stable isotopic compositions of their skeleton are frequently used to reconstruct paleoceanographic conditions, including sewater temperature. However, microanalytical techniques, i.e. microdrill and SIMS, have shown that the $\delta^{18}O$ in lines of centres of calcification (LCC) are strongly depleted relative to the surrounding fibrous skeleton. These large amplitude, small length scale isotopic variations cannot be driven by changes in environmental parameters. Several models have been proposed to explain the observed variations, including models based on pH variations of the hypothetical extracellular calcifying fluid (Adkins *et al*., 2003, Rollion-Bard *et al*., 2003).

To document clearly the oxygen isotopic behaviour against the structure and the pH, we have performed ion microprobe $\delta^{11}B$ and $\delta^{18}O$ profiles cross-cutting the two main structures of *Lophelia pertusa* (the $\delta^{11}B$ values are discussed in an abstract by Blamart *et al*. (this conference)). The $\delta^{18}O$ data range from -2.61 to 3.41 ‰, which is in the range of variation obtained by microsampling. The LCC $\delta^{18}O$ values range from -2.61 to -1.17 ‰, with a mean value of -1.93 ‰ (n=13). The $\delta^{18}O$ values for the surrounding fibres are systematically heavier, ranging from 0.45 to 3.37 ‰, with a mean value at 2.41 ‰ (n=19). So the $\delta^{18}O$ values appear strongly correlated to the microstructure of the coral skeleton.

It was thought that this different behaviour of the $\delta^{18}O$ between fibres and COC was principally driven by variations of pH. The $\delta^{11}B$ data performed in parallel profiles demonstrate that there is no correlation between $\delta^{18}O$ and $\delta^{11}B$, and therefore no correlation with pH. Moreover, it was presumed from $\delta^{18}O$ data that LCC should have a higher pH than surrounding fibres and it is the contrary. This implies that the LCC and surrounding fibres do not derive from the same calcifying fluid. Therefore LCC and surrounding fibres are precipitated by different mechanisms, most likely which are controlled by specialized domains of the calicoblastic layer.

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Lamproite-hosted xenoliths of Vestfjella: Implications for lithospheric architecture in western Dronning Maud Land, Antarctica

I. ROMU AND A. LUTTINEN

Department of Geology, P.O.Box 64, FI-00014 University of Helsinki, FINLAND (ilona.romu@iki.fi, arto.luttinen@helsinki.fi)

Lamproite-hosted xenoliths from Kjakebeinet (73º47’ S, 14º53’ W), south Vestfjella, represent unique samples of the unexposed continental crust at the rifted margin of western Dronning Maud Land. The xenolith suite indicates 1) heterogeneity of the crust, 2) granulite facies metamorphic conditions, and 3) mainly igneous protoliths. Two leucocratic tonalite gneiss samples yielded U-Pb SHRIMP zircon ages of ~1.0–1.3 Ga (J. Jacobs, personal communication, 2006). Interpretation of mineral–whole-rock Sm-Nd isotope data on mafic granulites is complicated by lamproite overprint. The results imply compositional affinity to Proterozoic lower crustal xenoliths from Lesotho, South Africa (Rogers and Hawkesworth, 1982) and equilibration of the Sm-Nd -system during Grenvillean and Jurassic magmatic events. Overall, the lamproite-hosted xenoliths indicate extension of the Proterozoic Maud Belt crust to Vestfjella. These results and the presence of basalt-hosted Archean xenoliths at the nearby Muren (Luttinen & Furnes, 2000) imply that the Kjakebeinet lamproites erupted probably just at the Archean-Proterozoic lithospheric boundary.

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Experimental study of REE behavour during apatite dissolution in presence of iron and organic matter

T. RONCAL-HERRERO, N. MATHIEU, J. SONKE AND E.H. OELKERS

LMTG, Université de Toulouse, CNRS, IRD, OMP, 14 Av. E. Belin, F-31400 Toulouse, France (roncal@lmtg.obs-mip.fr; mathieunicholas@yahoo.fr; sonke@lmtg.obs-mip.fr; oelkers@lmtg.obs-mip.fr)

The absolute concentration and distribution of Rare Earth Elements (REE) in many natural aquatic systems is controlled by 1) the dissolution/precipitation rates and 2) the solubility of phosphate minerals (c.f. Poitrasson *et al*., 2004), which themselves may be influenced by the presence of iron colloids and aqueous organic acids. Taking account of the results of Kohler *et al*. (2005) the effect of iron colloids and dissolved organic acids on the behaviour of REE in natural fluids were determined by the dissolution of natural apatite ($Ca_5(PO_4)_3F$) in the presence of a variety of selected aqueous fluids. To best replicate natural system, experiments were performed in closed-system reactors at 25°C and pH 4 and 6. After a short initial period due to the presence of REE in the initial apatite, the reactive solutions become supersaturated with respect to rhabdophane ($REE(PO_4).6H_2O$), which buffers total REE concentration and alters the REE spectra. Complimentary synthetic lanthanum rhabdophane ($La(PO_4).6H_2O$) dissolution/precipitation experiments were used to determine the steady-state rates of this reaction and to determine aid in the interpretation of the apatite dissolution experiments.

Results to be presented will be used to assess the role of rhabdophane precipitation and the presence of iron colloids and dissolved organic acids during the chemical evolution of surface and near-surface waters. Further analysis of these results is used to access the applicability of aqueous REE speciation models to predict the composition of REE in natural waters.

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Hydrochemical characteristics of surface water in two boreal granitoidic settings, Eastern Sweden

PERNILLA RÖNNBACK AND MATS ÅSTRÖM

School of Pure and Applied Natural Sciences, University of Kalmar, SE-391 82 Kalmar, Sweden (pernilla.ronnback@hik.se, mats.astrom@hik.se)

The Baltic Sea and its terrestrial surroundings consist of a unique environment due to the brackish water and still active land uplift (up to 8-9 mm/year). Consequently, the near-coastal catchment areas are characterised by young and unweathered soils. The overall aim of this study was the increase the understanding of the chemical dynamics that control water chemistry in small natural catchments in this region, with focus on spatial and temporal trends. The work was done within the Swedish nuclear waste programme and two different areas were studied: Forsmark which has a carbonate-rich till and Laxemar with a carbonate-poor till. One of these will be selected as a deep repository for spent nuclear fuel.

Surface water (lake and stream water) were collected and analysed for major elements, nutrients and trace elements (U and REEs). The water sampling period lasted for nearly four years and continuous flow measurement were carried out over the last two years. Repetitive seasonal cycles in surface water chemistry have been observed each year along with seasonal cycles in stream discharge. The major findings were: (1) the concentrations of elements derived from rock weathering increased in stream water during flow, (2) sporadic intrusions of brackish water from the Baltic Sea resulted in strong increase in salinity (Na, Cl^-, Br^-, SO_4^{2-}), (3) a huge increase in biological activity during summer months resulted in decreased concentrations of NH_4^+, NO_3^- and Si and increased pH and concentrations of chlorophyll a, O_2, DON, POC, PON and POP, (4) the U concentrations were high at both areas and a possible source is reduced U-minerals in the overburden due to the young and unweathered soil and (5) the REE concentrations were low and characterised either by an increase in relative concentrations throughout the lanthanide series (Forsmark) or flat patterns (Simpevarp), and were by speciation modelling predicted to be carried as organic complexes.

Surface charge, ion adsorption and molecular dynamics at the α-SnO_2/water interface

J. ROSENQVIST[1], L. VLCEK[2], E. MAMONTOV[1], M. L. MACHESKY[3], P. T. CUMMINGS[2] AND D. J. WESOLOWSKI[1]

[1]Oak Ridge National Laboratory, Oak Ridge TN 37831, USA (rosenqvistjk@ornl.gov), (mamontove@ornl.gov), (wesolowskid@ornl.gov)
[2]Vanderbilt University, Nashville TN 37235, USA (lukas.vlcek@vanderbilt.edu), (peter.cummings@vanderbilt.edu)
[3]Illinois State Water Survey, Champaign IL 61821, USA (machesky@uiuc.edu)

Introduction

It has been hypothesized that the bulk dielectric constant (ε) of the oxide solid influences the structure of interfacial water as well as the nature of ion sorption at the interface.[1] To investigate this, we have studied cassiterite (α-SnO_2, with ε=9) using potentiometric titrations, quasielastic neutron scattering (QENS) and molecular dynamics (MD) simulations; and compare the results to previously obtained results for isostructural rutile (α-TiO_2, with ε=121).

Results and discussion

QENS experiments performed on nanosized powders of cassiterite and rutile, predominantly showing the 110 crystal face, indicated considerable differences in the dynamics of water molecules at the interface. Our MD simulation results showed excellent agreement with the measured relaxation times of interfacial water on the 1–100 ps time scale.

