

Determination of PVTX data and the phase change of crustal fluids

YOSHIHARU UCHIDA AND KENSHIRO OTSUKI

Department of Geoenvironmental Science, Graduate School of Science, Tohoku University (uchida@dges.tohoku.ac.jp; otsuki@dges.tohoku.ac.jp)

Crustal fluids are the aqueous solution of salts (NaCl, KCl, CaCl₂ etc.) and gases (CO₂, CH₄, N₂ etc.), most commonly a H₂O-CO₂-NaCl system. However, because of the effects of charged species, we have a little information on the phase change and the thermodynamic properties over the wide range of P and T, especially, around critical region for the ternary system. The equation of state (EOS) is the most important for understanding several geochemical processes. However, the EOS that is specified for high salinity (>25wt%) systems has not been also established yet, because experiments have not been done successfully around the critical point. In this study, we have determined the fundamental thermodynamic properties (PVTX relation and phase change) experimentally using new apparatus up to 200MPa and 600°C.

We have developed a new experimental apparatus, which is composed of a mini-piston/cylinder system set in the pressure vessel and CO₂ injector. PVT data is measured continuously and synchronously and error of measurement is within 1%. The phase change can be determined from differential V with respect to P or T. We verified the performance of our apparatus by comparing our experimental data with EOS for pure water, H₂O-CO₂ and H₂O-NaCl binary system over the P-T conditions attainable. Those results are in good agreement with preexisting EOS within accuracy of about 3%. Our experimental method serves for the determination of the thermodynamic properties on high saline crustal fluids with high CO₂ concentrations around critical region.

Preliminary geochemical results on the CO₂ Georeactor sequestration test at the Ogachi HDR site

A. UEDA¹, T. YAJIMA¹, H. SATO¹, A. OZAWA², H. KAIEDA³, H. ITO³, T. OHSUMI⁴ AND K. KATO⁴

¹Energy project & technology center, Mitsubishi materials Coro., 1-297 Kitabukuro, Omiya-ku, Saitama, Japan (a-ueda@mmc.co.jp; tyajima@mmc.co.jp; hsatoh@mmc.co.jp)

²Environmental Monitoring and Assessment, Mitsubishi Materials Natural Resources development Corp., 1-297 Kitabukuro, Omiya, Saitama, Japan (aozawa@mmc.co.jp)

³Central Research Institute of the Electric Power Industry, 1646 Abiko, Abiko-shi, Chiba, Japan (kaieda@criepi.denken.or.jp; ito_hisa@criepi.denken.or.jp)

⁴Research Institute of Innovative Technology for the Earth, 9-2 Kizugawa-dai, Kizu, Soraku-gun, Kyoto, Japan (ohsumi@rite.or.jp; koikato@rite.or.jp)

This paper reports a preliminary result of field experiments of CO₂ sequestration into the Ogachi HDR site, where a part of CO₂ will be expected to be fixed as carbonates by interaction with rocks (Georeactor; Ca extraction from rocks and carbonate fixation). The Ogachi HDR (Hot-Dry Rock) field is situated at the northeast Japan and have been studied to produce geothermal electricity.

Experimental Procedure

River water had been continuously injected (380 L/min, 15 MPa) into an injection well (OGC-1) and produced (40 L/min) from an production well (OGC-2) during the experiment (2 weeks). After the fluid flow rate became constant, CO₂ dissolved water (0.2 wt%) was injected with tracers (KI; 2kg/200L and uranine; 150g.18m³). The fluids from OGC-2 were geochemically monitored for their isotope and chemical compositions. The final output temperature at the OGC-2 well site is 127.5 °C.

Results and Discussion

During the experiments, major chemical compositions of fluids from OGC-2 are almost constant. The tracers are first detected at 34 hours after the injection and showed the maximum concentration at 67 hours. The dilution rates of the observed to injected concentrations of KI and uranine are calculated to be 6×10^{-5} and 1×10^{-3} , respectively. CO₂ concentrations in the fluids varied from 600 to 200 mg/L with time and showed no correlation with those of the tracers. This is due to the high dilution rate with reservoir fluids. In this field experiment, we could not discuss the fixation rate of CO₂ as carbonate.

Melting condition and origin of arc magmas beneath the Sengan region, Northeastern Japan

KENTA UEKI AND HIKARU IWAMORI

Department of Earth and Planetary Science, University of Tokyo, Japan
(kenta@eps.s.u-tokyo.ac.jp; hikaru@eps.s.u-tokyo.ac.jp)

Subduction zone processes play important roles in the evolution of the crust and mantle, yet are poorly constrained at present. Recent geophysical and geological studies suggest that there are periodical structures with about 50km wavelength in the mantle wedge and crust beneath Northeastern Japan (Tamura *et al.*, 2002). In this study, we investigate 3-D thermal and compositional states of the mantle wedge and crust beneath the volcanic front of Northeastern Japan, based on the compositional variations of volcanic rocks collected from 28 Quaternary volcanoes in a volcanic region, the Sengan region (30km-30km).

Volcanoes in the Sengan region are divided into two groups. Compositional variations of the first group can be reproduced by fractional crystallization from a basaltic magma, based on thermodynamic calculation using MELTS (Ghiorso and Sack, 1995). These volcanoes are mainly distributed on the outer rim of the cluster. Magma mixing between high-MgO andesite and dacite associated with fractional crystallization is observed in the second group, based on AFC calculation and mineralogy. The second group is distributed at the central part of the volcanic cluster associated with voluminous welded tuff and granitic pluton. Major element compositions of these voluminous silicic rocks show a similar range to those reported for partial melts of amphibolite (e.g. Beard and Lofgren, 1991).

Melting conditions in the mantle wedge have been estimated to minimize the difference between the composition of partial melt calculated at a given P , T , H_2O -content (Ghiorso *et al.*, 2002) and that estimated from the observed volcanic rocks, assuming olivine maximum fractionation. The estimated mantle condition shows that the mantle beneath the central part of the cluster has a higher H_2O -content than that beneath the outer rim. It is suggested that mantle-derived wet magma had supplied heat and H_2O to the crust and induced crustal melting/magma mixing at the central part of the volcanic cluster. On the outer rim, basaltic magma ascended to the surface without causing crustal melting.

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Radiocarbon analysis in tree rings of Yaku-cedar by AMS for investigating secular variation of atmospheric $^{14}C/^{12}C$ ratios

H. UENO¹, Y. MURAMATSU¹, H. MATSUZAKI² AND Y. SUNOHARA-TSUCHIYA²

¹Dept. of Chemistry, Gakushuin University, Tokyo, Japan
(uenohiroki@hotmail.com, yasuyuki.muramatsu@gakushuin.ac.jp)

²Micro Analysis Laboratory, Tandem accelerator (MALT), University of Tokyo, Japan

Atmospheric radiocarbon is produced in the stratosphere by cosmic ray reaction with nitrogen ($^{14}N(n,p)^{14}C$). The produced ^{14}C enters into the carbon cycle in the air, and it is absorbed photosynthetically by plants. Therefore, by measuring $^{14}C/^{12}C$ ratio in tree rings, it is possible to obtain information on the secular change of cosmic ray intensity.

In this study, we have used an old cedar tree (1680 year-old) from Yaku island (Kagoshima Prefecture, Japan). Samples (about 20mg) were collected from annual tree rings, and then α -Cellulose, which is immovable constituent and recorded $^{14}C/^{12}C$ ratios at the time of the absorption, was extracted by treatments with acid and alkaline. The obtained α -Cellulose (about 3mg) was oxidized to CO_2 and purified with a glass vacuum line. Then it was reduced to pure graphite which was used as a target (about 1mg) for the determination by Accelerator Mass Spectrometry (AMS).

Using a small sample size, as mentioned above, we could measure $^{14}C/^{12}C$ ratios with reasonable precision and accuracy by AMS at MALT. Results obtained at this time are shown in Fig.1 (for the period 524-775 A.D.) together with the IntCal04 data. The values were not on the straight-line, which is extrapolated from the year 1950 with the half-life of ^{14}C , suggesting there were considerable variations of the ^{14}C production. Some periods (e.g. around 660A.D.), in which $\Delta^{14}C$ values were higher than those of IntCal04, were observed. Since IntCal04 was mainly composed from western data, our results from Yaku-cedar should be useful to understand secular variation of $^{14}C/^{12}C$ ratios in Japan.

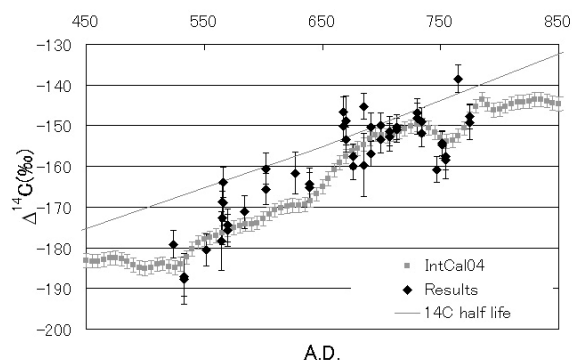


Figure 1. Results together with the IntCal04 values.

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Nb-Ta oxide minerals in granites and pegmatites: Tracers of magmatic to post-magmatic evolution

P. UHER AND P. CHUDÍK

Dept. of Mineral Deposits, Comenius University, Bratislava, Slovakia (puher@fns.uniba.sk)

Accessory Nb-Ta oxide minerals occur in some highly fractionated granites and granitic pegmatites. Their internal zoning, compositional variations and breakdown products are sensitive indicators of magmatic to post-magmatic evolution of the parental rocks.

Regular fine to coarse oscillatory zoning of columbite-tantalite and Nb,Ta-rich rutile with repeated Nb- and Ta-rich zones indicates their primary magmatic crystallization. Increasing Ta/Nb, (Nb+Ta)/Ti and Mn/Fe ratios in the Nb-Ta phases traces the degree of magmatic fractionation, whereas W, Sn, Sc, Zr, Y, U and Mg contents reflect mainly their local compositional environment. Moreover, presence of Ti,Fe³⁺-rich Nb-Ta minerals (titanian ixiolite, rutile) could serve as an indicator of higher oxygen-fugacity (fO_2) conditions in comparison to the Ti-poor, Fe²⁺-rich ordered columbite-tantalite + ferrotapiolite assemblage. Minerals of the fooridite-thoreaulite series (Sn²⁺Nb₂O₆ – Sn²⁺Ta₂O₆) represent an example of primary magmatic phases in specific Sn-rich and low fO_2 pegmatitic environment in contrast to common occurrence of cassiterite + W,Ti-rich Nb,Ta minerals (columbite-tantalite, ixiolite, rutile) in rare-element tin-bearing leucogranites.

Late-magmatic to subsolidus alteration, recrystallization and breakdown of the primary Nb-Ta oxide minerals is widespread. Complex irregular convoluted zones reveal partial leaching and replacement of the primary phases; erratic Nb-Ta distribution is typical for the secondary columbite-tantalite. Mosaic patchy zoning of Nb-Ta-Ti phases manifest their recrystallization probably due to younger thermal/pressure metamorphic overprint. Subsidiary exsolution textures are typical for Fe³⁺,Ti,Sc,W,Sn-rich, primary Nb-Ta phases (e.g. Nb-Ta rutile, ixiolite); they indicate a breakdown of the primary phases and element redistribution during granite/pegmatite cooling and uplift.

Increasing of fluid activity and fO_2 during late- to post-magmatic stage caused a breakdown of Sn²⁺-bearing fooridite-thoreaulite and precipitation of secondary cassiterite + columbite-tantalite. Moreover, an influx of late-magmatic to hydrothermal Na,Ca-rich fluids facilitates replacement of columbite-tantalite, ixiolite and Nb-Ta rutile by fersmite, pyrochlore-group and other alkali-rich Nb-Ta minerals. Rarely, an activity of Sb,Pb-bearing hydrothermal fluids caused a precipitation of specific secondary Nb-Ta minerals (plumbomicrolite, stibiobetafite, stibiotantalite, Nb,Ta-rich roméite etc.).

Thermodynamic price tags for a wet mantle

G.C. ULMER¹ AND E. WOERMANN²

¹Geology Dept., Temple University, Philadelphia, Pa., 19122 (gulmer@temple.edu)

²Josef Ponten Str 57, Aachen-Richterich, Germany, D 52072

The exciting discovery of Wadsleyite as mineral host for hydrogen or as a 'hydrous material' in the mantle has redox-equilibria-implications relative to other published redox models for the Earth's mantle. Such redox models for the Earth's mantle suggest that along the geotherm, shallow mantle conditions range from the log fO_2 given by the buffer (FMQ) to levels of redox of $\Delta(\text{FMQ}) = -2$. These models have been based on studies that include: (1) xenolith studies by several methods (as reviewed by Ulmer *et al.*, 1987) (2) stability of diamonds relative to other redox buffers (for example, Eggler and Baker, 1982 or Ulmer *et al.*, 1978). Most redox models for the Earth's mantle do incorporate more reduced conditions for greater depth in the mantle: the log fO_2 given by the buffer (IW) at the core mantle boundary is one logical reason for this model. Deeper xenolith studies also suggest this. (Haggerty and Tompkins, 1983 or Ulmer *et al.*, 1987). Even more reduced conditions for the mantle are implied by the abundant existence of the mantle mineral, Moissanite, (SiC) whose redox stability in log fO_2 can be represented by $\Delta(\text{IW}) \approx -8$ at pressures up to 9.0 GPa and temperatures up to 1730 K. Furthermore, the kinetics of oxidation of SiC exposed to carbonates or iron oxides from 2.0 to 15.0 GPa and temperatures as low as 1173 K has been measured in hours, not days or months! (Ulmer *et al.*, 1998)

To have mantle phases, either with hydroxyl, or as true hydrates, that can be compatible in the redox state of the mantle seems a problem? A companion manuscript at this meeting explores redox EOS calculations of water stability in the mantle. (*cf.*, Woermann *et al.*). To our thinking, one possibility may be the influence of defects in the Wadsleyite. No direct data yet seem available for this suggestion; it is by analogue to the large range of redox values demonstrated by defect olivines that this idea should be pursued.

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Uranium(IV) oxide surface reactivity

K.-U. ULRICH¹, A. SINGH¹, S.F. DIXON¹, E. SCHOFIELD²,
J.R. BARGAR² AND D.E. GIAMMAR¹

¹ Dept. of Energy, Environmental & Chemical Engineering,
Washington University, St. Louis, USA
(k.ulrich@seas.wustl.edu; giammar@wustl.edu)

² Stanford Synchrotron Radiation Laboratory, Menlo Park,
USA (bargar@slac.stanford.edu)

The success of bioremediation of uranium-contaminated sites will depend on the long-term stability of the U(IV) oxide formed by microbially induced reduction of soluble U(VI). This contribution is part of a research project establishing the local and long-range structure and reactivity of biogenic uraninite generated under different environmental conditions in comparison to its closest abiotic analog, UO_{2+x} ($0 < x < 0.25$). An abiotic uraninite solid was produced by thermal reduction of uranium peroxide with $\text{H}_{2(g)}$, yielding particles with a star-like prism shape and a size of ~ 700 nm. Powder XRD proved an fcc crystal lattice of cubic uraninite. Its stoichiometry was identical to that of a reference sample of $\text{UO}_{2.0}$, as shown by EXAFS spectroscopy.

The dissolution kinetics of abiotic uraninite have been examined in batch and flow-through experiments as a function of pH, dissolved inorganic carbon, and dissolved oxygen. Dissolution rate constants are calculated from a mass balance approach, accounting for equilibrium solubility and the decrease of particle size as dissolution progresses. Batch dissolution experiments under anoxic conditions have shown dissolved uranium concentrations close to or even higher than predicted from published thermodynamic data. In the range of pH 6 to 9, dissolution rate constants were on the order of $1.3\text{--}3.1 \cdot 10^{-13} \text{ mol m}^{-2} \text{ s}^{-1}$, but they increased by two orders of magnitude under atmospheric conditions. Under anoxic conditions, a flow-through experiment has shown an initial U-release peak, suggesting removal of more soluble U phases from the surface. However, carbonate as a complexing agent for U(VI) did not immediately change the dissolution kinetics of abiotic uraninite, but gradually altered its surface toward higher solubility, which was a reversible reaction.

Dissolved U(VI) showed high affinity for abiotic uraninite. Further experiments will quantify the adsorption/desorption reactions and test the effects of other divalent cations such as manganese, calcium, and magnesium. Among factors such as formation conditions, structural properties, and adsorption/desorption behavior, the surface reactivity and dissolution kinetics of uranium oxide are the most important factors for promoting immobilization and long-term stability in the subsurface.

Nd isotope mixing during thermal ionisation mass spectrometry: Implications for accurate ^{142}Nd measurements

D. UPADHYAY, E.E. SCHERER AND K. MEZGER

Zentrallabor für Geochronologie, Institut für Mineralogie,
Univ. Münster, Corrensstr. 24, 48149 Münster, Germany

Deviations from the exponential-law mass-bias curve are observed during some high-precision runs of the La Jolla Nd standard. The resulting measured isotope ratios ($X/144$) are generally higher than predicted by the exponential law (Fig. 1) and characterized by increased scatter. The onset of the deviations correlates with a distinct change in the mass-bias trajectory (from normal to reverse) of the isotope ratios.

Similar effects during Ca isotope measurements [1] were attributed to isotope mixing during mass spectrometry. For Nd isotopes, the effects of mixing during measurements are not clearly understood even though several studies have documented an apparent breakdown of the exponential mass-bias law [e.g., 2 and 3].

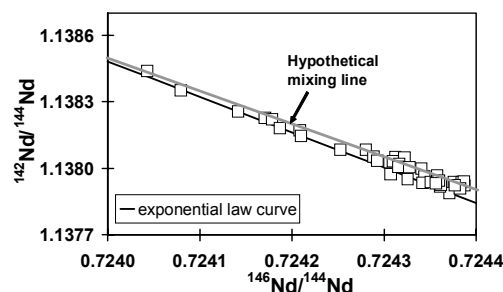


Figure 1: Deviations of the isotope ratios from the exponential curve during a run segment modeled as mixtures of ions from differentially fractionated sample reservoirs

This study shows that the divergence from exponential-law can be modeled as mixtures among reservoirs on the theoretical fractionation curve (Fig. 1). Such differentially fractionated reservoirs can form because of temperature gradients or heterogeneous sample distribution on the filament. Mixing of ions derived from these reservoirs can modify the composition of the ion beams significantly causing deviations from the exponential-law curve. Mixing results in an apparent reversal of mass fractionation because isotopically light ions from less fractionated reservoirs are ionized together with those from more fractionated ones.

Such mixing during mass spectrometry is a great concern when measuring the generally very small ^{142}Nd anomalies because deviations up to 56 ppm have been observed for the $^{142}\text{Nd}/^{144}\text{Nd}$ ratios. This deviation is far greater than the variations expected for most applications. The ultimate accuracy and reproducibility of the isotope ratios is dictated by the extent of isotope fractionation and mixing in addition to instrument electronics and ion counting statistics.

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Integrated air quality assessment - PM_{0.1} to PM₁₀ magnetic particles

M. URBAT, E. LEHNDORFF AND L. SCHWARK

Institut für Geologie und Mineralogie, Universität zu Köln, Cologne, Germany (m.urbat@uni-koeln.de)

Approach

In our multidisciplinary approach atmospheric air quality in the Greater Cologne Area (GCA, NW-Germany) was studied using pine needles as passive samplers. Here we report accumulation histories, particle size dependency and spatial distribution of remanent magnetic pollutants as to approximate the dust load. Environmental magnetic results are interpreted in conjunction with complementary trace element and persistent organic pollutant data.

Results

Variability between sites proves to be significantly higher than within sites. Established accumulation rates predominantly reflect anthropogenic emissions. Minor natural processes comprise canopy effects and abrasive removal of particles. Emission specific concentrations and grain size distributions (Fig. 1) are readily detected by magnetic parameters and allow for source allocation in spatially highly resolved data sets.

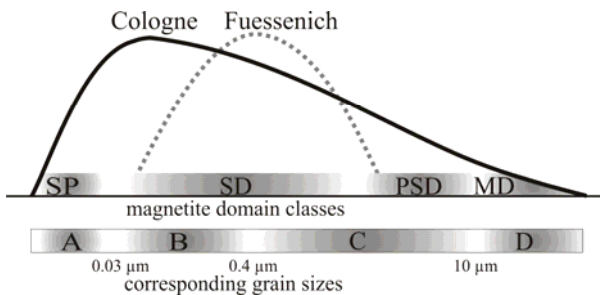


Figure 1 Hypothetical end-member grain size distribution curves for metropolitan location Cologne and rural station Fuessenich (adopted from Lehndorff *et al.* 2006)

Conclusions

The correlation of magnetic particles, trace elements and PAH yields a far more complete picture of air pollution in that source allocation is more readily achieved.

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Sub- μm size high precision analysis of $\delta^{18}\text{O}$ in zircon by SIMS

T. USHIKUBO¹, F. Z. PAGE¹, N. T. KITA¹, L. R. RICIPUTI², AND J. W. VALLEY¹

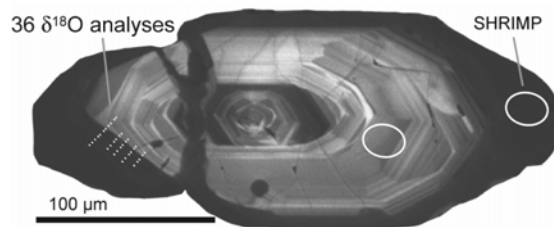
¹Dept. of Geology & Geophysics, Univ. of Wisconsin, Madison, WI, U.S.A. (ushi@geology.wisc.edu)

²Oak Ridge National Laboratory, Oak Ridge, TN, U.S.A.

Oxygen isotopic ratios ($\delta^{18}\text{O}$) of rocks provide important insights to understand igneous and metamorphic processes. Zircon is a valuable accessory mineral to study such processes because (1) it is common in igneous, metamorphic, and sedimentary rocks, (2) it provides U-Pb ages, and (3) it is retentive of primary composition. However, because zircons are small (typically 10 to 100 μm) with internal zonation, *in situ* microanalysis is required.

An *in situ* O isotopic analysis technique with $\sim 0.5 \mu\text{m}^2$ spot and an analytical uncertainty of 1.0 ‰ (1σ) has been developed using a Cameca ims 1280 SIMS. This technique was applied to a zoned zircon from a partially melted metasediment (Daniel's Road, near Saratoga Springs, NY) in the granulite-facies Adirondack Highlands [1], which consists of a detrital igneous core (1353Ma) and a metamorphic overgrowth (1019Ma) with $\delta^{18}\text{O}$ values of $\sim 6\text{‰}$ and 12‰ , respectively [2].

Five traverses with 2 μm steps, totaling 36 sub- $1\mu\text{m}$ $\delta^{18}\text{O}$ analyses, were performed to determine the $\delta^{18}\text{O}$ gradient at the core/overgrowth boundary that is clearly seen by CL. The figure shows the CL image of the sample and positions of $\sim 30 \mu\text{m}$ pits from previous SHRIMP U-Pb analyses and $\sim 0.8 \mu\text{m}$ dia. pits for $\delta^{18}\text{O}$ analyses of this study. We found a steep $\delta^{18}\text{O}$ gradient at the boundary that indicates O isotopic exchange between the core and the overgrowth occurred over a distance less than 2 μm . Modeled for a 50 Myr isothermal period [3], an O diffusion coefficient in zircon of $\sim 10^{-23} \text{cm}^2/\text{s}$ best fits the data. The preservation of such a steep gradient and the inferred low diffusion coefficient indicate that the zircon preserved $\delta^{18}\text{O}$ from crystallization through high-grade metamorphism. We envision that sub- μm stable isotope analyses will permit new investigations of materials that are rare, precious or zoned, including those of biological origin.



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PGE geochemistry, mineralogy and Os-isotope signature in the mantle-hosted ophiolitic chromitites from the Kahramanmaraş area, SE-Turkey

I. UYSAL¹, F. ZACCARINI², G. GARUTI³, T. MEISEL⁴,
M. TARKIAN⁵, M.B. SADIKLAR¹

¹Karadeniz Technical University, Trabzon-Turkey

²Granada University, Granada-Spain

³Modena and Reggio Emilia University, Modena-Italy

⁴Leoben University, Leoben-Austria

⁵Hamburg University, Hamburg-Germany

Mantle-hosted ophiolitic chromitites from the Kahramanmaraş area (SE-Turkey), have been investigated as to their chromite composition, Platinum-group elements (PGE) concentration and mineralogy, as well as Os-isotope geochemistry. Chromitites vary from Al-rich to Cr-rich, however they indifferently display enrichment in Os-Ir-Ru over Rh-Pt-Pd, with concentrations of PGE lower than 510 ppb. Consistently, the most abundant Platinum-group minerals (PGM) are Ru-Os-Ir sulfides and alloys. They occur as small grains (less than 15 µm), mainly included in fresh chromite. Base metals sulphide (BMS), Na-rich amphibole and rare phlogopite were also identified forming inclusions in chromite. Their textural position and morphology indicate that these inclusions are magmatic in origin. Based on textural relations, paragenesis and composition, it was possible to establish that PGE alloys crystallized before than PGE and BM sulfides, at temperature comprised between 1300 and 1000 degrees and under increasing sulphur fugacity. The presence of abundant hydrated primary silicates suggests that the Kahramanmaraş chromitites formed in the presence of water and volatile- and sodium-rich fluids. This observation is also supported by the Re/Os ratio relatively high, that points a mixing of mantle-derived Os with Os from a source characterized by relatively high radiogenic signature, possibly fluids originated in a supra-subduction zone (SSZ). If a SSZ setting is accepted, the concomitant presence of Al-rich and Cr-rich chromitites suggests chromite precipitation from melts varying in composition from back-arc basalts (Al-rich chromite) to boninites (Cr-rich chromite), possibly at different mantle levels (i.e. deep for the Cr-rich chromitites and close to the Moho-Transition Zone for the Al-rich ones).

Potential problems in the annealing of zircon

T. VÁCZI¹, L. NASDALA¹, R. WIRTH²,
B. WANTHANACHAISAEANG³ AND T. HÄGER³

¹Institut für Mineralogie und Kristallographie, Universität Wien, Austria (tamas.vaczi@univie.ac.at, lutz.nasdala@univie.ac.at)

²GeoForschungsZentrum Potsdam, Germany (wirth@gfz-potsdam.de)

³Institut für Geowissenschaften, Johannes Gutenberg-Uni. Mainz, Germany (wanthana@students.uni-mainz.de, tobias.haeger@uni-mainz.de)

Annealing experiments are often employed to study the recrystallisation behaviour and the real structure of radiation-damaged zircon. This includes dry annealing in air and hydrothermal annealing; in the latter case the reconstitution is controlled by fluid-driven reaction fronts (Geisler *et al.*, 2003). It is well-known that the temperature-induced recovery of strongly radiation-damaged zircon involves an intermediate stage (at about 900–1100 °C) where nearly amorphous ZrSiO₄ decomposes into oxides (Nasdala *et al.*, 2002). This is explained by the preferred nucleation of tetragonal ZrO₂ over ZrSiO₄ (Garvie, 1965). Dry annealing of moderately radiation-damaged zircon, in contrast, does not involve this intermediate stage but rather results in a gradual reconstitution of zircon.

We have found that under certain conditions ZrO₂ may also be observed in the annealing of lowly metamict zircon, and at temperatures as high as 1600 °C. For instance, we found baddeleyite on the surface, or in the entire volume, of annealed zircon crystals that were treated at 1400 °C. We attribute the high-temperature formation of baddeleyite to be an artefact, for which we see two potential causes. First, if volatile alkali elements are present in the furnace atmosphere, they may react with silica to form Na-silicate glass. Second, if annealing is done using corundum crucibles, there may be a reaction of the silica component with corundum (for instance by formation of mullite). The latter idea seems to be confirmed by recent observations that during high-temperature treatment of gem-quality ruby, baddeleyite may form at the surface of included zircon crystals (Wanthanachaisaeng *et al.*, 2006). It is therefore important to consider doing annealing experiments in a controlled environment (no contaminants reaching the sample) and choosing suitable materials (e.g., Pt crucibles).

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X-ray photoelectron spectroscopy study of coals with different rank

B. VALENTIM¹, A. COSTA¹, A. GUEDES¹, D. BOAVIDA²,
M. MARQUES¹ AND D. FLORES¹

¹Centro and Departamento de Geologia da Faculdade de Ciências da Universidade do Porto, Porto, Portugal (bvvalent@fc.up.pt)

²Instituto Nacional de Engenharia, Tecnologia e Inovação (INETI), Departamento de Engenharia Energética e Controlo Ambiental (DEECA), Lisboa, Portugal

Nowadays the increasing amounts of NO_x and N₂O converted from coal nitrogen, led to the investigation of the combustion processes and coal properties that contribute to maximise the nitrogen production and influence the variation in the emissions. Therefore it is important to determine the molecular structure of nitrogen in coal.