Titrations showed that the charging of the cassiterite surface is of the same magnitude as for rutile. However, for cassiterite we obtained virtually identical charging curves in RbCl and NaCl media, whereas charging on rutile is clearly different in the different media. Results from MD simulations indicate that the distribution of Rb^+/Na^+ on the two surfaces is quite different, thus providing an explanation for the observed results. Significant differences are also observed for Sr^{2+} adsorption, while Zn^{2+} adsorption is similar on the two mineral surfaces.

Using O-H bond distances obtained in ab initio and MD simulations together with hydrogen bonding schemes obtained from MD, we constructed a surface complexation model based on the MUSIC model[2] that was able to predict the observed charging and distribution of ions.

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Phase and melting relations of a residual garnet clinopyroxenite

A. ROSENTHAL[1] G.M. YAXLEY[1], D.H.GREEN[1], J. HERMANN[1] AND C.S. SPANDLER[2]

[1]Research School of Earth Sciences, Australian National University, Canberra (anja.rosenthal@anu.edu.au)
[2]Institute of Geological Sciences, University of Bern

Melting behaviour and high pressure phase relations of refertilised mantle comprised of mixed lithologies (e.g. discrete bodies of mafic eclogite or pyroxenites and diverse types of metasomatised, re-fertilised or depleted mantle) are poorly constrained, yet this information is essential for understanding the observed geochemical diversity of primitive magmas on Earth.

Our project is designed to explore the melting behaviour of subducted crust in an inhomogeneous, buoyant, upwelling mantle. We track a sequential process in which melts are redistributed from the (initially) low temperature melting of average oceanic crust, and then from the residues (garnet pyroxenite) until the solidus of the latter equals or exceeds the solidus of refertilised peridotite.

Composition Res-2 is the melting residue of an anhydrous altered MORB composition (GA2 of Spandler *et al*., submitted) at 5 GPa near the point of coesite out, and hence is a model for recycled eclogite which has lost a siliceous melt component during mantle upwelling. It is therefore depleted in incompatible minor elements, with 2.2 wt% Na_2O and a CaO/Na_2O ratio of 4.9. Res-3 is identical but has higher CaO/Na_2O ratio of 12.1.

The subsolidus phases of Res-2 & 3 are grt and cpx with accessory coesite/quartz. The solidus of Res-2 is at 1275°C at 3 GPa, 1400°C at 4 GPa, 1425°C at 5 GPa, and <1450°C? at 6 GPa. The solidus of Res-3 behaves similarly, but is at slightly higher T than that of Res-2 (1300°C at 3 GPa).

Low-degree melting (<10%) is eutectic-like. Once coesite is melted out, the grt-cpx cotectics control melt compositions and proportions with cpx>grt. However, with increasing degree of melting, cpx/grt ratios decrease until cpx is exhausted, leaving grt as the sole liquidus phase. In contrast, coesite-out for Res-3 remains approximately constant at ~50°C above solidus at all pressures. In residues of Res-3 the proportion of grt increases with P, and always exceeds that of cpx.

Melt compositions vary with increasing degree of melting from dacitic to basaltic for Res-2 at 3 GPa. However, at higher P, melts of Res-2 are generally much less silica rich, varying from andesitic to basaltic. This is similar to Res-3 at all pressures.

For both Res-2 & 3, Ti behaves incompatibly in cpx at all P-T conditions, but D^{Ti}[cpx/melt] decreases toward higher temperature. Na however, is incompatible at 3 GPa, but compatible at higher pressures.

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Late-stage removal of chalcophile elements from the mantle by sulfide liquid extraction to the core

L. ROSE-WESTON[1], D.C. RUBIE[1] AND J.M. BRENAN[2]

[1]Bayerisches Geoinstitut, University of Bayreuth, Germany (lesley.rose@uni-bayreuth.de)
[2]Department of Geology, University of Toronto, Canada

The U-Pb chronometer reveals a more protracted age of Earth core formation (65-85 Myr; Halliday, 2003) compared to the Hf-W chronometer (30-50 Myr; Kleine *et al*., 2005). These long-lived isotopic systems are ideal for determining the timescale of core formation because the parent-daughter ratios are fractionated by metal-silicate segregation, with moderately siderophile W and slightly siderophile Pb following metallic liquid into the core. The discrepant timescales suggest that a strong U/Pb fractionation took place sometime during the accretionary history of the Earth, that did not affect the Hf-W system (Wood and Halliday, 2005).

Under reducing conditions in the early Earth, liquid Fe metal separated from liquid silicate to form the core. With oxidation of the lower mantle and the continued accretion of volatile-rich material, it is likely that the later stages of Earth differentiation involved the formation of a FeNi-sulfide liquid (O'Neill, 1991). It has been suggested that because Pb displays chalcophile behaviour (Jones *et al*., 1993), contrary to W (Chabot and Jones, 2005; Jana and Walker, 1997), removal of a small portion of this sulfide 'Hadean matte' to the core may have depleted Pb from the mantle, disrupting the U-Pb chronometer (Hart and Gaetani, 2006). The abundance of other chalcophile elements in the mantle would also have been altered by this process, such as Te and Se, useful in evaluating Earth differentiation processes.

Partitioning of Pb, Te, and Se between liquid metal and liquid silicate are presented at 3 GPa and 2233 K, in which both the S content and fO_2 are gradually increased. At IW-2, the partition coefficients (D) for Te and Se show a 3-fold increase with the addition of ~10 wt% S to the metallic liquid, with D_{Te} increasing from 104±18 to 324±68, and D_{Se} from 30±6 to 90±13. A marked increase in D_{Pb} was observed by Ballhaus *et al*. (2006) with the addition of S at low pressure. Similar to Se and Te, higher pressures may increase the magnitude of D_{Pb}, suggesting that segregation of some 'Hadean matte' equilibrated at high P-T conditions in a magma ocean, may have been a significant factor in disrupting the U-Pb age of core formation on the Earth.

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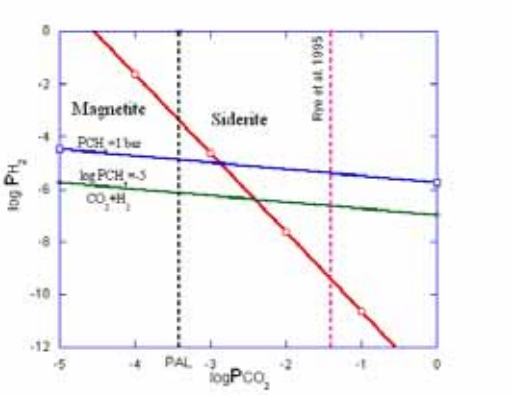
Constraints on atmospheric H_2 from banded iron formations

MINIK T. ROSING[1] AND DENNIS K. BIRD[2]

[1]Nordic Center for Earth Evolution, University of Copenhagen, Øster Voldgade 5-7, 1350 København K, Denmark. (minik@snm.ku.dk)
[2]Dept. of Earth and Environmental Sciences, Stanford University, Stanford 94305, CA, USA. (bird@pangea.stanford.edu)

Quartz-magnetite banded iron formations are ubiquitous throughout the Archaean geologic record. Models for the composition of the Archaean atmosphere and ocean must therefore be compatible with the widespread precipitation of magnetite from the ocean. At 25 C magnetite is stable relative to siderite only when the partial pressures of H_2 and CO_2 are so low that their reaction to form methane cannot sustain reproduction by methanogenic organisms (Sleep and Bird, 2007).



If we assume ocean temperatures ~ 25 C and a partial pressure of CO_2 in the atmosphere ~ present value, magnetite stability is only possible at H_2 pressures below ~0.0001 bar. At the maximum CO_2 pressures allowed by Precambrian palaeosols (Rye *et al*., 1995), the hydrogen pressure would be further 5 orders of magnitude lower.

The common presence of magnetite in Archaean sediments is therefore not compatible with models that favour an early Archaean atmosphere characterized by high hydrogen mixing ratios (Tian *et al*., 2005) or with suggestions that H_2 nourished an extensive biosphere prior to the evolution of oxygenic photosynthesis (e.g. Tice and Lowe, 2004).