X-ray Photoelectron Spectroscopy (XPS) analyses were performed in vitrinite-rich coals of increasing rank to determine the nitrogen functionalities (pyridine at 398.8 eV, pyrrol around 400.2 eV, quaternary nitrogen around 401-402 eV and nitrogen-oxide around 403 eV). Nitrogen in the studied coals was found to be predominantly pyrrol. However, the coals storage procedure determined the degree of nitrogen oxidation and the other nitrogen functionalities (Fig. 1 and 2). Due to this fact, the ratios of pyridinic to pyrrolic nitrogen and pyridinic to quaternary nitrogen vary with increasing rank and also with the oxidation of the coals. The analyses of a set of non-oxidised coals with rank lower than 1.41% vitrinite reflectance permitted the observation of the decreasing of pyrrolic and quaternary nitrogen and an increase of the pyridine with increasing coal rank.

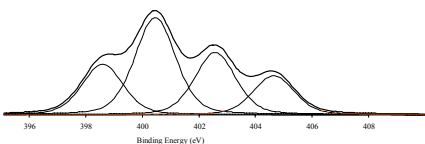


Figure 1: Representative XPS spectra of nitrogen (1s) obtained on oxidised coal.

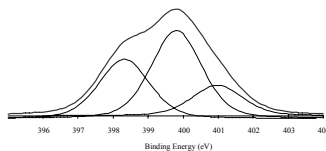


Figure 2: Representative XPS spectra of nitrogen (1s) obtained on non-oxidised coal.

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Synthetic isotope mixtures for the calibration of ion current ratio measurements in carbon and oxygen in carbon dioxide

S. VALKIERS, M. VARLAM AND M. BERGLUND

Institute for Reference Materials and Measurements, EC-JRC, B-2440 Geel (B)

Different sets of synthetic isotope mixtures for the calibration of carbon and oxygen ion current ratio measurements obtained by mass spectrometry have been prepared by mixing carbon dioxide isotopically enriched in ¹⁸O (^{nat}C¹⁸O₂) and natural carbon dioxide (^{nat}C^{nat}O₂), and by mixing different natural CO₂ gases with slightly different carbon and oxygen isotopic compositions [1].

These mixtures act as Primary Standards to the SI-scale for carbon and oxygen isotope amount ratio measurements in CO₂. They will help to anchor existing carbon Isotope Reference Samples (i.e. NBS19, IAEA-CO-9) and therefore offer the basis for comparability of carbon (and oxygen) isotope measurement results, without any assumptive correction for the oxygen isotopes.

Via such 'absolute' isotope amount ratio measurements of carbon and oxygen on CO₂ produced from the Primary Standard to the VPDB-scale NBS19, calibrated by means of synthetic isotope mixtures, 'absolute' isotope amount carbon and oxygen ratios corresponding with the zero point of the VPDB conventional scale were calculated to be $R_{13/12} = (11\ 137\ 6 \pm 16) \cdot 10^{-7}$ and $R_{18/16} = (208\ 824 \pm 48) \cdot 10^{-8}$ respectively.

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Evidence of the earliest crust on Earth

JOHN W. VALLEY

Dept. of Geology & Geophysics, University of Wisconsin,
Madison, WI, 53706, USA, (valley@geology.wisc.edu)

Understanding the earliest crust on Earth has long been considered the realm of planetary geology. Since all crust older than 4 Ga was apparently destroyed on Earth, older mafic to ultramafic rocks from Mars and the moon provided analogs. However, growing evidence from zircons is finally providing direct testimony of the first 500 myr on Earth.

Detrital and xenocrystic zircons older than 4.0 Ga, without identified parent rocks, are found in highly mature conglomerates and sandstones, and occasionally in granites, almost exclusively from the northern Yilgarn of Western Australia. The oldest grains cluster at 4.35 to 4.4 Ga and are among the most intensely studied samples on Earth. Compositions and ages are variable within single grains and careful study involves imaging and in situ analysis correlated to textures [1]. Many zircons have younger overgrowths or altered domains, and bulk ages should be interpreted with caution. Some zircons are actually small “rocks”, containing a granitic suite of inclusions including: quartz, K-feldspar, and plagioclase [2]. No evidence of shocked zircon (planar elements, reidite) has yet been reported in spite of careful examination by optics and SEM. Mildly elevated $\delta^{18}\text{O}(\text{Zc})$ indicates that low temperature processes involving liquid water altered protoliths of parent magmas. Equally high $\delta^{18}\text{O}$ is not found in zircons from mafic rocks in young ocean crust [3] or from the moon [4]. A number of tests support these results as primary including: magmatic zoning, U-Pb concordance, Th/U, type 1 REE profiles [1], and slow diffusion rates in zircon [5]. The picture emerges of an early Earth with differentiated buoyant crust, cool (perhaps cold) surface temperatures, and oceans, which was hospitable for the emergence of life by 4.2 Ga and perhaps earlier.

The composition of the earliest crust and its tectonic setting are less constrained. Nd, Hf, and Pb isotopes have long pointed to early formed protocrust. Recently, $^{176}\text{Hf}/^{177}\text{Hf}$ ratios and low Ti in zircons were interpreted to indicate the existence of wet S-type granites, continental crust, and plate tectonics before 4.4 Ga [6], but questions remain [7].

Why are rocks older than 4.0 Ga preserved on Mars and the moon, but not Earth? Impacts and melting, commonly cited culprits, were important on all bodies. Plate tectonics, if a factor on early Earth, would have subducted zircons along with rocks. Perhaps surface rocks on Earth merely weathered away in an early low pH atmosphere and zircons are the only recognizable relicts. If so, deeper rocks should have escaped and may still await discovery.

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Fractionated HSE in suboceanic mantle: Assessing the influence of refertilization processes on upper mantle peridotites

D. VAN ACKEN^{1,2}, H. BECKER^{1,2}, F. WOMBACHER¹,
R.J. WALKER², W.F. McDONOUGH², R.D. ASH² AND
P.M. PICCOLI²

¹Freie Universität Berlin, Institut für Geologische
Wissenschaften (dvana@zedat.fu-berlin.de;

hbecker@zedat.fu-berlin.de, fwo@zedat.fu-berlin.de)

²Department of Geology, University of Maryland
(rjwalker@geol.umd.edu; mcdonough@geol.umd.edu,
rdash@geol.umd.edu, piccoli@geol.umd.edu)

The Totalp ultramafic massif in Eastern Switzerland consists of peridotites interlayered with pyroxenites, that have been exposed on the seafloor of the Jurassic Ligurian ocean. Petrographic observations, whole rock major element and Re-Os data in peridotites from the Totalp massif suggest refertilization of the peridotites by percolating melt parental to the associated pyroxenites. Here, we examine the behaviour of other highly siderophile elements (HSE).

Peridotites from the Totalp massif have Ir contents between 1.7 and 4.3 ppb, typical for mantle-derived lherzolites. Osmium abundances range from 2.7 to 5.2 ppb, Ru abundances range from 4.8 to 12.7 ppb, both within the range previously reported for mantle peridotites. Os/Ir_N and Ru/Ir_N are broadly chondritic to slightly suprachondritic within a range of 1.0 to 1.9 and 1.3 to 1.9, respectively. Platinum abundances range from 2 to 7 ppb; Pt/Ir_N varies from subchondritic to slightly suprachondritic within a range from 0.72 to 1.19. Palladium abundances range between 4 and 15 ppb, Re abundances between 0.21 and 0.76 ppb. In a few samples, Pd/Ir_N and Re/Ir_N are enriched by factors of up to 4 and 5, respectively, compared to typical upper mantle lherzolites.

Associated pyroxenites are enriched in incompatible PPGE while compatible IPGE have slightly lower abundances compared to the peridotites. Websterite layers display Pd/Ir_N as high as 40 and Re/Ir_N of up to 9; Pt/Ir_N and Ru/Ir_N are only slightly elevated, to factors of up to 3.8 and 2.1, respectively.

Single grain in situ analyses of Ni-Fe-sulfides (pentlandite, pyrite, godlevskite; alongside native copper) in pyroxenites by LA-ICP-MS yield roughly chondritic Os/Ir and chondritic to suprachondritic Ru/Ir and Pd/Ir of up to 23 and 50, respectively. Re/Ir is subchondritic to slightly suprachondritic by a factor of 2. Both HSE abundances and inter-element HSE ratios vary significantly within one sample, indicating heterogeneous distribution of HSE on grain to thin section scale.

In summary, whole rock and in situ single grain HSE data indicate that melt migration by mafic mantle derived melts produced suprachondritic Pd/Ir and Re/Ir and negligibly affected Pt and more compatible HSE.

Transient landscape evolution following uplift in the Southern Ecuadorian Andes

V. VANACKER¹, F. VON BLANCKENBURG², G. GOVERS³
AND P.W. KUBIK⁴

¹University of Louvain, Department of Geography, Louvain-la-Neuve, Belgium (vanacker@geog.ucl.ac.be)

²University of Hannover, Institute for Mineralogy, Hannover, Germany (fvb@mineralogie.uni-hannover.de)

³University of Leuven, Physical and Regional Geography, Leuven, Belgium (Gerard.govers@geo.kuleuven.ac.be)

⁴Paul Scherrer Institute, Institute of Particle Physics, ETH Hoenggerberg, Zurich, Switzerland

Fluvial systems are driving landscape evolution in active tectonic settings. Examining differential denudation rates associated with specific channel and hillslope morphology contributes to understand the transient response of a landscape following uplift. Here, we explore the relationship between landscape morphology and erosion by quantifying basin-wide denudation rates of various morphological zones in the Southern Ecuadorian Andes. Cosmogenic radionuclides (¹⁰Be) in quartz of river sediment were employed to constrain basin-wide denudation rates (10⁴-10⁵ yr). Along an east-west transect across the Cordillera Real, we carefully selected small basins (< 250 km²) to cover a wide range of morphological settings, and to be representative of specific areas of transient adjustment. Channel and slope morphology vary systematically from east to west, reflecting the transition from high-relief, strongly dissected topography in the eastern side of the Cordillera Real into relatively low-relief topography in the Inter-Andean valley. Basin-wide denudation rates range by nearly two orders of magnitude, from ~ 4 mm/kyr to ~ 400 mm/kyr, and show good correlation with channel and hillslope steepness indices.

The spatial pattern of differential denudation rates across the Cordillera Real reflects the transient adjustment of the landscape to rapid river incision following tectonic uplift. Relative high denudation rates (> ~200 mm/kyr) are measured in the eastern part of the Cordillera Real, where slopes and channels are steep and actively adjusting to rapid incision of the trunk stream. Basin-wide denudation rates are about ten times lower in the central part of the Inter-Andean valley. The presence of smooth concave river profiles indicates that the incision signal has not yet propagated into the Inter-Andean valley.

The consequence of Quaternary changes in chemical weathering rate for ocean chemistry

D. VANCE¹, G.L. FOSTER¹ AND D.A.H. TEAGLE²

¹Bristol Isotope Group, Department of Earth Sciences, Univ. Bristol, Bristol BS8 1RJ, UK (d.vance@bristol.ac.uk, g.l.foster@bristol.ac.uk)

²National Oceanography Centre, Univ. Southampton, Southampton SO14 3ZH, UK (dat@noc.soton.ac.uk)

Modern riverine chemistry and discharge is commonly used to estimate the long-term flux to the oceans of the many chemical species that have their primary source in the continental crust. Here we suggest that measurements of many modern rivers, only a few thousand years after a glacial period, are not representative of the long-term flux and we quantitatively assess the implications of such a suggestion for key marine geochemical budgets.

Blum and co-workers [e.g. 1] first developed the idea that physical grinding during glacial periods of the Quaternary was followed by rapid chemical weathering of fresh soils during the warm, wet conditions of interglacials. Recently [2], Pb isotopic records of the oceans were shown to be consistent with pulses of rapid weathering during the early stages of interglacials. The consequences for long-term Quaternary chemical weathering rates and the Sr isotopic record of seawater have been explored previously [1]. Here we focus on another important implication: that the instantaneous weathering rates implied by modern riverine cation flux are higher than the long term average. In our estimation, for regions that were glaciated 20 kyr ago but that are now ice-free, present day chemical weathering rates are a factor of 3 to 4 higher than the average rate for the past 2 to 3 Myr.

This finding has major implications for long-standing problems in ocean chemistry. For example, it remains a puzzle that the hydrothermal flux of Sr required to balance the modern riverine flux is much greater than is suggested by the extent of alteration of the oceanic crust [3]. Indeed, while there is growing convergence between ocean floor hydrothermal fluid flux estimates based on independent tracer exchanges [e.g. 4] and simple thermal calculations, estimates based upon the oceanic ⁸⁷Sr or Mg balances that rely on the quantification of the modern riverine flux are more than an order of magnitude greater. For elements such as Sr and Mg, with long oceanic residence times, modern riverine measured fluxes do not provide appropriate estimates of the long-term inputs. The changes in weathering rates also imply dramatic variation in the supply of alkalinity and nutrients to the ocean, with consequences for atmospheric CO₂.

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Global Neodymium - Hafnium isotope systematics – Revisited

T. VAN DE FLIERDT¹, S.L. GOLDSTEIN¹, S.R. HEMMING¹,
M. FRANK² AND A.N. HALLIDAY³

¹Lamont-Doherty Earth Observatory, Columbia University,
Palisades, U.S.A., (tina@ldeo.columbia.edu)

²IfM-GEOMAR, Leibniz Institute for Marine Sciences, Kiel,
Germany, (mfrank@ifm-geomar.de)

³University of Oxford, Oxford, U.K., (alexh@earth.ox.ac.uk)

Combined Nd and Hf isotope analyses have become widely used in solid Earth geochemistry studies, but their application for low-temperature processes is still limited. The residence time for both of these elements in the ocean is thought to be similar (500 – 2000 years) and there is a growing number of studies addressing the sources of Nd and Hf as well as internal cycling processes in the ocean. In the case of Nd, these studies have been accompanied by a number of emerging applications of Nd isotopes as a tracer for past water mass mixing and ocean circulation, since the Nd isotopic composition of various archives in the ocean has been shown to record the Nd isotopic composition of ambient seawater reliably. Due to very low concentrations of Hf in seawater and hydrothermal fluids, and associated analytical difficulties of measuring Hf isotope compositions, our overall understanding about fractionation processes and internal cycling of Hf in the ocean is not as well developed as for Nd. However, recent studies have shown that direct measurements of seawater and river waters are feasible.