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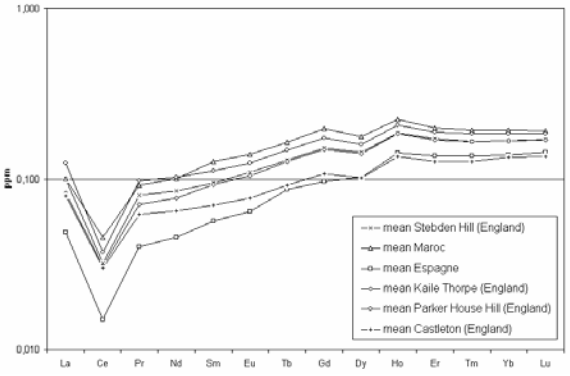
Mississippian microbial carbonates: Test for the validation as proxy for marine REE geochemistry

B. ROSLEFF-SÖRENSEN, M. ARETZ AND H.U. KASPER

Universität zu Köln, Instiut für Geolgie und Mineralogie, Zülpicher Str. 49a, 50674 Köln, Germany (Beke.Rosleff-Soerensen@gmx.de)

First results suggested that recent microbial carbonates are so far the best proxy material for the record of marine REE-patterns (Webb & Kamber 2000). The results were confirmed by further tests on Archean (Kamber & Webb, 2001, Kamber *et al*., 2004) and Devonian (Northdurft *et al*., 2003) microbial carbonates.

To further validate this proxy, REE and some additional trace elements of microbial carbonates were analysed from several locations from the upper Visean (Carboniferous) of England, Morocco, and Spain. Very clean microbial material was chosen by thin-section studies and analysed by ICP-MS. All samples show very smooth REE-patterns that perfectly display the REE-geochemistry characteristics of modern seawater as e.g. LREE depletion, positive La- and Gd- and negative Ce-anomalies. The nearly marine Y/Ho-Ratio as well as the contents of Zr, Sc, Hf and Th suggest very low terrigenous contamination.



While accompanying non-microbial carbonates show the same REE-pattern as the microbial ones, they have a significantly lower absolute REE content and are therefore less readily accessible for analysis.

Slight differences exist in REE content of the different locations. Potential interrelation with the local paleogeographic situation, e.g. by incorporation of variable degrees of terrigenous input requires further examination.

Our data confirm the results by Webb & Kamber (2000) that microbial carbonates are so far the most reliable and additionally easiest accessible proxy for fossil marine REE-geochemistry. They do not show the fractionation problems of skeletal carbonates, incorporate high REE content and are overall relativly resistive to diagenetic overprint.

Further investigations to illucidate the possibilities of application to paleogeographic and paleooceanographic reconstructions are necessary.

Carbonate and anhydrite veins from altered gabbroic oceanic crust (Atlantis Massif, MAR 30°N)

M. ROSNER[1], W. BACH[1], B. PEUCKER-EHRENBRINK[2], J. ERZINGER[3] AND B. PLESSEN[3]

[1]University Bremen, Germany, (mrosner@uni-bremen.de)
[2]Woods Hole Oceanographic Institution, USA, (behrenbrink@whoi.edu)
[3]GeoForschungsZentrum Potsdam, Germany, (erz@gfz-potsdam.de, birgit@gfz-potsdam.de)

Atlantis Massif is an Oceanic Core Complex (OCC) that formed in the past 1.5-2.0 Myr at the intersection of the Mid-Atlantic Ridge and the Atlantis fracture zone. IODP Hole U1309D, drilled in the central part of the Atlantis Massif OCC, is the third-deepest hole in oceanic lithosphere with a core recovery of 75%. Gabbros and troctolites are the dominant rock types (92%), followed by ultramafic (~5%) and basaltic (~3%) rocks. The magmatic sequence is metamorphosed and fractured, and fluid flow during uplift resulted in the formation of several generations of late-stage veins that record sub-seafloor water-rock interactions. Below the diabase-dominated top section of U1309D carbonate veins are the most abundant late-stage vein type. Macroscopic anhydrite veins occur only at about 740 mbsf.

Carbon, O and Sr isotope compositions of the calcites do not vary systematically down-hole. The $^{87}Sr/^{86}Sr$ ratios are relatively unradiogenic and span a limited range between 0.7043 and 0.7051. Oxygen and C isotope ratios are both isotopically light displaying $\delta^{18}O$ (VSMOW) values of about 10‰ and $\delta^{13}C$ (VPDB) values of about -4‰. Oxygen isotope compositions of calcites yield minimum precipitation temperatures between 150° and 220°C (assuming seawater $\delta^{18}O$ for the fluid). The temperature could have been significantly higher, if the fluid had exchanged oxygen with basement. For instance, if the $\delta^{18}O$ value of the precipitating fluid was 2‰, like in the Rainbow hydrothermal fluids, calculated formation temperatures would be 30° to 50°C higher. In fact, Sr isotope ratios of the carbonate veins approach values for high-temperature hydrothermal systems such as Rainbow or Logatchev. Unlike in the calcites from detachment fault rocks from the 15°20'N Fracture Zone area, however, the calcites from Site U1309D lack carbon isotope signatures for thermal methanogenesis. Hence, temperatures were likely not higher than 300°-350°C.

Two massive cm-wide single anhydrite veins were recovered at about 740 mbsf at Site U1309D. For the anhydrite veins we obtained $^{87}Sr/^{86}Sr$ ratios of 0.70774 for core 150R3 and 0.70631 for core 153R3. As the Sr isotope composition of anhydrites from 1309D and 504B are similar we infer that 1309D anhydrites may also have formed in the down-flow limb of a hydrothermal convection cell, from seawater that has been heated to about 150°C and has had limited opportunity to exchange Sr with the basement.

Seismic constraints on deep Earth structure and mantle melts

SEBASTIAN ROST

Institute of Geophysics and Tectonics, School of Earth and Environment, University of Leeds, Leeds LS2 9JT, United Kingdom (s.rost@leeds.ac.uk)

Seismic results of recent years characterize Earth's lowermost mantle to be highly heterogeneous on many scale lengths. Structures found using seismic means include sharp horizontal discontinuities (although strong topography on these might be present), thin ultra-low velocity zones (thin regions of strongly reduced seismic velocitites), anisotropy and large anomalously slow regions with sharp vertical boundaries. Therefore, the lowermost mantle and core-mantle boundary region is a likely location of untapped, "hidden" reservoirs in the Earth which might be detectable by seismic means.

The scales of these heterogeneities span several magnitudes from 1000's of km to the smallest detected structures with scalelengths of only a few 10's of km. Smaller structures are likely and their detection depends on increased seismic resolution.

These results indicate a highly dynamic and complicated region that can only be understood by combining seismological, geochemical, geodynamical and mineral-physical results. Current models of the lowermost mantle, the D″ region and the core-mantle boundary include the post-perovskite phase transition to explain the D″ discontinuity and possibly other regional layers, partial melts to explain ultra-low velocity zones and chemically distinct regions to both explain large-scale and small-scale structures.

This presentation will highlight recent seismological results of the structure of the D″ discontinuity focussing on the structure of the structure of the post-perovskite phase transition beneath the Cocos plate (central America). The second part of the presentation will focus on the fine scale structure of ultra-low velocity zones. The seismic data sampling ultra-low velocity zones can be well explained by the existence of dense partial melts in thin layers. Geodynamic modeling shows that ultra-low velocity zones could be the dominant structures at the edges of large-scale thermo-chemical piles as have been detected beneath the Pacific and Africa. These partial melts could be iron enriched and might be connected to plume genesis.

The Italian contribution to stardust

A. ROTUNDI[1], G.A. BARATTA[2], J.R. BRUCATO[3], L. COLANGELI[3], G. FERRINI[4], V. MENNELLA[3], M.E. PALUMBO[2]

[1]Dip. Scienze Applicate, Università degli Studi di Napoli "Parthenope", Napoli, Italy (rotundi@uniparthenope.it)
[2]INAF-Osservatorio Astrofisico di Catania, Catania, Italy
[3]INAF-Oss. Astronomico di Capodimonte, Napoli, Italy
[4]Novaetech s.r.l., Città della Scienza, Napoli, Italy

We report combined micro-infrared, micro-Raman, and Field Emission Scanning Electron Microscope analyses of five particles collected by the Stardust spacecraft during its fly-by of comet 81P/Wild2 on 2 January 2004 and returned back to Earth on January 2006.

The CH_2/CH_3 ratios inferred from the infrared data are greater than those seen in organics in the diffuse interstellar medium, possibly indicating the presence of longer or less branched aliphatic chains. The micro-Raman data offer insights on the state of order of the carbonaceous component present in the particles. A comparison with spectra of Interplanetary Dust Particles (IDPs) and meteorites yields for most of the particles analyzed that the cometary carbonaceous material span a similar range to those of IDPs and the most primitive meteorites (see Figure 1).

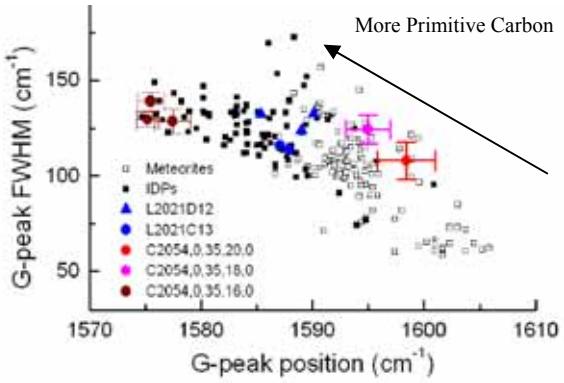


Figure 1: FWHM versus peak position for the G band measured for Stardust particles and IDPs (circles and triangles, LANDS team) compared to several IDPs (Wopenka 1988; Raynal *et al*. 2001) and Meteorites (Raynal *et al*. 2001).

Hydrated minerals seem to be present in one particle which seem to contain also carbonates, but further investigations with other techniques need to be performed to confirm these findings. Analyses interpretation is difficult because of the presence of aerogel mixed with the grain.

The analysed grains result to be: 1) rich in complex organic compounds; 2) compositionally and structurally heterogeneous. Suggesting that cometary particles consist of a mixture of subgrains of various sizes and compositions.

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Diagenetic evolution of the Hooggenoeg Formation: Implication for Archean seawater composition

VIRGILE ROUCHON[1], BEATE ORBERGER[1], AXEL HOFMANN[2] AND DANIELE L. PINTI[3]

[1]Université Paris Sud, Laboratoire IDES UMR 8148, 91405 Orsay cedex, France. (virgile.rouchon@u-psud.fr)
[2]University of KwaZulu-Natal, Durban, South Africa
[3]UQAM-McGill-Geotop, Montreal, Canada

The reconstruction of the composition of the Archean atmosphere and ocean relies on scarce data and much theoretical modeling. We provide new constraints on this issue by studying the mineralogy and geochemistry of Archean sediments. The low-grade metamorphic Hooggenoeg Formation (HFm) of the Barberton greenstone belt is an extensive low-grade Paleoarchean volcano-sedimentary sequence, ideal for studying primitive diagenetic processes. The 3.45 Ga Upper HFm comprises a rhyodacitic volcanic complex with associated volcaniclastic sediments that locally overlie pillow basalts and hydrothermal orthochemical carbonaceous cherts. Detrital material was mainly derived from rhyodacites that were affected by an event of K-Si metasomatism prior to erosion. Phenocrysts, matrix and glass fragments were replaced by quartz-sericite-orthoclase and Ti-oxides still co-existing with primary apatite and zircon. After deposition, the detritus was cemented by early diagenetic microquartz. Silicification mainly resulted in SiO_2 dilution, as the trace element signatures (REE, HFSE) of the sedimentary source rocks were preserved.

Sandstones and conglomerates were affected by carbonatization (up to 40% vol.), as carbonate minerals replaced the diagenetic quartz cement and detritus. Three types of carbonate textures were sequentially formed: 1) Oscillatory zoned ankerite rhombs, 2) aggregates of ankerite-pyrite-sericite and 3) ankerite-calcite-albite-kaolinite. EPMA of carbonates revealed Na/Cl molar ratios of ~1 similar to seawater. The bulk $\delta^{13}C_{PDB}$ of carbonates ranges from +1.9 to +2.3 ‰, typical of a marine origin. The $\delta^{18}O_{SMOW}$ is homogeneous at +15 ‰, similar to deep-burial carbonates (120-160°C equilibrated with -2 ‰ < $\delta^{18}O_{SMOW}$ < +2 ‰ fluids). Regionally extensive seawater-basalt interaction zones that are developed below the sedimentary sequence provided large amounts of dissolved SiO_2, Fe^{2+}, Ca^{2+} and Mg^{2+}. The CO_2-acidic (biologically unbuffered) ocean was in favorable conditions for early-diagenetic abiological silica cementation as opposed to carbonates. Trapped pore-fluids dissolved silicates as a result of temperature increase during burial. The related pH increase allowed carbonate precipitation at higher burial depth. This diagenetic evolution (silica→carbonates) is reversed compared to that observed in Phanerozoic sedimentary basins. Thermodynamic calculations will allow the determination of 3.45 Ga seawater-pH and related atmospheric P_{CO2}.

CAIs in Rumuruti chondrites

S. S. ROUT AND A. BISCHOFF

Institut für Planetologie, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany (suryarout@uni-muenster.de)

Rumuruti chondrites (R-chondrites) are a group of chondritic meteorites that are highly oxidised, poor in metals, olivine rich (with high Fa content of ~39 mol%), and have high $\Delta^{17}O$ values. Barely any description of Al rich objects has been reported till now (Bischoff and Srinivasan, 2003; Berlin, 2003). Here, we present the results of our search and analysis of CAIs and Al-rich objects in the R-chondrites.

We studied 14 R-chondrites (NWA 753, 755, 1472, 1476, 1477, 1478, 3364, Rumuruti, Dhofar 1223, Acfer 217, Dar al Gani 013, Hughes 030, Hammadah al Hamra 119, and Sahara 99537) and found 102 Ca,Al-rich objects (87 CAIs, 13 Al-rich chondrules and 2 spinel-rich fragments). Based on the mineralogical characterisation by SEM and electron microprobe the inclusions can be grouped into seven classes:
(1) Concentric spinel-rich inclusions (30). These CAIs have abundant spinel and based on the presence or absence of major different phases can be subdivided into three groups:
(a) 18 CAIs dominantly consist of a spinel core rimmed by Al-rich diopside. (b) Five of the spinel-rich CAIs also contain abundant fassaite. These CAIs have a rim of diopside occasionally including olivine. (c) Within seven inclusions besides spinel abundant Na- and/or Cl-rich alteration products (probably nepheline and/or sodalite) were observed within the cores rimmed by diopside and, rarely, by olivine.
(2) One concentric hibonite-rich CAI has been found.
(3) Concentric fassaite-rich CAIs (3 spherules) have no rims and contain either hibonite or spinel and/or olivine and ilmenite as additional phases.
(4) Complex spinel-rich CAIs are the most abundant variety of CAIs (50): Based on their mineral abundances these CAIs can be subdivided into four other groups: (a) Two inclusions have also abundant hibonite. (b) 29 inclusions are rich in plagioclase (anorthite and/or oligoclase), and have sometimes fassaite. All the oligoclase-rich CAIs are devoid of any rims, but others generally have an Al-rich diopside rim. (c) 11 of the complex spinel-rich CAIs have major fassaite and Na- and/or Cl-rich alteration products mainly showing a complex mixture of spinel, fassaite, and alteration products. All CAIs have a diopsidic rim. (d) Complex spinel-rich CAIs with abundant Na-,Cl-rich alteration products (8) occasionally having a diopsidic rim.
(5) Three complex diopside-rimmed CAIs with minor fassaite and/or alteration products in the core and having a complex texture were found.
(6) 13 Al-rich chondrules were analysed.
(7) Two Al-rich (spinel-rich) fragments were found, whose relationship of these fragments to other types of inclusions described above is uncertain.

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Constraints on lithospheric enrichment and crustal contamination in the central Rio Grande Rift (New Mexico, U.S.A.): Volatile and trace-element variability in basaltic melt inclusions

M.C. ROWE AND J. C. LASSITER

Department of Geological Sciences, University of Texas at Austin, Austin, TX 78712 (rowem@mail.utexas.edu)

Many basalts erupted during the early stages of rifting throughout the southwestern United States have a preferential enrichment in water-soluble elements relative to insoluble elements leading to high ratios of water-soluble to insoluble elements, e.g. Ba/Nb, K/Nb, and Sr/Nd. These high ratios are characteristic of "arc-like" or "subduction-related" basalts often found in volcanic arcs. Numerous studies have suggested that these basalts originate from melting of a mantle source that has undergone hydrous metasomatism as a result of shallow subduction of the Farallon Plate beneath western North America during the Laramide orogeny (80-40 Ma).

We have analyzed olivine- and orthopyroxene-hosed melt inclusions from Rio Grande Rift (New Mexico, U.S.A.) tholeiites and alkaline basalts for major-, trace-, and volatile-element concentrations in conjunction with whole rock geochemistry. If prior petrogenetic models requiring melting of hydrous metasomatized mantle are correct, then melt inclusions from lavas with an "arc-like" signature (e.g. elevated Ba/Nb or Sr/Nd) should be enriched in volatile species such as water and Cl.