The global Nd-Hf isotope systematics can be described by two linear arrays in Nd-Hf isotope space, the global silicate Earth array (“the terrestrial array”) and the global ferromanganese crust and nodule array (“the seawater array”). The offset between these two arrays provides evidence for the sources and mechanisms by which these elements are added to seawater. However, the reason for this offset is under debate, with the two preferred hypotheses being (i) incongruent release of Hf during continental weathering and (ii) hydrothermal supply of Hf to seawater.

In this paper we revisit the cause for the offset of the seawater array from the terrestrial array using simple mass balance considerations. We use these calculations for a test to what degree the seawater array can be a product of preferential weathering of “non-zircon minerals” of the upper continental crust, implying retention of zircons in the solid residue of weathering. Lutetium-Hf and Sm-Nd evolution and mixing calculations show that the global seawater array can be generated with continental sources only. On the other hand, a predominantly hydrothermal origin of Hf in the ocean is not possible because the seawater Hf isotopic composition is significantly less radiogenic than hydrothermal sources and requires a minimum contribution of 50% continental Hf. While hydrothermal sources may contribute some Hf to seawater, continental contributions are unambiguously required to balance the budget.

Reaction between ascending melt and peridotite: An experimental investigation

G. VAN DEN BLEEKEN¹, O. MÜNTENER^{1,2} AND P. ULMER³

¹Institute of Geological Sciences, University of Bern,
Switzerland (greg.vandenbleeken@geo.unibe.ch)

²Institute of Mineralogy and Geochemistry, University of
Lausanne, Switzerland (othmar.müntener@unil.ch)

³Institute for Mineralogy and Petrology, ETH Zürich,
Switzerland (peter.ulmer@erdw.ethz.ch)

Melt-rock reaction in the upper mantle is known from a variety of ultramafic rocks and is an important process in modifying melt composition on its way from the source to the surface. Evidence for depletion or enrichment by melt percolation is found in ophiolites, mantle xenoliths, and mantle sections exposed along MOR's. It includes disequilibrium textures, changes in major-to-trace element compositions and isotopic ratios.

In this experimental study, we present a consistent set of data to evaluate the compositional and time-dependent evolution of ascending magma over a range of temperatures and pressures as a function of initial melt and peridotite compositions. In order to simulate melt-peridotite reaction processes, we perform nominally dry piston cylinder experiments with a 3-layered setup: a bottom layer composed of vitreous carbon spheres (serving as a melt trap) overlain by a peridotite layer and on top a “melt layer” corresponding to a primitive MORB composition. The peridotite layer is mixed from pure separates of orthopyroxene, clinopyroxene and spinel (Balmuccia peridotite), and San Carlos olivine. Melt from the melt layer is forced to move through the peridotite layer into the melt trap. Therefore this setup allows us to simulate reactive melt flow, as opposed to other experimental studies in which diffusion is the main driving force for reaction between a melt and a mantle rock.

Experiments have been conducted at 0.8 GPa with peridotite of variable grain sizes, in the temperature range 1200 to 1320°C. In this P-T range, representing conditions encountered in the thermal boundary layer beneath MOR's, migrating melt is subjected to fractionation, whereas the peridotite is partially melting (solidus around 1260°C). Results show a strong dependence between phase relations in the melt layer and changes in the modal composition of the peridotite layer. Textural and compositional evidence demonstrate that reaction between percolating melt and peridotite occurs by a combination of dissolution-reprecipitation and, to a lesser degree, by solid-state diffusion. Glass compositions in our melt layers resemble those from crystallization experiments on the pure starting liquid at similar P-T conditions (Villiger *et al.*, J. Petr., 2007), but change progressively in the peridotite layers. Silica and alkali enrichment are the most significant changes.

Unravelling the sources of silica in early-Archaean cherts with silicon isotopes

S.H.J.M. VAN DEN BOORN¹, M.J. VAN BERGEN¹,
P.Z. VROON² AND W. NIJMAN¹

¹Department of Earth Sciences, Utrecht University, Utrecht,
The Netherlands (boorn@geo.uu.nl)

²Faculty of Earth and Life Sciences, Free University
Amsterdam, Amsterdam, The Netherlands
(pieter.vroon@falw.vu.nl)

Significant controversy exists regarding the origin of silica in early-Archaean cherts and the mechanism of their formation. Solving these questions is opportune, since recent studies have used oxygen and silicon isotopic signatures of cherts to infer high temperatures for early-Archaean oceans (Knauth and Lowe, 2003; Robert and Chaussidon, 2006). For example, do these cherts represent primary precipitates from a silica-saturated Archaean ocean or are they the products of hydrothermal emanations (Kato and Nakamura, 2003)?

We present silicon isotope data for a suite of samples from well-studied chert outcrops (3.0-3.5Ga) in the Pilbara greenstone belt (Western Australia). Our samples cover a range of depositional environments, and include both stratiform and dike cherts. Based on mineral assemblages (sericite, Ti-oxide and zircon versus Fe-(oxy)hydroxides), major element chemistry (e.g. Al₂O₃ content) and Eu and Y/Ho anomalies, we distinguish chemically precipitated cherts (C-cherts) from silicified-precursor cherts (S-cherts). The silicon isotopic composition ($\delta^{30}\text{Si}_{\text{NBS28}}$) of C-cherts ranges from -1.6‰ to 0.7‰, whereas S-cherts are all positive and range from +0.1‰ to +1.1‰. The observed trend for C-cherts is attributed to mixing between ³⁰Si-depleted hydrothermal fluids and ³⁰Si-enriched seawater. S-cherts, on the other hand, are inferred to be products of pervasive silicification of volcanic precursor material by seawater. Hence, we envisage the involvement of three main reservoirs of silica in the formation of Archaean cherts: (1) seawater; (2) hydrothermal fluids; and (3) precursor sediments or rocks. We show that Si isotopes are particularly effective in discriminating seawater from hydrothermally derived silica. In addition, the silicon isotopic composition of chert-dike samples facilitates the distinction between silicified precursor fragments (e.g. entrained sediments that slid into cracks from the sea floor) and purely chemical precipitates.

Our findings point to multiple modes of chert formation in the early Archaean, which has important implications for the interpretation of their geochemical signatures in terms of seawater properties.

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Genesis of intermediate to silicic igneous rocks at the end of the Sveconorwegian (grenvillian) orogeny

J. VANDER AUWERA, M. BOGAERTS AND O. BOLLE

Department of Geology, University of Liège, Belgium
(jvdauwera@ulg.ac.be)

The origin of voluminous granitoids at convergent plate margins and in postcollisional settings is a key question in understanding the evolution of the continental crust. In southern Norway, the end of the Sveconorwegian collision orogeny (1.13-0.9 Ga) was marked by the emplacement of abundant ferroan, metaluminous granitoids (0.96-0.95 Ga) mainly in the center of the Telemarkia terrane. These granitoids are dominated by intermediate to silicic compositions but rare mafic facies do also occur. We present here a quantitative assessment of the possible process linking these mafic facies to the dominant intermediate compositions using a combination of available major and trace elements as well as experimental data. Fractional crystallization of an ilmenite bearing noritic cumulate from the parent mafic composition produces a residual liquid with an appropriate intermediate composition after 67 % crystallization. There is also a good match between the calculated and observed trace elements as well as H₂O contents of the residual liquid. However, the calculated La and Ce contents are lower than the observed ones. 20% to 30% non modal batch melting of an amphibolitic source equivalent in bulk composition to the mafic facies also provides a good match between observed and calculated major and trace elements composition. Moreover, considering an H₂O content of the amphibolitic source of 1.25%, the produced intermediate liquid has an H₂O content ranging from 4 to 6 wt % in agreement with experimental constraints on the H₂O contents of the intermediate facies (5-6 wt % H₂O). This degree of partial melting is in agreement with modelled melt escape threshold which allows segregation and transfer of magma towards the upper crust. Thus both fractional crystallization and non modal batch melting satisfactorily predict the geochemical features observed in the granitoids and it is possible that both processes occurred simultaneously. Interestingly, both processes produce abundant mafic rocks, either as cumulates or residues, which must be equivalent to twice as much as the observed granitoids. As geological and geophysical evidence for large volumes of dense mafic rocks in the mid sveconorwegian crust is lacking, we suggest that these dense mafic rocks were produced in the lower crust but at a pressure lower than about 1 GPa as the low La/Yb of this magmatic suite precludes the involvement of garnet in their petrogenesis. Formation of these granitoids thus contributed to the vertical stratification of the proterozoic continental crust from a mafic lower crust to a more evolved upper crust.

Thermochronological age – elevation profiles, denudation rates and relief development

PETER VAN DER BEEK

Laboratoire de Géodynamique des Chaînes Alpines,
Université Joseph Fourier, Grenoble, France
(pvdbeek@ujf-grenoble.fr)

Sampling age – elevation profiles has become a standard technique in thermochronology to determine temporal variations in denudation rates. In general, however, these analyses have considered the problem as one-dimensional, implicitly assuming that the samples record a common thermal history because the profile is vertical or denudation rates are regionally constant, and thus neglecting potential effects of topography or laterally varying denudation rates on age-elevation profiles. Although the influence of temporally steady-state topography on thermochronological age-elevation profiles is well understood, the potential effects of transient topography have not as yet been addressed in detail.

We explore the capacity of low-temperature thermochronology data, in particular thermochronological age-elevation profiles, to provide joint constraints on the denudation and relief history of mountain belts. To answer the question whether we can differentiate regional changes in exhumation rate from relief changes by analyzing thermochronological age-elevation profiles, we combine a three-dimensional thermal-kinematic model to predict thermal histories and thermochronological ages from an input denudation and relief history, with an inversion scheme based on the neighborhood algorithm. We explore both synthetic data and a new thermochronological (zircon and apatite fission-track, apatite (U-Th)/He) dataset collected along an age-elevation profile in the French western Alps, a region that has experienced modest tectonic activity but intense glaciation during the last few myr. Our results suggest that multiple thermochronometers are required along an elevation profile to discriminate between different denudation and relief history scenarios, and that relief has increased significantly in our study area over the last few myr, possibly resulting from focused glacial valley erosion during Quaternary glaciations.

Blueschist-facies rehydration of eclogites: Constraints on subduction channel fluid-rock interaction from the Tian Shan (China)

F. VAN DER STRAATEN¹, V. SCHENK¹, T. JOHN² AND J. GAO³

¹Institut für Geowissenschaften and SFB 574, University of Kiel, Germany (fs@min.uni-kiel.de)

²Physics of Geological Processes (PGP), University of Oslo, Norway (timm.john@fys.uio.no)

³Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, PR China (gaojun@mail.igcas.ac.cn)

Exhumed eclogites from orogenic belts may show a retrograde blueschist-facies overprint with still preserved eclogite-facies relics. This overprint occurs during uplift when infiltrating fluids cause the growth of hydrous minerals such as sodic amphibole, epidote and white mica. We are studying this rehydration process and its P-T-X conditions to unravel the source of the retrograde subduction fluids and the exhumation path.

In eclogites from the Tian Shan, garnet, omphacite and rutile represent the assemblage of the eclogite stage. If a blueschist-facies overprint has occurred, omphacite and garnet are partially replaced by glaucophane, white mica and epidote. This rehydration was associated with massive growth of carbonate, pointing to an infiltration of an H₂O- and CO₂-rich fluid. Whole-rock major and trace element analyses show an increase of LILE (K, Cs, Rb and Ba) and volatiles in the rehydrated blueschist, presumably incorporated in white mica. The increase of Mn, Mg, Fe and CO₂ leads to the precipitation of ankerite. Partially dissolved apatite, epidote minerals and garnet released significant amounts of REE, Pb, Sr, U and Y into the infiltrating fluid. From mass-balance calculations it is evident that up to 25 % of the REE were mobilized while the eclogite has been transformed to blueschist.

Based on geothermobarometry, the P-T evolution during rehydration under blueschist-facies conditions is characterized by contemporaneous cooling and decompression. The most likely uplift path is the so called ‘subduction channel’ which is the serpentinized part of the mantle wedge above the downgoing slab. Fluids can infiltrate eclogites, rehydrate them and force their uplift because of reduced density and the resulting buoyancy. In addition, this process is aided by the high H₂O-content and the modified rheology of the mantle wedge. The observed data indicate that the subduction channel fluids do not only change the petrophysical properties due to metamorphic reactions, they also induce metasomatic changes in the reacting rocks.

¹⁴C lipid biomarker ages in surface sediments off the five great Russian arctic rivers

BART E. VAN DONGEN^{1,2} IGOR SEMILETOV³ AND
ÖRJAN GUSTAFSSON¹

¹Stockholm University, Dept. of Applied Environmental Science, Stockholm, Sweden,
(orjan.gustafsson@itm.su.se)

²University of Manchester, School of Earth, Atmospheric and Environmental Sciences, Manchester, United Kingdom,
(Bart.vandongen@manchester.ac.uk).

³International Arctic Research Center, University of Alaska Fairbanks, Fairbanks, Alaska, USA,
(igorsm@iarc.uaf.edu)

Numerical climate models forecast an amplified warming in the Arctic continental region, making it reasonable to expect that substantial effects of global warming will be first observed here. This will involve effects on the huge amounts of 'old' organic matter stored in Siberian soils. However, existing studies are inconclusive whether there is currently a climate-warming induced release of 'new' old carbon from the land. Therefore, surface sediments off the five Great Russian Arctic Rivers (GRARs), spanning 140 deg longitude, were investigated for their lipid biomarker composition and high molecular weight (HMW) *n*-alkanes and *n*-alkanoic acids were isolated and used for compound-specific radiocarbon analysis (CSRA) to obtain information on the ¹⁴C-based reservoir age of the OM currently released from the Russian-Siberian permafrost.

In contrast to the F_{modern} bulk values, which show a decrease across the climosequence from 0.69-0.83 in the west to 0.39-0.50 in the east, CSRA of both the isolated HMW *n*-alkanes and *n*-alkanoic acids indicate on average the release of relative older terrestrial material organic material (OM) by the Western GRARs (F_{modern} 0.24-0.34), compared to the Eastern (F_{modern} 0.31-0.50).

Global warming is expected to affect the permafrost areas in the continental Siberian Arctic, causing them to shrink. This will probably lead to a deeper water penetration of the soil and, consequently, the liberation/transport of 'older' terrestrial material stored in these layers. The eastern GRARs CSRA results indicate that the majority of the source of this terrestrial OM transported to the estuaries in these areas are originating from the 'top' (relative younger) part of the soil. In contrast, the western areas are presently much less influenced by permafrost, indicating that the water can penetrate deeper and consequently can liberate/transport 'older' OM to the estuaries. In addition, this 'older' OM is most likely more degraded, which agrees with the biomarker analyses.

Although this benchmark study suggests presently no major release of remobilized 'old' OM through the eastern GRARs, the results of the western GRARs shows how amplified warming in the Arctic might influence the stored OM; a scenario which would have major implications for the global carbon cycle and climate.

Effect of self-consistently generated plate tectonics on stirring by mantle convection in a 3-D spherical shell

HEIN VAN HECK¹ AND PAUL J. TACKLEY²

¹Institut für Geophysik, ETH Zürich, Switzerland
(grotebaas@hotmail.com)

²Institut für Geophysik, ETH Zürich, Switzerland
(ptackley@ethz.ch)

The stirring of heterogeneities by mantle convection is a key process in explaining geochemical observations, but to date most studies have been performed in only two-dimensional geometry. If 3-D convection has only poloidal motion, then its stirring efficiency is similar to that of 2-D convection [Coltice and Schmalzl, 2006], but the presence of toroidal motion could make a major difference because it can lead to chaotic stirring paths even in a steady-state flow [Ferrachat and Ricard, 1998].

Toroidal flow is mainly associated with plate motions. Two previous studies have assessed the influence of steady-state present-day plate motions on mantle stirring [van Keken and Zhong, 1999; Stegman *et al.*, 2002]. Here we instead study flows in which time-dependent plate tectonics is self-consistently generated by the rheology, similar to [Tackley, 2000] but in a spherical shell, and has a toroidal:poloidal ratio in the range observed for the Earth. Several diagnostics are used to measure the efficiency of dispersion and stretching and their spatial variation. Stirring in plate tectonics convection is compared to stirring in other convective flows that have similar convective vigor and wavelength but without plate tectonics. Three-dimensional "plate tectonic" flows are also compared to equivalent two-dimensional flows, in order to test whether the findings of [Coltice and Schmalzl, 2006] still hold when toroidal motion is also present in the 3D cases. The effect of 'realistic' depth-dependence of viscosity and other material properties is also assessed.

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Geochemistry of micas associated with tantalum mineralization in the Tanco pegmatite, Canada

M. VAN LICHTERVELDE¹, R.L. LINNEN², M. GRÉGOIRE³,
D. BÉZIAT⁴ AND S. SALVI⁴

¹Bundesanstalt für Geowissenschaften und Rohstoffe,
Stilleweg 2, D-30655 Hannover, Germany.
(marieke.lichtervelde@bgr.de)

²Department of Earth Sciences, University of Waterloo,
Waterloo, ON, N2L 3G1, Canada

³CNRS-UMR5562 DTP OMP, University Paul Sabatier, 14
Av E. Belin, F-31400 Toulouse, France

⁴CNRS-UMR5563 LMTG OMP, University Paul Sabatier, 14
Av E. Belin, F-31400 Toulouse, France

Tantalum is a high-tech metal which is mainly mined from rare-element pegmatites. Although the mineralogy of tantalum is well constrained, very little is known about the mineralizing processes, and in particular the role of fluids in the formation of Ta ore. In many Ta deposits, the high-grade Ta ore is associated with late micaceous alteration of central pegmatite zones. Such metasomatism was commonly interpreted as hydrothermal (i.e., due to aqueous pegmatitic fluids). However, the recent discovery of melt inclusions with extremely high concentrations of volatiles (H₂O, B, F, etc...) has provided an alternate explanation. Such melts could be at the origin of the metasomatic alteration commonly encountered in granitic pegmatites.

In the Tanco pegmatite, one of the world's major tantalum deposits, micas are common accessory phases that are intimately associated with the successive stages of Ta mineralization, from the wall zone to the central zone where micaceous replacement is pervasive. The different generations of micas, both primary and secondary, associated with Ta oxides, were analyzed by electron microprobe and LA-ICP-MS in order to investigate the magmatic-metasomatic transition in the Tanco pegmatite. Their chemical composition trends permit to determine whether they crystallized from a melt or an aqueous fluid.

The primary micas range from dioctahedral muscovite to trioctahedral lepidolite and show high Li-F as well as Ta (100 to 250 ppm) contents. On the other hand, replacement micas consist of end member muscovite with high B and low Li-F and Ta (around 40 ppm) contents. The B-rich and Na-Li-Ta-poor compositions of replacement micas compared to primary micas suggest that they crystallized from a B-rich aqueous fluid. This fluid would have coexisted with a late Li-rich, Ta-saturated melt, which is consistent with an immiscibility model as advocated by Veksler and Thomas (2002).

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Aluminum diffusion and Al-vacancy association in MgO

JAMES A. VAN ORMAN¹, CHEN LI^{1,2},
KATHERINE CRISPIN¹ AND YINGWEI FEI³

¹Case Western Reserve University, jav12@case.edu

²University of Arizona, Department of Geosciences

³Geophysical Laboratory, Carnegie Institution of Washington

Periclase, with end-member formula MgO, is the second most abundant mineral in Earth's lower mantle and may play a significant role in chemical exchange across the core-mantle boundary. Aluminum and other trivalent cations diffuse very rapidly through periclase, orders of magnitude faster than divalent cations such as Mg. This is opposite to what is observed in most silicate minerals, where highly charged cations are generally among the slowest diffusing species. The culprit appears to be a highly mobile defect associate consisting of a cation vacancy electrostatically bound to a trivalent cation [1]. Lidiard [2] developed the theory for divalent cation diffusion in alkali halide crystals, and we extend it to describe the functional dependence of trivalent cation diffusivity on concentration in alkaline earth oxides. The theory is applied to Al diffusion profiles in MgO obtained from experiments over a wide range of pressures and temperatures (1 atm to 25 GPa and 1577 to 2273 K). A family of synthetic diffusion profiles was calculated numerically, for various combinations of Al-vacancy pair diffusivity and binding energy, and the best fit for each experimental profile was determined by chi-square minimization. The binding energy for all but one experiment is in the range 0.45-0.62 eV, slightly lower than theoretical values [3] of 0.65-0.71 eV, and shows no clear dependence on temperature or pressure. The activation energy for Al-vacancy pair diffusion is 2.1 eV, and the activation volume is 2.9 cm³/mol.

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Reconciling ^{210}Pb deficits with the physics of melt extraction

JAMES A. VAN ORMAN¹ AND ALBERTO E. SAAL²

¹Case Western Reserve University, Department of Geological Sciences, (james.vanorman@case.edu)

²Brown University, Department of Geological Sciences, (Alberto_Saal@brown.edu)

Short-lived intermediate daughters in the uranium decay series have a broad range of half-lives suitable for timing melt production and transport processes beneath mid-ocean ridges. The discovery two decades ago of ^{226}Ra excesses in mid-ocean ridge basalts constrained the time between Ra-Th fractionation and eruption to be on the order of 1000 years or less. The recent discovery of ^{210}Pb deficits, correlated with ^{226}Ra excesses in mid-ocean ridge basalts [1], indicates that the timescale must be much shorter still—less than 100 years.

A critical question is what part of the melting process the ^{210}Pb - ^{226}Ra disequilibrium is timing. If the fractionation can only be produced during partial melting in the mantle, then the observed disequilibrium implies melt transport rates on the order of km/yr, which would present a serious challenge to our physical understanding of melt extraction. Another possibility is that the ^{210}Pb - ^{226}Ra disequilibrium results from crustal processing. Numerical models have shown that shallow-level diffusive exchange with gabbroic cumulates is capable of producing ^{226}Ra excesses (or deficits) in the melt [2,3]. We have found that the same process leads to ^{210}Pb deficits.

A plagioclase or clinopyroxene grain interacting with its surroundings develops internal steady-state daughter concentration profiles, which represent a balance of radioactive production and decay and diffusive fluxes³. Because the half-life of ^{210}Pb is short compared to the timescale for Pb diffusion, the spatial distribution of ^{210}Pb activity within each mineral closely follows that of ^{226}Ra . Ra is much less compatible than Pb, and ^{210}Pb is thus more depleted within the interior of the mineral grain than it would be if partitioning equilibrium were achieved. The result is that ^{210}Pb is absorbed far more readily than ^{226}Ra from any melt it comes in contact with, leaving the melt with a ^{210}Pb deficit. This deficit develops rapidly, and reaches a steady-state value on a timescale comparable to the half-life of ^{210}Pb , about 20 years. The magnitude of the deficit is only weakly dependent on the enrichment of the melt and on the relative diffusivities of Ra and Pb in the minerals, but is sensitive to the melt/rock ratio and to the relative mineral/melt partition coefficients of Ra and Pb. A typical value of the $^{210}\text{Pb}/^{226}\text{Ra}$ activity ratio following gabbro exchange is ~ 0.1.

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Carbon and iron isotopic evidence for photosynthesis in a 3.5 Ga old shallow marine depositional environment

M. A. VAN ZUILEN¹, C. THOMAZO¹, B. LUISAIS² AND P. PHILIPPOT¹

¹Laboratoire Géobiosphère Actuelle et Primitive, Institut de Physique du Globe de Paris, CNRS & Université Denis Diderot, France, (vanzuielen@ipgp.jussieu.fr) thomazo@ipgp.jussieu., frphilippo@ipgp.jussieu.fr,

²CRPG-CNRS, Vandoeuvre-les-Nancy, France, (luisais@crpg.cnrs-ancy.fr)

Different abiologic and biologic models exist for the oxidation of Fe(II)aq in the upper part of the Archean ocean; UV-induced photochemical reactions, anoxygenic photosynthetic iron oxidation, or reaction with free oxygen generated by oxygenic photosynthesis. In the O₂-poor, and CO₂-rich Archean ocean these processes would have competed with direct precipitation of Fe-carbonates. Here we discuss the origin of Fe-oxides that occur in the 3.49 Ga old Chert-Barite-Unit of the Dresser Formation at North Pole (Pilbara Drilling Project, Western Australia). This unit represents a shallow water depositional environment within a volcanic caldera, and has experienced low-grade metamorphism (<350°C). It consists from bottom to top of bedded cherts, barite-sulfide beds, and bedded Fe-rich carbonates. An underlying network of barite- and silica-feeder dikes suggests syndimentary hydrothermal activity. Towards the top of the unit, a succession of thin alternating bands of hematite and Fe-rich carbonate occurs, that includes kerogenous laminations that resemble typical microbial mats. These laminations display a $\delta^{13}\text{C}$ (-30 to -18‰), that is distinctly different from the $\delta^{13}\text{C}$ of kerogen in the underlying silica dikes (-34 to -31‰). The isotopic discrepancy between these two pools of kerogen cannot be explained by metamorphism. The hematite bands display a strong positive $\delta^{56}\text{Fe}$ (+0.1 to +1‰), compared to the Fe-rich carbonates (-0.6 to +0.4‰) and underlying barite-sulfide beds (-0.7 to -0.4‰). These petrographic and isotopic observations exclude abiologic oxidation of Fe(II)aq by UV-induced photolysis, and suggest that oxygenic and/or anoxygenic photosynthesis were directly involved in the formation of Fe-oxides in this Early Archean shallow marine depositional environment.

Geochemical characteristics of the Quaternary volcanic rocks from Hatay region, Southern Turkey: Evidence for lithospheric mantle source

E. VAROL¹, R. FREI², M. ALPASLAN³, M. A. KURT³
AND A. TEMEL¹

¹Hacettepe University, Dept. of Geol. Engineering, 06800, Beytepe-Ankara, Turkey (elvarol@hacettepe.edu.tr; atemel@hacettepe.edu.tr)

²Geological Institute University of Copenhagen, Oster Voldgade 10, DK-1350 Copenhagen, Denmark (robertf@geol.ku.dk)

³Mersin University, Department of Geology, 33343, Çiftlikköy-Mersin, Turkey (malpaslan@mersin.edu.tr; malikurt@mersin.edu.tr)

The Hamam-Reyhanli (Hatay) region located in southern part of Turkey, consists of two distinct phases of Quaternary basaltic volcanism that display different geochemical characteristics. The first phase includes alkaline basalts and the second one tholeiitic basalts with SiO₂ contents ranging from 45.55-46.4 and 48.94-50.56 respectively. The former group contain high LILE, LREE, low HREE, Y contents, low Sr and high Nd isotopic values and display negative K, positive Nb, Ta anomalies as compared with the latter group. The geochemical data indicate that all the volcanic rocks are derived from a metasomatically enriched mantle source. The crustal contamination is not an important process in the evolution of the samples. The trace elements and isotopic characteristics of both group suggest that they were derived by partial melting of different depth of a lithospheric mantle source. The higher La/Yb, Zr/Y and La/Nb (<1) ratios reveal that the first group volcanic rocks are derived from a deeper mantle source than the second group.

The relative tempo of weathering and erosion controls supergene metal accumulation

P.M. VASCONCELOS

The University of Queensland, Earth Sciences, Brisbane, Qld, Australia (paulo@earth.uq.edu.au)

When the balance between weathering and erosion favors the former, chemically and mineralogically stratified weathering profiles may develop. Weathering may promote the supergene enrichment of mineralized lithologies or the formation of ore deposits from unmineralized substrates. In the first case, weathering is an ore-enrichment process; in the second, weathering is an ore-forming process. Geochronological constraints indicate that under conducive climatic and tectonic conditions, supergene enrichment of some ore deposits may occur extremely fast (less than 1 Ma; e.g., Ok Tedi). Weathering geochronology, on the other hand, indicates that supergene ore bodies in stable cratonic areas may be continuously exposed to weathering for more than 70 Ma (e.g., Carajás). Protracted exposure suggests that some supergene deposits may not reflect any one specific climatic condition, but record the combined effects of changing climates through time. Variations in precipitation, evapotranspiration, vegetation cover, and biological activity ultimately control the composition of the weathering solutions and the mechanisms affecting the dissolution, transport, and redeposition of ore elements in supergene systems. Weathering geochronology and cosmogenic isotope studies provide quantitative constraints on longevity of weathering profiles, rates of physical and chemical erosion, and rates of supergene transport and redistribution of ore elements in supergene systems. Particularly significant are contributions from ⁴⁰Ar/³⁹Ar geochronology of supergene Mn-oxides and alunite-group sulfates; (U-Th)/He dating of supergene Fe-hydroxides; and ²⁶Al, ¹⁰Be, and ³He constraints on erosion rates. Results from these studies reveal that most supergene ore bodies preserved on the surface of the planet are younger than ca. 70 Ma (some much younger); resulted from protracted and episodic dissolution and reprecipitation of ore minerals, with effective leaching of deleterious elements; and are preserved in areas of low to very low (less than 1 m.Myr⁻¹) erosion rates. The application of these analytical approaches on a global scale indicates that paleoclimates in the late Cretaceous-early Paleocene, the early Eocene, and the early to mid Miocene were especially conducive to weathering-driven ore forming processes.