In melt inclusions from Rio Grande Rift tholeiites and alkaline basalts Cl/K and Cl/Nb ratios broadly correlate with Ba/Nb and Sr/Nd. In melt inclusions with high Ba/Nb and Sr/Nd ratios (up to 32 and 31, respectively), Cl/Nb (~20-35) and Cl/K (0.04-0.08) ratios are also elevated. Similarly, tholeiitic basalts with lower Ba/Nb and Sr/Nd possess low Cl/Nb and Cl/K ratios (Cl/Nb 8-17; Cl/K 0.02-0.04), more consistent with ratios observed in fresh MORB (Cl/Nb 3-8; Cl/K 0.02-0.04). However, at a given Ba/Nb ratio, Cl/Nb ratios are generally low compared to melt inclusions from present day arc and backarc basalts from the Casacade range in western North America.

The observed correlation between Cl enrichment and "arc-like" trace element ratios is consistent with a model for generation of Rio Grande Rift basalts through melting of variabily metasomatized mantle. However, partial melting and assimilation of continental crust could potentially produce qualitatively similar trends. No overall systematic variation in Ba/Nb, Sr/Nd or Cl/K is evident relative to the host Mg#, although within an individual sample host phenocryst compositions are restricted. Future in situ water and Pb-isotope analyses of melt inclusions will further constrain the role of crustal contamination and mantle source enrichment in the generation of the Rio Grande Rift basalts.

Sulfate reduction across a salinity gradient in hypersaline coastal pans

ALAKENDRA N ROYCHOUDHURY[1] DONOVAN PORTER[1] AND DONALD COWAN[2]

[1]Department of Geological Sciences, University of Cape Town, Rondebosch, 7700 Cape Town, South Africa (alakendra.roychoudhury@uct.ac.za; dporter@geology.uct.ac.za)

[2]Department of Biotechnology, University of the Western Cape, Bellville, 7535 Cape Town, South Africa (dcowan@uwc.ac.za)

The impact of salinity on the metabolic activity of sulfate-reducing bacteria in five highly saline to hypersaline coastal pans was studied using a radioactive tracer ($^{35}SO_4^{2-}$) technique. We recorded sulfate reduction at the higher *in situ* porewater salinity (422) than previously reported. The depth-integrated sulphate reduction rates (integrated to 12 cm) varied from 6 to 241 mmol m^{-2} d^{-1} and were also among the highest ever reported rates. The reduction rates decreased down-core and, surprisingly, were highest in the winter season when the lowest sediment temperatures were encountered.

High salt concentrations did not inhibit sulfate reduction rates. Rather, higher rates were measured at pans with higher *in situ* salinities. In laboratory slurry incubation experiments, sediments from the saltpans were treated with increasing salt concentrations. Regression analysis suggested that the short term response of microbial consortia to up-shock was an increase in sulfate reduction activity up to salinities of 350 – 400 and 200 – 300, in hypersaline and highly saline pans, respectively. Beyond these salinities, the cells showed evidence of reduced activities.

Suprisingly, sulfate reduction rates also show an increase with increasing sulfate concentration of up to 600 mM. This is unusal, as for sulfate reduction, the highest reported half-saturation constant values in the literature lie below 10 mM. Does this suggest that there is a third sulfate transport mechanism that becomes active among sulfate reducers thriving in hypersaline environments?

Migmatisation in the Central Alps lasting 10 m.y.

D. RUBATTO[1], A. BERGER[2], C. GREGORY[1], J. HERMANN[1] AND M. ENGI[2]

[1]Research School of Earth Sciences, ANU, Canberra 0200 Australia (daniela.rubatto@anu.edu.au; joerg.hermann@anu.edu.au; courtney.gregory@anu.edu.au)

[2]Institut für Geologie, Universität Bern, Switzerland (berger@geo.unibe.ch; engi@geo.unibe.ch)

The southern part of the Central Alps underwent Barrovian style metamorphism that reached partial melting at upper amphibolite facies conditions. Previous geochronological constraints indicated that melting occurred in the Oligocene, around 29-32 Ma, with cooling extending into the Miocene.

SHRIMP U-Pb dating of zircons from migmatite suite from the southern Central Alps yielded variable and distinct ages between circa 31 and 22 Ma. A similar age range is recorded by the U-Th-Pb system of allanite. This range in ages is found not only across different samples, but also within single samples. For example, a leucosome from the locality of Bellinzona contains zircon grains with inherited Permian cores remnants of the magmatic protolith. The cores are overgrown by three zircon rims with different internal zoning and chemical composition, which yield distinguishable ages at circa 31, 26 and 23 Ma. In the locality of Valle Arbedo (25 km to the E) similar migmatites show distinct zircon overgrowths at circa 31, 28, 23, and 22 Ma. For all of the zircon overgrowths the inclusions, trace element composition and Ti-in-zircon thermometry indicate growth in the presence of melt at similar temperatures between 600 and 700 °C. Therefore, we conclude that this region of the Central Alps repeatedly underwent melting at similar conditions over an extended period of at least 10 Ma.

These geochronological constraints support a model where episodic melting is controlled by the availability of aqueous fluids (Berger *et al*., 2007). Local infiltration of aqueous fluid in rocks of different composition thus produced diachronous melting episodes. The southernmost part of the Central Alps evidently remained at temperatures above the wet granite solidus for at least 10 million years.

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New constraints on conditions of core formation and the light element content of the Earth's core

D.C. RUBIE AND D.J. FROST

Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany, (dave.rubie@uni-bayreuth.de)

The concentrations of light elements in the Earth's core must have been set by metal-silicate equilibration during core formation, as was likely the case for the moderately siderophile elements. It has been shown recently that equilibration conditions of core formation can be constrained by the partitioning of FeO between liquid Fe-alloy and silicate melt in a magma ocean, based on the mantle composition and the light element content of the core (Rubie *et al*., 2004; Asahara *et al*., 2007). This is because the partitioning of FeO into liquid iron increases strongly with increasing temperature (and therefore magma ocean depth), thus decreasing the FeO content of the mantle and increasing the O content of the core. Based on a simple core formation model, Asahara *et al*. (2007) estimated that the maximum depth of metal-silicate equilibration was ~1700 km, which would have resulted in a maximum of ~8 wt% oxygen in the core. However, lower limits could not be constrained because the oxygen content of the starting (chondritic) composition is poorly constrained.

Traditionally, experimental data on the metal-silicate partitioning of siderophile elements have been used to constrain the conditions of core formation, for which an estimate of the prevailing oxygen fugacity is required. However, for a given metal-silicate bulk composition, the oxygen fugacity is fixed by the partitioning of FeO, which is a function of pressure and temperature only. Therefore we are developing core formation models based on the combination of FeO and moderately siderophile element partitioning. The model bulk composition is chondritic with an initial oxygen content that can be varied. Liquid metal and liquid silicate are assumed to equilibrate near the base of a magma ocean (defined by the peridotite solidus) and the compositions and relative proportions of the two phases are calculated using mass balance combined with formulations describing the partitioning of FeO and siderophile elements as a function of P and T. The results enable new constraints to be placed on (i) conditions of metal-silicate equilibration and therefore magma ocean depth, (ii) the bulk oxygen content of the Earth and (iii) the oxygen content of the Earth's core.

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Fluid-rock interactions recorded by kinetic fractionation of Li isotopes

ROBERTA L. RUDNICK[1], WILLIAM F. MCDONOUGH[1], FANG-ZHEN TENG[2] AND MICHAEL A. W. MARKS[3]

[1]Department of Geology, University of Maryland, College Park, MD, 20742, USA
[2]Department of the Geophysical Sciences, The University of Chicago, Chicago, IL, 60637, USA
[3]Universität Tübingen, AB Mineralogie und Geodynamik, D-72074 Tübingen, Germany

Li diffuses relatively rapidly through minerals and fluids and this, coupled with the large differences in diffusivities between its two isotopes (Richter *et al*., 2003), can lead to large kinetic isotopic fractionations parallel to the diffusion pathways. Thus, Li isotopes can be used to trace fluid-rock interaction. Here we summarize three different pluton-country rock settings that illustrate the controls and limits on kinetic Li isotopic fractionation. Lithium diffused over distances of >30 m from the Li-rich Tin Mt. pegmatite into metamorphic country rocks along fluid-filled grain boundaries accompanied by large, kinetically induced isotopic fractionations (>30‰, Teng *et al*., 2006). Li diffused over an order of magnitude further into the country rocks than other fluid-mobile trace elements (e.g., Na, Rb, Cs and Sb), making Li perhaps the most sensitive tracer of fluid-rock interaction amongst the lithophile elements. In contrast, metapelitic country rocks surrounding the Onawa granodiorite are not enriched in Li, reflecting the low Li content of the intrusion (45 ppm) relative to the country rocks (130 ppm) and hence the lack of a chemical potential gradient to drive diffusion. Indeed, Li content of the metapelites decreases by a factor of two adjacent to the pluton, reflecting the loss of Li during metamorphic devolatilization (Teng *et al*., 2007). The constant δ^7Li in the country rocks is consitent with equilibrium fractionation during Li loss via Rayleigh distillation at the temperatures of metamorphism (>500^{o}C). Finally, large, kinetic Li isotopic fractionations are observed perpendicular to the contact between an alkali syenite and granitic country rocks of the Ilímaussaq Complex, Greenland (Marks *et al*., 2007). Here, however, the syenite is barely enriched in Li relative to the country rocks (25 vs. 14 ppm, respectively), and this concentration difference is not large enough to account for the large isotopic fractionations observed over distances of up to 150 m (δ^7Li $\geq$ –9 in the granite country rocks and $\leq$ +16 in the syenite). These large fractionations reflect the circulation of isotopically heavy, Li-bearing fluids adjacent to the syenite-granite contact.

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Studies of continent stability using joint petrological and geodynamical models

L.H. RÜPKE, N.S.C. SIMON AND Y.Y. PODLADCHIKOV

Physics of Geological Processes, University of Oslo, P.O.Box 1048 Blindern, N-0316 Oslo, Norway, (lars.rupke@fys.uio.no)

Continents are remarkably stable features of our dynamic Earth. Extreme examples of this are Archean cratons, which have resisted erosion by lithosphere delamination and mantle convection for billions of years. However, continents are not stable under all conditions. In fact, delamination of continental lithosphere has been related to intra-plate volcanism and uplift in the absence of shortening. The main goal of this study is to identify and quantifying the key factors that control the stability of continental lithosphere.

To simplify this task we regard lithosphere delamination as a Rayleigh-Taylor instability. Rayleigh-Taylor instabilities have been extensively studied analytically, numerically and experimentally - also with regard to continent stability. It is clear from these studies, that the growth rate of the instability is primarily controlled by the density and viscosity contrast. The density (and viscosity) contrast between the lithosphere and asthenosphere is a complex function of temperature, pressure and, often neglected, chemical and mineralogical composition. Chemical composition can vary significantly among different continents and it may well be that chemical and mineralogical variations determine if the lithosphere is gravitationally stable or not. To test this hypothesis, we use a joint petrological and geodynamical approach. The petrological model is based on a companion study (Simon *et al*. 2007 – this volume), which explores the dependence of mantle density on chemical composition using thermodynamics. The key metamorphic reaction for continental stability is the garnet-in reaction. The location of this reaction in p-T space is strongly dependent on the Cr_2O_3/Al_2O_3 ratio, while the amount of formed garnet mainly depends on the Al_2O_3 content. This suggests that relatively fertile mantle compositions rich in aluminum will tend to destabilize continental roots. To quantify the effect of mantle composition on continent stability, we will integrate thermodynamically computed densities for various mantle compositions into a geodynamic flow model. Using this joint petrological and geodynamic model, we will explore for which mantle composition continents are stable over geological time and define a critical enrichment for which continental lithosphere becomes gravitationally unstable.

Prebiotic chemistry in iron-rich water medium: Fixation of cyanide as Prussian Blue

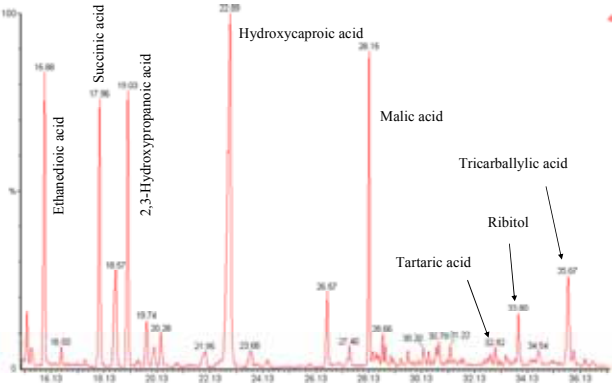
M. RUIZ BERMEJO, C. MENOR SALVÁN,
S. OSUNA ESTEBAN AND S. VEINTEMILLAS VERDAGUER

Centro de Astrobiología (CSIC-INTA). Ctra. Torrejón-Ajalvir km 4.2, Torrejón de Ardoz E-28850, Spain (ruizbm@inta.es)

Water based aerosols are ubiquitous in the actual troposphere and it has been suggested that they could play an important role as prebiotic micro-reactors in the origin of life. The salinity and pH of the aqueous phase may have an important influence in the gas-liquid interfaces, which are expected to be special sites for relevant prebiotic reactions (1). The presence of the Archean banded iron formations strongly suggests that dissolved iron (ferrous ion) was present in high quantities in the ancient sea and it has been postulated that the ancient sea had a salinity of the 1.5 to 2 times the modern value and its pH ranged between 4 to 10 (depending of the author).

In this work, we explore the effects of pH (between 5.8 to 9.8) in the generation of biomolecules in prebiotic simulation experiments using aqueous aerosols of saline iron rich solutions and spark discharges in a suitable prebiotic atmosphere.

In all experiments, we observed that the presence of ferrous iron leads the formation of Prussian Blue, a strongly reduction the final pH of the aqueous pool and the lack of small molecules in the raw of reaction. Under the assayed conditions the Strecker reaction is inhibited and the formation of heterocycles is stopped but a rich mixture of carboxylic acids is obtained (Fig. 1). Therefore, independently of the pH, in the studied range, the ferrous ion seems to have an important influence in the formation of the organics and their precursors.



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Differences in REE distribution patterns of the fault tectonites in the Huize Carbonate-hosted Zn-Pb-(Ag-Ge) district, Yunnan, China

HAN RUN-SHENG[1], LIU CONG-QIANG[2]
AND HUANG ZHI-LONG[2]

[1] Kunming University of Science and Technology; Southwest Institute of Geological Survey, Geological Survey Center for Non-ferrous Mineral Resources, Kunming 650093, P.R.C (hrs661@yahoo.com.cn)

[2].Institute of Geochemistry, CAS, Guiyang 550002, P. R. C. (hzligcas@hotmail.com)

The Huize Zn-Pb-(Ag-Ge) district is a typical representative in the Sichuan-Yunnan-Guizhou metallogenic region. Two groups of NE-, NW-extending fault structures are mostly developed. The Lower Carboniferous Baizuo Formation (C_1b) is the most important ore-hosted stratum.

Differences in REE distribution patterns of the fault tectonites are closely related to the lithologic character of the protolith, the extent of water/rock interaction and faults' differences in their mechanics properties. As for the protoliths of the same lighologic character, the extent of fluid/tectonite interaction and the mechanics properties of faults are the two major factors affecting REE distribution patterns. Tectonic activities occurred mainly during the metallogenic stage. Differently trending fault tectonites belong to different types owing to different tectonic properties, so there would be some difference in the extent of interaction of fluids with the rocks, as well as in their REE composition and REE distribution patterns. The NE-trending faults are compression-compresso-shear faults, where mineralized cataclastic (clastoporphyritic) rocks, clastic rocks and mylonite were dominated and their forming environment was relatively reductive relative to the NW-trending fault zone, unfavorable to the interaction of ore fluids with rocks. So, the rocks there are relatively enriched in HREE and show a variety of REE distribution patterns: Eu-enrichment type and Eu-depletion type; the NW-trending faults are of tensile nature during the metallogenesis, mostly characterized by mechanical destruction and the formation of breccia, cataclastic (clastoporphyritic) rocks and similar REE distribution pattern (LREE-enrichment-HREE-flat type) to those of strata (C_1b).

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Formation of high alumina phases in sediments and soils of different ages without inherited weathering products

HANS RUPPERT[1] AND GEORG GRATHOFF[1,2]

[1]Geosciences Centre, University of Goettingen, Germany, (hrupper@gwdg.de)
[2]Department of Geology, Portland State University, USA, (GrathoffG@pdx.edu)

We investigated the mineralogy and geochemistry of moraine forest soils in the former ice-covered granitic areas in Kings Canyon and Yosemite National Parks (Sierra Nevada, California), soils on sand dunes at the Pacific coast in Oregon (USA), as well as moraine profiles in the Dry Valley (Antarctica). The profiles did not contain any inherited weathered phases. So the neoformed phases represent the weathering products and help us decipher the weathering processes. Grain sizes of <0.2µm and 0.2-2µm were separated and analyzed by X-ray diffraction and electron microprobe. The solution to separate the clay size fraction was filtered with a 0.1µm filter and analyzed by ICP-AES, to determine the colloid and dissolved element chemistry.