Petrogenesis of fayalite granitoids: New insights from metapelitic xenoliths

P. VÁSQUEZ¹, G. FRANZ¹, J. GLODNY² AND
R.L. ROMER²

¹Technische Universität Berlin, Ackerstraße 71-79, 13355,
Berlin, Germany. (pauvasquez@yahoo.es)

²GeoForschungsZentrum Potsdam, Telegrafenberg, 14473
Potsdam, Germany.

Fayalite-bearing granites are fairly uncommon granitoids, related mainly to alkaline and evolved magmatism usually associated with intraplate settings or anorogenic magmatism. Fayalite granitoids have recently been reported from the Cobquecura Pluton of Central Chile, SW margin of Triassic Gondwana. We discuss their petrogenesis in the light of their geochemical and isotopic characteristics. The Cobquecura Pluton is an epizonal, partly fayalite-bearing intrusive suite, composed mainly of gabbro and granite. Both fayalite-granitoids and gabbros contain hercynite-rich metapelitic xenoliths with a composition different to the metamorphic basement in the area, but similar to that expected for the (restitic) lower crust.

The Cobquecura rocks (SiO₂ = 48 - 76 wt.-%) are sub-alkaline, with high FeO*/(FeO*+MgO) ratios. REE patterns are fairly flat (La_N/Sm_N = 1.12 - 3.39; Lu_N/Gd_N = 0.59 - 0.76). Patterns are nearly parallel, with steeper slopes for the LREE as typical for fractional crystallization processes. However, the fayalite-granitoids are richer in REE-content than the fayalite-free granites despite the higher SiO₂-content of the latter. The trace element signature of metapelitic xenoliths in gabbros and fayalite-granitoids differs from the metapelitic basement in the area. The xenoliths are richer in compatible elements, and their overall chemical signature is very similar to that of the fayalite-granitoids. Fayalite granites have high ⁸⁷Sr/⁸⁶Sr_i (~0.707) for their corresponding εNd values (-0.6 to -0.7). Pb-isotopic fingerprints of the fayalite granite (²⁰⁶Pb/²⁰⁴Pb = 18.22 - 18.25, ²⁰⁷Pb/²⁰⁴Pb = 15.64 - 15.62 and ²⁰⁸Pb/²⁰⁴Pb = 38.13 - 37.8) are similar to those of the metapelitic xenoliths (²⁰⁶Pb/²⁰⁴Pb = 18.22 - 18.39, ²⁰⁷Pb/²⁰⁴Pb = ~ 15.6 and ²⁰⁸Pb/²⁰⁴Pb = 37.62 - 38.25).

The origin of fayalite granites has been discussed in terms of (i) fractionation from a mafic magma and (ii) partial melting of a dehydrated source, like granulites of the lower continental crust. The restitic nature of the pelitic xenoliths suggests that they come from the middle or lower crust. The major element behaviour suggests that the fayalite granites are a product of fractionation from the gabbros of this suite. However, close similarities between xenoliths and fayalite granites in terms of Pb isotope and trace element signatures point to Fe-rich medium or lower continental crust assimilation as an important process in fayalite granitoid petrogenesis.

A reassessment of prebiotic sources of carbon in the early Earth

ARON VECHT

Aron Vecht and Associates. London NW11 7DL, England
(phosphors@vecht.com)

A major reassessment of the sources of carbon is required to explain a range of anomalies associated with carbon distribution in the early earth and in the post Hadean periods.

Among these we might list:-

A. The early earth crust whether sub-continental:-acidic or granitic, or sub-oceanic:-basic or basaltic contains a very small concentration of carbon, less than 100 ppm. The sedimentary rocks which are assumed to be directly or indirectly derived from these materials contain well over 5% of carbon.

B. The earliest sources of carbon can not be assumed to have been derived from living matter and a prebiotic source of carbon must have existed in realistic quantities. Even if the micro-structural and isotopic evidence for the existence of life around 3.8Ga is assumed, which is an open question, a source of carbon must be established.

C. The large deposits of methane hydrates as well as the more recent sources of methane (Lake Kivu) cannot be explained as purely to organic sources.

To explain the above anomalies we wish to propose the concept of 'reactive minerals'. We believe that a considerable number of reactive minerals exist well below the earth's surface. Such minerals would react with water, water vapour and/or oxygen when approaching the surface. We could cite carbides and sulphides as examples, more specifically calcium and aluminium carbide. It is well known that these compounds are stable at high temperatures but react if exposed to water or oxygen. In the former case they would initially yield methane or acetylene if confined to a neutral or reducing environment, or under oxidising conditions they would yield CO₂. This in turn would form carbonates and at higher temperatures result in the formation of oxides and silicates.

The existence of such reactive minerals would explain how pre-biotic sources existed from which living matter could have developed. It will also show that our present figures regarding the actual carbon content of the earth are low and true values would now be in line with the carbon content of other planets and interstellar materials.

Kinetics of liquid immiscibility in the system K_2O - CaO - FeO - Al_2O_3 - SiO_2

I.V. VEKSLER¹, A.M. DORFMAN², R. WIRTH¹ AND D.B. DINGWELL²

¹GeoForschungsZentrum Potsdam, Telegrafenberg, Potsdam, D-14473 Germany (veksler@gfz-potsdam.de)

²Ludwig-Maximilian University, Theresienstrasse 41, Munich, D-80333 Germany (dingwell@lmu.de)

Our previous experiments on natural ferrobasic liquids showed that silicate liquid immiscibility may be seriously hampered by slow kinetics, metastable crystallization of tridymite, and the formation of sub-micron immiscible emulsions. Here we present new experiments on three synthetic compositions in the system K_2O - CaO - FeO - Al_2O_3 - SiO_2 . Two of the selected compositions lie inside the known miscibility gaps on the joins fayalite-orthoclase-silica and fayalite-hedenbergite-orthoclase-silica. The third composition lies on the anorthite-fayalite cotectic, well outside of known regions of stable or metastable liquid immiscibility. The charges in sealed Fe containers were first kept for 24 hours at a constant super-liquidus temperature, and quenched. Then, they were rapidly re-heated to the same temperature, and subjected to in situ centrifugation for 4 hours under acceleration of 1000 g. The aim of centrifugation was to distinguish between sub-liquidus emulsions due to quench, and those that may have formed by stable, super-liquidus immiscibility. The final glasses were studied by electron microprobe and transmission electron microscopy (TEM).

High-temperature super-liquidus emulsions formed in all the three compositions. The emulsions showed a remarkable stability, and did not completely break during centrifugation. Phase separation appears to be the fastest in the Ca-free composition on the fayalite-orthoclase-silica join. Here individual droplets readily grow to sizes of dozens and hundreds of microns, and merge to continuous liquid pools. The growth, coalescence and settling of droplets are significantly slower in the Ca-bearing fayalite-hedenbergite-orthoclase-silica composition. However, the most interesting and unexpected result was the formation of very fine, sub-micron emulsion in the composition on the anorthite-fayalite cotectic, where immiscibility had never been reported. The emulsion quenched to optically transparent glass, and could be revealed only by high-temperature centrifugation, electron microprobe profiles, and TEM.

Our results imply that the kinetics of silicate liquid immiscibility strongly depends on melt composition and viscosity. In some compositions, immiscibility may not develop beyond sub-micron scale for hours or days, and can be overlooked in conventional static experiments. If actual regions of silicate immiscibility are broader than presently thought, the petrogenetic role of immiscibility should be also revisited. In nature, large, slowly cooling magma chambers appear to offer enough time, and the best conditions for a full development of silicate liquid immiscibility.

Molecular and isotopic biogeochemistry of Neoproterozoic sediments in the Rio de la Plata Craton

M. VELASQUEZ¹, J.E. SPANGENBERG¹, C. GAUCHER² AND P.C. BOGGIANI³.

¹Institut of Mineralogy and Geochemistry, University of Lausanne, Switzerland; Mariluz.Velasquez@unil.ch, (Jorge.Spangenberg@unil.ch)

²Faculty of Sciences, Department of Geology, Montevideo, Uruguay; (gaucher@chasque.net)

³Institute of Geosciences, University of Sao Paulo, Brazil; (boggiani@usp.br)

The Upper Ediacaran Arroyo del Soldado group (ASG) in Uruguay and Corumbá group (CG) in SW-Brazil were deposited on the same passive continental margin of the Rio de la Plata Craton. They contain a largely unmetamorphosed sedimentary sequence of alternating siliciclastic and carbonate rocks, that have been investigated by inorganic and organic geochemical methods in order to get new insight about changes in climate and chemistry of oceans during the Neoproterozoic in SW-Gondwana.

We report isotopic data from carbonates ($\delta^{13}C_{carb}$ and $\delta^{18}O$) and associated organic carbon ($\delta^{13}C_{ker}$ and $\delta^{15}N_{ker}$), together with hydrocarbon distribution and concentrations of major, trace and rare earth elements (REE). The $\delta^{13}C_{carb}$ values display coeval excursions in the two groups (ASG, CG) and range from -5.7 to 5.7‰. Dolostones from the Bocaina Formation in CG show the lowest $\delta^{13}C_{carb}$ values, a typical signature of cap carbonates worldwide. The $\delta^{13}C_{ker}$ values varying from -26.4 to -22.8‰ in CG and from -27.4 to -12‰ in the ASG reflect variations in the primary composition of organic matter as well as in the productivity rate during deposition. The $\delta^{15}N_{ker}$ values in the CG samples range between -3.3 to -3.1‰, suggesting a primary contribution of cyanobacteria. More positive $\delta^{15}N_{ker}$ values (1.8 to 5.2‰) in the ASG samples reflect most probably a higher planktonic contribution. Positive $\delta^{13}C$ and $\Delta^{13}C_{carb-ker}$ excursions, higher concentrations of redox sensitive elements (Mn, Fe, U and V), REE, and variations in the Ce anomaly in dark organic limestones of both groups can be explained by an increased bioproductivity and preservation of organic carbon at unusually high rates of sedimentation.

The main resolvable compounds in the gas chromatograms of the hydrocarbon saturated fraction are *n*-alkanes in the C_{12-30} (maxima at C_{21}) and C_{14-35} (maxima at C_{26}) ranges for CG and ASG samples respectively, in both cases with no odd-even predominance. Most samples have a hump of unresolved complex mixture in the C_{17-30} range. The predominance of $C_{>18}$ of *n*-alkanes in the ASG samples confirm a marine planktonic input. The biomarker distribution (extended C_{29} to C_{34} hopanes, steranes) in the organic limestones of the CG are diagnostic for not strictly anaerobic bacteria and a diverse community of algae.

Open tube combustion method of organic samples for stable carbon isotope analysis

T. A. VELIVETSKAYA¹, A. V. IGNATIEV¹ AND
S. I. KIYASHKO²

¹Far East Geological Institute FEB RAS, Vladivostok, Russia
(velivetskaya@mail.ru)

²Institute of Marine Biology FEB RAS, Vladivostok, Russia
(sekiyash@mail.ru)

A simple and effective conversion method of organic carbon into carbon dioxide for analysis of stable carbon isotopes ($\delta^{13}\text{C}$) in samples of solid and liquid substances and sedimentary rocks is presented. The conversion of organic carbon of the samples is carried out in a quartz reactor connected to a vacuum line for CO_2 freezing and purification. A solid organic sample mixed with CuO is placed at the reactor bottom and the reactor is subsequently filled up with a granular CuO . One end of the CuO column is preheated up to 850°C while the other end of the column in contact with the sample is kept at ambient temperature. Then, heating of the sample (850°C) and remainder of the column is performed. The preheated part of the column provides the efficient conversion of carbon into CO_2 . The reactor for conversion of volatile organic carbon compounds is filled in with a granular CuO . The column of CuO is heated to 850°C . Volatile liquid organic samples are introduced into the reactor through a septum using a micro syringe. Complete conversion is 10 minutes for solid samples and 3 minutes for volatile liquids. Precision of $\delta^{13}\text{C}$ analysis for solid and volatile liquid organic substances is $\pm 0.1\text{‰}$ and $\pm 0.04\text{‰}$ respectively.

The method presents an alternative to the well established sealed tube methods for combustion of organic material (Buchanan and Corcoran, 1959, Sofer, 1980)

The procedure of preparing the samples for combustion is simplified owing to the use of open tubes instead of sealed ampoules. The repeated use of reactors reduces considerably the consumption of expensive materials. Simultaneous use of several reactors enhances the economical aspects of the method. The method of carbon conversion demonstrates a high accuracy of $\delta^{13}\text{C}$ analysis for solids and liquids. Validity of results is confirmed by the comparison with data obtained by the universally recognized sealed tube combustion method and analysis of international standards reference materials.