Results:

1. In the soils of the Sierra Nevada with soil solution pHs around 6, the fraction 0.2-2µm has fairly high Al_2O_3/SiO_2 ratios close to 1, which are approximately factor 5 higher than the ratios of the source material. Vermiculite is the main clay minerals formed during the last 10-20ky. The 60-80ky old soils in Kings Canyon additionally may contain gibbsite. Mobile nutrient elements such as K, Mn, Mg, and Ca are enriched in the uppermost horizons, because of mobilization by plant roots and accumulation in the humic rich upper soil section by plant debris. This trend is more pronounced in the older profile.

2. In the 120ka old soil profile of the sand dune in Oregon (pH around 5), the 0.2-2µm fractions in the 0-90cm section show Al_2O_3/SiO_2 ratios close to 1, 20 times higher than that of the bulk material. In the section below 90cm, the Al_2O_3/SiO_2 ratios increases to 4. Inverse to that is the trend of the Al/Si ratio in the separation solutions (0-90cm: Al_2O_3/ SiO_2 ratio of ~11, below 90cm: ~3). We suppose, that dis-solved or colloidal organic complexes extremely enriched in alumina are translocated from the upper soil horizon into the deeper profile facilitated by the enormous pore space. On the way down the organic ligands are oxidized leading to preci-pitation of Al-rich phases such as allophane and gibbsite.

3. The composition of the clay fraction of the profile from Dry Valley has low Al_2O_3/SiO_2 ratios close to 0.3, which are close to that of the parent rock. The separation solution is higher in Si (0.7-5.1ppm SiO_2) and lower in Al (0.0-0.7ppm Al_2O_3). No trends of the element contents with age (20ka, 200ka, 2000ka) are discernible. Although the soil solution has pH-values between 8.8 and 10.2, the chemical weathering is insignificant, presumably because of lacking plant material which promotes chemical weathering.

^{238}U-^{230}Th and ^{226}Ra-^{230}Th crystal ages at Volcán Quizapu: A prime location for studying magma mixing processes on short time scales

P. RUPRECHT[1], K. M. COOPER[2] AND G. W. BERGANTZ[1]

[1]Department of Earth and Space Sciences, University of Washington, Box 351310, Seattle, WA 98195-1310, USA (ruprecht@u.washington.edu; bergantz@u.washington.edu)
[2]Department of Geology, University of California, One Shields Avenue, Davis, CA 95616-8605, USA (kmcooper@geology.ucdavis.edu)

Despite significant innovation in textural, crystal-chemical analysis as well as U-series and diffusion age dating of igneous materials, the physical processes associated with measured time scales are unclear. For example, there is often discordance between diffusion ages and absolute ages of mineral separates derived from U-series (^{238}U-^{230}Th and ^{226}Ra-^{230}Th) disequilibria, and the two techniques may be measuring different processes. A simple system with well defined boundary conditions is necessary to understanding the information contained in ages measured by different techniques. We present U-series data for the historic eruptions of Volcán Quizapu, Chile, (5 km^3 of lava in 1846/47 and 4 km^3 of pumice in 1932). Both dacitic eruptions of Volcán Quizapu were accompanied by andesitic recharge magma. The lavas of the earlier eruption show extensive but incomplete mixing and mingling, while the plinian eruption of 1932 displays less interaction between the recharge and host magmas.

^{238}U-^{230}Th ages industinguishable from the eruption age and Ra-Th ages of 2-3.5 ka for plagioclase and hornblende separates indicate a relatively short and simple magmatic evolution of Volcán Quizapu that stresses the dominance of short time scales processes associated with the magma mixing. This simplicity, along with the well-constrained repose time between the two major eruptions, makes Volcán Quizapu a perfect location to further investigate the information provided by diffusion and short-lived radioactive isotopic clocks. ^{226}Ra-^{230}Th dating of selected populations from the recharge and host magmas will allow us to integrate textural and crystal-chemical information with crystal ages. In addition, tracking changes in phenocrysts from recharge magma that were not evacuated during the first eruption, but remained in the reservoir and subsequently erupted in the second pulse has the potenital to unravel the interplay between diffusion, crystal growth and resorption during a simple magma overturn.

Photoluminescence recovery upon annealing of fergusonite

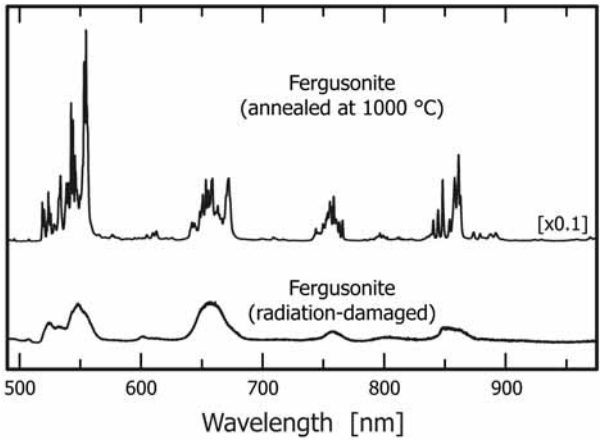
K. RUSCHEL[1], L. NASDALA[1], M. GAFT[2], C. SCHNIER[3] AND J. SCHLÜTER[4]

[1]Institut für Mineralogie und Kristallographie, Universität Wien, Austria (katja.ruschel@univie.ac.at; lutz.nasdala@univie.ac.at)
[2]Physics Group, The Open University of Israel, Raanana, Israel (michael_g@itlasers.com)
[3]GKSS, Geesthacht, Germany (christian.schnier@gkss.de)
[4]Mineralogisch-Petrographisches Institut, Universität Hamburg, Germany (jochen.schlueter@uni-hamburg.de)

Fergusonite [general formula $YNbO_4$], due to its actinide content, is commonly found in the metamict state. In dry annealing experiments, the majority of structural recovery occurs at temperatures of >800 °C (Tomašić *et al.*, 2006). This process involves intermediate formation of tetragonal α-fergusonite below ~1000 °C and monoclinic β-fergusonite above this temperature.

We have studied changes in laser-induced photoluminescence (PL) spectra, which are dominated by emissions of centres related to rare-earth elements (REE), upon gradual reconstitution of the crystallinity. For this, a metamict fergusonite sample from Madagascar (Th 1.9 wt%, U 4.3 wt%) was subjected to dry annealing for 100 h at different temperatures. Analogous to observations on annealed zircon (Nasdala *et al.*, 2002), annealed fergusonite yields considerably intensified PL (Fig. 1). General sharpening of bands at higher annealing temperatures is due to increasing crystal field effects and indicates recovery of the fine structure.

Figure 1: Photoluminescence spectra of natural and annealed fergusonite, dominated by trivalent REE (Nd, Er, Pr, Ho, Tm) emissions.



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Worlds frozen in time: Dawn explores 1 Ceres and 4 Vesta

C. T. RUSSELL

Institute of geophysics and planetary physics and department of earth and space sciences, university of california, los angeles, USA (ctrussell@igpp.ucla.edu)

Dawn is a low-cost planetary mission that uses ion propulsion to rendezvous with and orbit the two most massive members of the asteroid belt, 1 Ceres and 4 Vesta. Our current understanding of Ceres is based almost entirely on remote sensing while our understanding of Vesta is based predominantly on cosmochemical evidence obtained from the Howardite-Eucrite and Diogenite meteorites. These data suggest that these two bodies are quite dissimilar: Ceres being wet with perhaps a 100 km thick ice mantle covered with dust and Vesta being dry with a basaltic surface similar to the moon. Both bodies have clearly undergone thermal evolution to reach their current state but, we believe, did so rapidly in the first 1 – 3 million years of the early solar system well before the larger terrestrial planets were formed. The surfaces of these two survivors of the collisional environment established with the formation of the gas giants have remained frozen in time allowing the Dawn mission to effectively travel not only in space but also take us backward in time to learn the conditions at the earliest epoch of our solar system. Dawn carries redundant framing cameras, a visible infrared mapping spectrometer and a gamma ray and neutron detector. These instruments together with radiometric data provide geologic context, minerological data, elemental composition and internal structure. Vesta will be orbited in 2011 and Ceres in 2015.