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Sulfide mobility during melt percolation: Implications for PGE and Os isotopes from the Oman ophiolite

M. VELZ¹. AND G. BRÜGMANN²

¹Institut für Geologie u. Mineralogie, Uni Köln, Zùlpicher Str. 49b, 50674 Köln. (Michaela.kurth@uni-koeln.de)

²Max-Planck-Institut für Chemie, Abt. Geochemie, Postfach 3060, 55020 Mainz. (bruegman@mpch-mainz.mpg.de)

This study is focused on the origin of Os isotope heterogeneity in the Oman ophiolite in the context of melt percolation and sulfide mobility. Basically, two different sulfide populations occur: (1) *Residual peridotites* contain pentlandite (Pn) and chalcopyrite (Cp). Cp occurs either as thin lamellae or at the margin of Pn. In subgroup 1a, the grain sizes of the rare sulfides range from 10-60 μm . They are associated with opx as spherical inclusions, or they are located at triple junctions of olivines. Sulfides of subgroup 1b occur typically as interstitial, subhedral or anhedral grains with curvilinear boundaries. The grains sizes frequently range from 100 to 400 μm and they are closely associated with spinel and/or cpx, suggesting precipitation from an immiscible sulfide melt. (2) *Non-residual peridotites and pyroxenitic dikes*: The relative abundance of sulfides strongly increases from the residual group to the non-residual group. The primary sulfide assemblage is composed of massive pyrrhotite + Cp + Pn. Large sulfide grains (up to 700 μm) are attached to coarse grained, subhedral cpx and/or spinel. The 1a type residual peridotites have very depleted trace element abundances (e.g. $\text{Yb}_\text{N}(\text{cpx}) \sim 1.1$; $\text{Ti}_\text{N}(\text{cpx}) \sim 0.3$), $(\text{Pd}/\text{Ir})_\text{N}$ ratios of < 1 and low $^{187}\text{Os}/^{188}\text{Os}$ ratios ($^{187}\text{Os}/^{188}\text{Os}_{(t=90\text{Ma})} = 0.1149$ and 0.1169). The unradiogenic Os compositions yield Re depletion ages of ~ 2 Ga. Type 1b residual peridotites have chondritic to suprachondritic Os isotopic ratios ($^{187}\text{Os}/^{188}\text{Os}_{(t=90\text{Ma})} = 0.1234$ to 0.1318) and $(\text{Pd}/\text{Ir})_\text{N} \sim 1$ to 2 . Samples from the non-residual group have suprachondritic Os isotopic ratios ($^{187}\text{Os}/^{188}\text{Os}_{(t=90\text{Ma})} = 0.1367$ to 0.1675). The PGE and REE abundances of pyroxenitic dikes ($\text{Os} = 0.13$ ng/g; $\text{Pd} = 6$ ng/g; $(\text{Pd}/\text{Ir})_\text{N} = 40.4$) resemble those of mantle-derived melts. The PGE and REE distribution patterns of the non-residual peridotites are similar to or transitional between those of the residual peridotites and the pyroxenites. In a $^{187}\text{Os}/^{188}\text{Os}_{t=0}$ vs $1/\text{Os}$ diagram the radiogenic samples define a mixing line having a depleted mantle and radiogenic pyroxenitic dykes as end members. It is suggested that the initial PGE and Os isotopic composition of the Oman mantle has been locally chemically overprinted by percolating melts, dissolving and re-precipitating sulfide liquids. In regions of high melting degrees and/or high melt/rock ratios, the initial PGE budget and Os isotope composition of a mantle rock may be completely replaced by sulfides derived from an Os radiogenic source.

Estimates of particle fluxes and boundary scavenging in the seawater around the Kerguelen Plateau using $^{230}\text{Th}_{\text{xs}}$ and ^{231}Pa

C. VENCHIARUTTI¹, C. JEANDEL¹, M. ROY- BARMAN²
AND R. FREYDIER³

¹LEGOS, OMP/UMR5566, 14 av. Edouard Belin, 31400
Toulouse

(venc@legos.obs-mip.fr, jeandel@legos.obs-mip.fr)

²LSCE/IPSL, 91198 Gif-sur-Yvette

³LMTG, OMP, 14 av. Edouard Belin, 31400 Toulouse

The Kerguelen Ocean and Plateau compared Study (KEOPS, 19 Jan.- 13 Feb. 2005) took place in the wake of Kerguelen, characterized by a recurrent bloom allocated to natural fertilisation due to iron rich shelf inputs.

Particle dynamics (settling velocities, residence times) and dissolved/particle exchanges (boundary scavenging) are essential to understand the mechanisms responsible for the fertilisation over the Plateau. This work proposes to use two oceanic radionuclides ^{230}Th and ^{231}Pa –both decay products of soluble and conservative U and sensitive to scavenging- as particle dynamic tracers.

The measured dissolved and particulate ^{230}Th and ^{231}Pa data are consistent with other published data for near shelf area and open-ocean site. Dissolved excess ^{230}Th (noted $^{230}\text{Th}_{\text{xs}}$) distributions increase linearly with depth down to 700 m at most of the stations. This linear trend reaches the bottom (1550 m) for both tracers at Kerfix, located west of the Kerguelen Plateau, with dissolved concentrations ranging from 0.6 to 11 fg/kg and from 0.02 to 1.8 fg/kg for $^{230}\text{Th}_{\text{xs}}$ and ^{231}Pa respectively.

A reversible scavenging model using the $^{230}\text{Th}_{\text{xs}}$ dataset allowed us to estimate scavenging rates ($k_f \approx 0.3-0.9 \text{ y}^{-1}$), remineralization rates ($k_r \approx 1-5 \text{ y}^{-1}$) and partition coefficients (average $K = 0.15 \pm 0.06$). Assessed particle settling velocities S are 800 m.y^{-1} at Kerfix and surprisingly lower over the biologically productive Plateau with ca. 500 m.y^{-1} . These latter velocities are nevertheless consistent with the high mineralization rates characterizing this area. The deep layers of the three stations located east of the Plateau display depleted tracer distribution (ca. 50% of the Th stock is lost) interpreted as reflecting intense scavenging due to the presence of nepheloid layers.

Single column procedure for quantitative separation and recovery of cadmium (Cd) for high precision isotope analysis by MC-ICP-MS

SOPHIE VERHEYDEN¹, CLAUDE MAERSCHALK¹,
ALYSSA E. SHIEL² AND NADINE MATTIELLI¹

¹DSTE - Université Libre de Bruxelles (ULB) CP 160/02 Av
F.D. Roosevelt, 50, 1050 Brussels, Belgium.

(sophie.verheyden@ulb.ac.be)

²Dept. Earth and Ocean Sciences. University of British
Columbia 6339 Stores Road, Vancouver, V6T 1Z4
Canada.

Cadmium isotope analyses gain increasing interest since terrestrial Cd isotopic compositions can be measured with higher resolution and precision. However, Cd isotopic studies face analytical challenges related to potential low Cd contents, non-spectral matrix effects as well as molecular (M^{40}Ar^+ and M^{16}O^+) and elemental isobaric interferences of Sn (112, 114, 116), In (113) and Pd (106, 108, 110) (Wombacher *et al.*, 2003). As a result, complete isolation of Cd from its sample matrix is important.

We propose a novel Cd separation procedure based on the Pb separation described in Lugmair and Galer (1992) as an interesting alternative to the current procedures of Wombacher *et al.* (2003) and Cloquet *et al.* (2005). The present chromatographic method is performed on a single stage micro column with AG1-X8 anion-exchange resin with a total processed acid volume of 7 ml.

For the 14 estuarine suspended particulate matter (SPM) samples passed through the column, total Cd recovery is better than 96%. The separation procedure removes more than 98% of the Sn present in the sample. Potential problematic elements such as Mo and Zr, inducing molecular interferences during MC-ICP-MS analyses, are not present (not detected with a Thermo Finnigan *element 2* HR-ICP-MS) in the Cd fraction and the recovery of Zn is less than 0.6%. No problematic presence of major elements (Na, K, Mg, Ca) was detected suggesting that a single column procedure should be sufficient for subsequent isotopic measurements on a MC-ICP-MS. Some Pb (up to 2% of the initial Pb) and Cr (up to 10%) are still present in the Cd fraction. A second processing on the same column displays a recovery of better than 96% Cd ($n=3$), no Sn, nor Zn and only 0.2% of Pb is recovered in the Cd fraction.

The $\delta^{114/110}\text{Cd}$ value obtained on four duplicate (total chemistry) SPM samples is of $0.17 \pm 0.06(2\text{sd})\text{‰/amu}$ against our in-house B-JMC Cd standard.

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CosmoCalc: An Excel add-in for cosmogenic nuclide calculations

PIETER VERMEESCH

Institute of Isotope Geology and Mineral Resources,
ETH-Zürich, (cosmocalc@gmail.com)

Today, we are facing a paradoxical situation: on the one hand, a better understanding of cosmogenic nuclide systematics has improved the accuracy of cosmogenic nuclide dating. But on the other hand, the increased sophistication of these method has been an obstacle to their widespread use. CosmoCalc is an add-in to MS-Excel developed with the intention to alleviate this problem. The program as well as a spreadsheet with test data can be downloaded from the CosmoCalc website (<http://cosmocalc.googlepages.com>).

CosmoCalc presently implements four scaling models: Lal, Stone, Dunai and Desilets. Although the more recent models such as those by Dunai and Desilets are significantly more sophisticated than the early scaling model by Lal, they are just as easy to use in CosmoCalc. It is equally simple to compute topographic, snow and self-shielding factors. The nuclide concentrations and the product of the scaling and shielding factors are the only input required for all further calculations.

CosmoCalc uses the ingrowth equation of Granger and Smith, which is a summation of four exponentials: one for neutrons, two for slow muons and one for fast muons. Default values for the various parameters in this equation are those advocated by Granger, but alternative values can also be set.

Banana plots are sophisticated devices which depend on a large number of parameters, such as the production rates at sea level and high latitude, the scaling model, and the relative proportions of the various production mechanisms. CosmoCalc flexibility allows different kinds of Al-Be and Ne-Be plots to be generated on the fly.

CosmoCalc implements two numerical techniques to solve the non-linear systems of ingrowth equations. The default is Newton's method, which is a very fast and exact algorithm. The Metropolis algorithm is offered as a computationally more intensive, yet also more robust, alternative.

Different scaling models use different kinds of geographic input. For example, Lal's scaling model uses elevation whereas Stone uses atmospheric pressure and Dunai and Desilets atmospheric depth. Furthermore, Lal and Stone use geomagnetic latitude whereas Dunai uses geomagnetic inclination and Desilets cutoff rigidity. To facilitate the comparison of the various scaling models, CosmoCalc provides some easy-to-use conversion tools.

Regardless of the scaling model of preference, it is crucially important to use the same scaling model for the unknown sample and the calibration sites. For this reason, CosmoCalc specifies the production rates not explicitly but implicitly, by specifying the raw measurements of the calibration sites. The program comes with a set of default calibration sites, but this list can be modified by removing and adding new sites.

The 940-864 Ma granites of the Yenisey Ridge and Taimyr foldbelts, western margin of the Siberian Craton: Geochemistry and geodynamics

A.E. VERNIKOVSKAYA, V.A. VERNIKOVSKY AND
A.M. YASENEV

Institute of Geology & Mineralogy, Russian Academy of
Sciences, Novosibirsk (tonya@uiggm.nsc.ru)

The 940–864 Ma granites occur within Meso- to Neoproterozoic greenschist and amphibolite facies metamorphic rocks of the ancient terranes in the Yenisey Ridge and Taimyr accretional belts of the western margin of the Siberian craton (Vernikovskiy and Vernikovskaya, 2001; Pease *et al.*, 2001; Vernikovskiy *et al.*, 2007).

In all studied plutons, the granites have slightly peraluminous (rarely metaluminous) chemical compositions with widely variable Sm-Nd and Rb-Sr isotopic data, which allows referring to these rocks as S- and transitional I- to S-types granites. The S-type granites with epsilon Nd_(940-885Ma) = -7.14 – -4.48, ⁸⁷Sr/⁸⁶Sr_i = 0.71206 – 0.72163 and zircon saturation temperatures (T_{Zr}) approximately 800°C were generated on the early stage of the collisional process from crustal transitional hot- to low-temperature melts, according to Miller *et al.* (2003). The granites of transitional I- to S-type were formed on the final stage of the collisional event from mantle-crustal low-temperature ($T_{Zr} < 800^{\circ}\text{C}$) melts with epsilon Nd_(894-864-Ma) = -2.8 – +0.04 and ⁸⁷Sr/⁸⁶Sr_i = 0.7070 – 0.7192. On this stage the most evolved granitic melts are formed, having low Ca, Mg and REE contents and enrichment in Si and K.

It is likely that the 940 – 864 Ma granites were part of a microcontinent prior to the accretion and collision of its blocks (or terranes) with the Siberian continent.

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The Neoproterozoic alkaline rocks of the Yenisey Ridge, western margin of the Siberian Craton: Mineralogy, geochemistry and geochronology

I.V. VERNIKOVSKAYA^{1,2}, E.B. SAL'NIKOVA³,
A.E. VERNIKOVSKAYA², N.YU. MATUSHKIN^{1,2} AND
A.M. YASENEV^{1,2}

¹Novosibirsk State University, Russia, (visit irena@mail.ru)

²Institute of Geology and Mineralogy, Russian Academy of Sciences, Novosibirsk

³Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences, St. Petersburg

The Srednetatarka alkaline massif is composed of ijolites, forming the central zone and foyaites making up the outer ring area. These medium to coarse grained rocks were intruded by pegmatite dikes. The main minerals are alkali feldspar (mainly microcline), nepheline, aegirine (or aegirine-augite), alkali amphibole (mainly arfvedsonite) ± lepidomelane, ± eudialyte, ± astrophyllite-kupletskite. Among accessory minerals there are titanite, fluorite and zircon.

Enrichment of Zr, Nb and Ce in titanite and astrophyllite-kupletskite from foyaites was discovered using electron microscope investigation and x-ray spectroscopic analyses. The water enriched fluid inclusions in fluorite from ijolite have homogenization temperatures from 175 °C to 200 °C. Thus, the crystallization of fluorites was in the postmagmatic stage of the Srednetatarka massif formation.

The rocks of the Srednetatarka massif are highly fractionated and enriched in Rb, Th, U, Nb, Ta, Hf, Zr, Tb and Y, and depleted in Ba, Sr, P and Ti. They also have large REE contents (Σ REE = 123 - 362 ppm), LILE enrichment ($La_N/Yb_N=8-16$) and negative Eu anomalies (Eu/Eu* changes from 0.2 to 0.9).

The Srednetatarka foyaites yielded a U-Pb titanite age of 698±2 Ma. Together with the previously-dated 696 Ma (Ar-Ar, biotite) trachydolerite of the Zakhrebetninsk complex (Postnikov, 2005), these intrusive rocks are the oldest alkaline rock of the Yenisey Ridge which could be formed in anorogenic setting.

One of the most interesting facts about these alkaline rocks is that Nb, Ta, Zr mineralization and a Al deposit associate with the Srednetatarka massif.