Site-specific, size-dependent reactivity of Al-oxide nanoparticle surfaces

JAMES R. RUSTAD[1], JIANWEI WANG[1] AND WILLIAM H. CASEY[1,2]

[1]Department of Geology, University of California, Davis, One Shields Avenue, Davis, CA 95616

[2]Department of Chemistry, University of California, Davis, One Shields Avenue, Davis, CA 95616

We use molecular dynamics calculations to estimate water-exchange rates for a series of aluminum (oxy)hydroxide compounds. These include the $Al(H_2O)_6^{3+}$ monomer; the ε-Keggin ion $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+/8+}$ (Al_{13}); the $[Al_2O_8Al_{28}(OH)_{56}(H_2O)_{26}]^{18+}$ (Al_{30}) aqueous polyoxocation; the surfaces of Al-oxyhydroxide minerals boehmite (AlOOH) and gibbsite ($Al(OH)_3$); and the aluminosilicate mineral kaolinite ($Al_2Si_2O_5(OH)_4$)**.** X-ray structural data can be used in conjunction with rate data from ^{17}O NMR studies[2] to test predictions of reactivity trends at a site-specific level. The molecular dynamics calculations here tie these structurally diverse systems together into a simple structure-reactivity trend based on Al-water bond lengths, and highlight the role of the Al_{13} and Al_{30} ions in systematically bridging the structural gap between the hexaaquo ion and the oxide surfaces.

Water-exchange rates were calculated for each species using the reactive-flux method. The rate constant is taken as $k=\kappa k_{TST}$ where k_{TST} is the transition state rate constant and κ is the transmission coefficient. κ is highly variable across the spectrum of reactive sites, ranging from 0.1 to 0.001.

Overall, the estimates of τ^{298} for the aluminous minerals are surprisingly short, falling within the range of $\sim 10^{-8}$-10^{-10} s, close to those for alkali and alkaline-earth metal ions. Waters bound at the edges of the minerals will exchange rapidly with bulk waters and with other ligands. The fast rates for these surface sites are consistent with the long Al-water bond lengths and also follow the general trend that rates increase, and $\Delta H^{\ddagger}$ values decrease, with increasing size and decreasing charge/Al ion of the complex.

This framework provides, for the first time, a means for estimating kinetic parameters for individual sites at aqueous polynuclear ions and oxyhydroxide surfaces. This result is enormously important for environmental chemistry where treatment of reactions at the aqueous-mineral interface is a long-standing problem. The structure-reactivity relation presented here places the ligand-exchange properties of extended interfacial systems on a new site-specific, quantitative footing.

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Potential temperature and volatile contents in mantle plume of Siberian trap province

I.D. RYABCHIKOV

Institute for Geology of Ore Deposits, Russian Academy of Sciences, 119017, Moscow, Russia, (iryab@igem.ru)

Magmatism in the Siberian CFB province is mainly represented by the voluminous lava flows of tholeiitic plateau basalts and subordinate amounts of highly magnesian volcanics and dyke rocks These highly magnesian rocks are strongly enriched in incompatible trace elements and are characterized by high LREE/HREE ratios. It suggests that their primary magmas were near solidus melts formed at high pressures. P-T conditions of the generation of these hi-Mg melts must be nearly identical with the P-T parameters characterizing magma-generating mantle plume.

To assess the formation conditions of hi-Mg Siberian magmas we investigated melt and fluid inclusions in the phenocrysts of these rocks, which were analyzed for major and trace elements (EMPA and SIMS methods). High Ti/Na ratios and high normative olivine contents in the melt compositions recalculated to the condition of equilibrium with mantle peridotites imply, that initial pressure of magma-generation is in the range of 7–9 GPa.

Ion microprobe data for reheated melt inclusions in phenocrysts from Siberian rocks show low concentrations of volatile and fluid-mobile components. H_2O/Ce ratios in melt inclusions from picrobasalts and meimechites are significantly lower than from MORBs and many OIBs. This implies that the source of Siberian magmas was even poorer in water by comparison with the depleted mantle. The same relations are observed for the ratios of a number of other volatile and fluid-mobile components to their non-volatile geochemical analogues, like B/Ce, Pb/Nd etc.

Low levels of volatiles contents imply that the estimates of near-solidus temperature based on comparison with volatile-free systems would not be changed significantly. Comparison of the estimated from melt inclusion data pressures with experimental data shows that the temperature of rising plume material was ca 400°C higher by comparison with convecting upper mantle at the same depth. This proves that plume material arrived from deep levels in the mantle.

Tracking subduction zone fluxes off slabs, across arcs, and into the mantle: B-Li isotopic evidence

JEFFREY G. RYAN

Department of Geology, University of South Florida, 4202 East Fowler Ave., Tampa, FL, 33620; (ryan@shell.cas.usf.edu)

New light element abundance and B and Li isotopic results from forearc settings and samples reflecting deep recycled mantle soruces have begun to complete the picture of subduction zone chemical cycling for the fluid-mobile elements (FME). Progressive boron and FME declines with increasing metamorphic grade in forearc "subduction complex" massifs (i.e., Bebout *et al* 1999), are complemented by signatures observed in diapiric serpentinites and associated fluids erupting in the Mariana forearc, which preserve dramatic enrichments in B and select FME, but are not elevated in most large-ion lithophiles (Savov *et al* 2005). Declines in B and $\delta^{11}B$ across volcanic arcs point to continued removal from slabs by metamorphism, and depleted B and $\delta^{11}B$ in ocean island lavas suggest deeply recycled slabs are stripped of boron. B isotopic variations in forearcs point to extensive boron removal at low temperatures, as the $\delta^{11}B$ of slab materials (~0 to -3‰ on average) are substantially lower than that of Mariana forearc serpentinites (+13 - +18‰: Benton *et al* 2004) or of B-enriched arc lavas. High $\delta^{11}B$ releases at shallow depths indicate isotopic "lightening" of the slab, such that the $\delta^{11}B$ systematics in arc lavas require inputs both of downdragged forearc mantle materials with high B and $\delta^{11}B$, and of a B depleted, low $\delta^{11}B$ slab component.

Li isotopic variations in the forearc mantle are divergent, with serpentine muds showing uniform $\delta^{7}Li$ indicating equilibrium with high $\delta^{7}Li$ porefluids, while entrained ultramafic clasts record highly variable $\delta^{7}Li$. Relatively high D_{Li} for mafic minerals (especially Mg-rich sheet silicates) combined with high Li diffusion rates result in exceptionally diverse $\delta^{7}Li$ in mantle-derived ultramafic samples. However, $\delta^{7}Li$ in young volcanic rocks from all tectonic settings are remarkably unifom, ranging from +3‰ to +6‰, indicating buffering by a uniform, Li-rich upper mantle reservoir, and/or limited Li isotopic change due to subduction zone chemical proccesing, despite evidence for Li and $\delta^{7}Li$ depletion in eclogitic rocks (Zack *et al* 2003). Interestingly, substantial $\delta^{7}Li$ changes can occur over time in lavas from "dying" subduction systemss, suggesting that such changes may only be observed when processes that homogenize the mantle (i.e., wedge convection) shut down.

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Chemical weathering in the Han River Basin, South Korea: Carbonate and silicate weathering

J.-S. RYU[1, 2], K.-S. LEE[1], H.S. SHIN[1] AND H.-W. CHANG[2]

[1]Division of Isotope Geoscience, Korea Basic Science Institute (jsryu@kbsi.re.kr; kslee@kbsi.re.kr; h2shin@kbsi.re.kr)
[2]SEES, Seoul National University (changhow@snu.ac.kr)

This study focuses on the fluvial geochemistry of the Han River, South Korea to determine its chemical weathering rate and associated CO_2 consumption rate. The Han River draining approximately 26,000 km^2 is the largest river in South Korea in terms of water discharge and the total river length, and consists of two major tributaries: the North Han River (NHR) and the South Han River (SHR). A remarkable difference in basin geology (silicate vs. carbonate) between the NHR and the SHR provides a good natural example to understand the processes of weathering and the influence of basin geology on water quality.

In this paper we report dissolved major elements and Sr isotopic compositions of a total of 58 samples collected seasonally from the Han River system for two years (2000 and 2006). A big difference in the concentration of dissolved loads is observed between the NHR and the SHR: the NHR is much lower in total dissolved solids (TDS), Sr, and major ion concentrations relative to the SHR, while higher in Si concentration and $^{87}Sr/^{86}Sr$ ratios.

Using the forward model, it is calculated that the dissolved loads of the NHR are primarily from silicate weathering (55±11%) with relatively smaller portion of carbonate weathering (30±14%), whereas those of the SHR mainly from carbonate weathering (82±3%) with minor portion of silicate weathering (11±4%). These results are consistent with geological characteristics of their drainage basin: silicate rocks in the NHR vs. carbonate rocks in the SHR. Unlike the NHR basin, sulfuric acids derived from sulfide dissolution play an important role in carbonate weathering in the SHR basin because of widely distributed coal-containing sedimentary strata. Silicate weathering rate (SWR) of the NHR basin is much higher than that of the SHR basin, indicating higher CO_2 consumption rate in the NHR basin.