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Hf and Nd isotopic composition of sediments, old and new

J.D. VERVOORT¹, T. PLANK², P.J. PATCHETT³ AND
J. PRYTULAK⁴

¹School of Earth and Environmental Sciences, Washington State University, Pullman, WA 99164, USA (vervoort@wsu.edu)

²Department of Earth Sciences, Boston Univ., Boston, MA, 02215, USA (tplank@bu.edu)

³Department of Geosciences, University of Arizona, Tucson, AZ, 85721, USA (patchett@email.arizona.edu)

⁴Department of Earth Sciences, Univ. Bristol, Bristol, UK, BS8 1RJ (j.prytulak@bristol.ac.uk)

We examine the Hf and Nd isotopic data for over 200 sediment samples in order to constrain Lu-Hf and Sm-Nd isotope systematics in the silicate Earth. The samples we have analyzed include sediments preserved on the continents and deposited in the ocean basins previously published [1] as well as unpublished data from >120 samples from 14 DSDP and ODP sites, chosen to represent the full range of sediment types and depositional environments. The most striking feature of the sediment data, as previously noted [1], is the strong positive correlation between Hf and Nd isotopes in these diverse terrigenous sediment samples. This sediment Hf-Nd array is coincident with the Hf-Nd mantle array as defined by MORBs and OIBs and collectively has been termed the terrestrial [1] or crust-mantle array. This array radiates from a depleted end-member with radiogenic Nd and Hf ($\epsilon_{Nd} \sim -10$; $\epsilon_{Hf} \sim -16$) toward evolved crustal values with very negative ϵ_{Nd} and ϵ_{Hf} values and represents mixing between components derived from the depleted mantle and components derived from continental crust.

The most prominent exceptions to this array, noted in the early Hf-Nd work on sediments [2,3], are ferromanganese crusts and nodules and metalliferous clays, which lie along a shallow slope above the terrestrial array. This anomalous array of authigenic sediments appears to represent, at least in part, the isotopic composition of seawater. This "seawater array" most likely results from the preferential dissolution of high Lu/Hf phases that are easily weathered such as apatite in old continental crust [4,5]. Regardless of the deviation from the terrestrial Hf-Nd array by metalliferous sediments and seawater, the tight coherency of the sediment Hf-Nd array with the OIB array indicates efficient mixing within the mantle through convection and on the Earth's surface through diverse sedimentary processes, and also effective transfer between the two through the recycling of crustal materials via subduction zones.

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Trace element partitioning between Mg-hastingsite and alkali basaltic melt in volcanic environment

MARCO VICCARO, CARMELO FERLITO AND
RENATO CRISTOFOLINI

Dipartimento di Scienze Geologiche, Università di Catania,
Corso Italia 57, 95129 Catania, Italy (m.viccaro@unict.it)

The occurrence of amphibole with no evidence of re-equilibration under low pressure conditions is rather rare in volcanic environment. The occurrence of a Mg-hastingsitic amphibole in trachybasaltic volcanic rocks of the 2001 eruption at Mt. Etna (Italy) has drawn the attention of many authors. However, the most intriguing character was found in tephra related to the most violent explosive phases of the event, whose textures show the original equilibrium at high- P_{fluid} between the amphibole and the surrounding glassy groundmass. This has allowed to calculate new accurate trace element partition coefficients (from LA-ICP-MS data) between Mg-hastingsite and basaltic-trachyandesite melt, well represented by the coexisting glass. Pressure and temperature conditions have been constrained on the grounds of geophysical and petrological data at 250 MPa and 980°C respectively.

Element	$A_{\text{mph/melt}}D$	Element	$A_{\text{mph/melt}}D$
La	0.366	Rb	0.063
Ce	0.671	Ba	0.564
Pr	0.959	Th	0.025
Nd	1.230	U	0.020
Sm	1.539	Nb	1.223
Eu	1.646	Ta	0.686
Gd	1.337	Sr	0.521
Tb	1.601	Zr	0.584
Dy	1.492	Hf	0.863
Ho	1.676	Sc	2.233
Y	1.498	V	2.065
Er	1.280	Cr	0.366
Yb	1.248	Co	2.094
Lu	1.267		

In detail, commonly incompatible trace elements such as Nb and Ta can be more easily incorporated in the amphibole than Th, U and LREE. This means that, if Mg-hastingsite fractionation occurs in magma reservoirs, the trace element signature of the residual melt can be strongly affected, with a significant increase in the melt of trace element ratios such as U/Nb, Th/Ta, La/Nb, La/Ta. This can have a great importance especially for those systems where amphibole is unusual, so that its role as a phase fractionated from the magma can be recognised from uncommon trace element ratios.

Lithium-bearing pegmatite resources at Fregeneda-Almendra pegmatitic field (Spain & Portugal)

R. VIEIRA, A. LIMA, E. R.-ROBLES AND T. MARTINS

U.P – Geology Centre, Portugal (romeu.vieira@fc.up.pt)

Introduction

A geological exploration is being carried out in the Fregeneda-Almendra region. This field has different types of pegmatite veins, defined according to their mineralogy, morphology and internal structure. The veins intrude a pre-Ordovician E-W metasediments belt and are located to the north of the syn-Hercynian Méda-Penedono-Lumbrales complex. This complex is mainly composed of a two-mica, peraluminous leucogranite. The veins have a zoned spatial distribution: the barren pegmatites are located near to the granitic complex and the rare-element enriched bodies occur further to the north. The Li-rich pegmatites are discordant, emplaced along the regional fracture system N-S to N030° E. Metamorphism isograd decreases with the distance from the granite and parallel to its contact: from sillimanite to chlorite isograd.

Methodology

Based on a stream sediment survey, the Li content of 2529 samples was analysed. Data was statistically studied and overlapped on region geological maps. This approach lead to the recognition of petalite- and spodumene-bearing pegmatites non identified until that moment.

Petalite- and Spodumene-bearing veins

Petalite-bearing veins only occur in the Portuguese part of the field. They are emplaced in the andalusite-sillimanite zone. Pombal and Vales outcrops exhibit a maximum extension of 500m and 10m width. The bodies do not show an evident internal zonation. Mineralogy assemblage is feldspars, quartz, and petalite as major constituents; minor muscovite, montebrazite and cassiterite. Fe-Mn phosphates and apatite appear as accessory minerals. Geochemical bulk analyses allow us to say that these veins are peraluminous ($A/CNK > 1$), have low SiO_2 content and $\text{Na}_2\text{O} > \text{K}_2\text{O}$. They are also impoverished in Fe(t), MgO and CaO.

Spodumene-bearing veins outcrop close to the limit of the biotite/chlorite isograd. Vau and Alberto mine have variable thicknesses of 4m to 15m. Internal zonation is not observed. Mineralogy is simple: feldspars, quartz and spodumene as major constituents; minor muscovite, montebrazite and petalite; beryl, Fe-Mn phosphates and cassiterite as accessory minerals. Further studies are required.

Final Remarks

Stream-sediment geochemistry is a powerful tool on Li-pegmatite exploration and allowed an improvement on the pegmatitic field petrogenetic understanding. It also provided the increase of mineral resources for ceramics and glass industry, which already consume material from this region.

Sm-Nd and Rb-Sr isotopic systematics of suspended sediments transported by the Solimoes and Madeira Rio: New insights about erosion and sediment provenance in the Amazon basin

J. VIERS¹, M. RODDAZ¹, N. FILIZOLA², F. GUYOT, F³, SONDAG¹ AND G. BOAVENTURA⁴

¹LMTG, Université de Toulouse, CNRS, IRD, Toulouse, France (viers@lmtg.obs-mip.fr)

²CEMETHI, Universidade do estado do Amazonas, Brazil

³LMTG, Université de Toulouse, CNRS, IRD, Casilla 18 1209 Lima 18, Peru (Jean-Loup.Guyot@ird.fr)

⁴Universidade do Brasilia, Brasilia, Brazil

The Amazon basin is the world's largest Cenozoic fluvial basin with an actual drainage area of $5.8 \cdot 10^6 \text{ km}^2$ and a depositional area of approximately $2.5\text{-}3 \cdot 10^6 \text{ km}^2$. It supplies about 7% of the suspended load (Filizola and Guyot, 2004) to the world's oceans. Filizola and Guyot (2004) give a mean annual suspended sediment flux close to $600 \cdot 10^6 \text{ t.yr}^{-1}$ at Obidos (Para state, Brazil). Ninety seven percent of this amount is contributed by Andean tributaries (62% from the Solimões River and 35% from the Madeira River).

This study reports the Sm-Nd and Rb-Sr isotopic systematics of materials being transported today by the Solimoes Rio and Madeira Rio during the year 2004. Within the ORE (Environmental Research Observatory) HyBam (Hydrology of the Amazon Basin) (<http://www.ore-hybam.org>) monthly samples are collected from the Solimoes River at Manacapuru station (Amazonas state, Brazil) and from the Madeira River at Porto Velho station (Rondonia state, Brazil) (see Hybam website for more details).

The Nd isotopic composition ranges from -8.9‰ to 9.9‰ and from -10.8‰ to -12.1‰ for the Solimoes and Madeira suspended sediments, respectively. The $^{87}\text{Sr}/^{86}\text{Sr}$ ranges from 0.713 to 0.717 and from 0.728 to 0.740 for the Solimoes and Madeira, respectively.

The purposes of this work are 1/ to assess possible systematic temporal variation in the Sm-Nd and Rb-Sr isotopic characteristics of the sediments, 2/ to use these potential differences of isotopic composition to constrain the geographic provenance of these sediments and the importance of bank erosion, and 3/ to estimate a global isotopic signature for sediments transported today by the Amazon River to the Atlantic ocean that can have important implications for the marine geochemistry of Nd.

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Carbon and hydrogen isotopic compositions of petroleum hydrocarbons to trace alteration processes in reservoirs

A. VIETH, R. ELIAS AND H. WILKES

GeoForschungsZentrum Potsdam, Telegrafenberg, D-14473 Potsdam, Germany (vieth@gfz-potsdam.de, elias@gfz-potsdam.de, wilkes@gfz-potsdam.de)

Hydrocarbons in petroleum reservoirs are subjected to viable abiotic and biotic alteration processes, such as evaporative fractionation, water washing and biodegradation. These processes cause significant changes in the molecular composition of the crude oil and therefore lead to a decrease in petroleum quality (e.g. lower API gravity, higher viscosity, higher TAN). Hence, the producibility of the respective fluids is negatively affected and the total volume of petroleum in place is reduced. Among the different alteration processes, biodegradation is responsible for the quantitative most important compositional changes in a petroleum reservoir, and therefore the ability to assess the extent of biodegradation is of particular interest for the petroleum industry.

Microbial processes favour the conversion of molecules containing lighter isotopes and therefore biodegradation leads to an enrichment of compounds with heavier isotopes (^{13}C , D) in the residual fraction. In general, hydrogen isotope fractionation tends to be at least one order of magnitude higher than carbon isotope fractionation, indicating higher sensitivity in the assessment of microbial degradation processes.

Recently it was shown that carbon isotope ratios of light hydrocarbons can be used to evaluate biodegradation processes in the Gullfaks reservoir, offshore Norway (Vieth and Wilkes 2006). However, it became clear that both source and also maturity effects have to be well constrained when using carbon isotope ratios for the assessment of biodegradation. In contrast to laboratory experiments, the hydrogen isotope ratios of light hydrocarbons in these crude oils from the Gullfaks field do not show a clear dependence on biodegradation processes. It is suggested that in petroleum reservoirs, besides differences in maturity and source, also the effects of hydrogen exchange between oil and formation water over geologic times have to be considered.

This study investigates the effects of biodegradation on carbon and hydrogen isotopes in crude oils. Here, we will present results of compound-specific isotope analysis on oil samples from different petroleum systems and demonstrate how carbon and hydrogen isotope ratios of petroleum hydrocarbons can be used to evaluate biotic as well as abiotic alteration processes in reservoirs.

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Simulating physical weathering of basalt on Earth and Mars

HEATHER VILES¹, BETHANY EHLMANN²,
TOMASZ CEBULA¹, COLIN WILSON¹, LISA MOL¹
AND MARY BOURKE³

¹University of Oxford, UK, (heather.viles@ouce.ox.ac.uk)

²Brown University, Rhode Island, USA
(bethany_ehlmann@brown.edu)

³Planetary Science Institute, Arizona, USA
(mbourke@psi.edu)

Background

Despite its importance as a surficial rock type on Earth and other planets, few studies have been made of the response of basalt to physical weathering. Heating and cooling, with or without salts and moisture, may have severe impacts on basalt clasts in many extreme environments (Leask & Wilson, 2003). We report here on an integrated programme of simulations investigating physical weathering of basalt under Earth (hot desert) and Mars conditions using a Fison's Environmental Cabinet and a specially constructed Mars Environment Simulation Chamber.

Methods

Small blocks (9 x 2.3 x 2.5 cm) of basalt were cut, and two groups prepared: (1) thermally pre-stressed and (2) thermally pre-stressed and immersed in saturated Na₂SO₄ solution. Sample strength was assessed before and after experimental weathering using a Grindosonic, and thin sections were produced for detailed petrological examination. Ambient, block surface and internal temperatures were monitored throughout the experiments. The Earth weathering regime was set up to reflect Negev desert conditions cycling between 296K and 345K; whilst the Martian regime cycled from 190K to 277K. Cycle length was 8 hrs. in each case. Both weathering regimes also included an element of radiative heating via lamps coming on for part of the heating cycle. The Mars weathering regime was carried out in 100% CO₂ atmosphere at 9 mbar pressure.

Results and conclusions

After 36 cycles under Earth and Mars conditions, changes in strength (few %) were apparent and some microscopic cracking was observed, although no visible weathering was produced. Blocks subjected to Mars-like conditions reacted differently to those subjected to Negev desert conditions especially with regard to whether salts caused strengthening or weakening.

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Arsenic in hydrothermal fluids from shallow vents in Baja California, México

R.E. VILLANUEVA-ESTRADA¹, R.M. PROL-LEDESMA²,
AND C. CANET²

¹Posgrado en Ciencias de la Tierra, Universidad Nacional Autónoma de México, México
(ventilas2000@yahoo.com)

²Instituto de Geofísica, Universidad Nacional Autónoma de México, México (prol@geofisica.unam.mx;
ccanet@geofisica.unam.mx)

Introduction

Dissolved arsenic concentrations in hydrothermal fluids from submarine (BC1, BC4 and BC6) (5 to 15 m depth) and intertidal hot springs (LP1 and SAN1, MAN1) from Bahía Concepción (Prol-Ledesma *et al.*, 2004) are higher than the permissible limit established by the Mexican government (0.05 mg/l). In the intertidal vents, there are Mn-oxides while in the submarine vents Fe-oxyhydroxides occur (Canet *et al.*, 2005). Here, we try to model the occurrence of arsenic by chemical speciation and the relation with precipitate mineralogy. The results are presented in the next table.

	Temp (°C)	pH	As (III)	As (V)	As total
BC1	87	6.0	10.4	0.04	10.41
BC4	87	6.0	6.1	0.03	6.14
BC6	87	6.0	9.3	0.04	9.34
LP1	61	6.5	4.8	0.04	4.81
SAN1	66	6.2	3.6	0.02	3.60
MAN1	40	7.0	2.0	0.03	2.00

Discussion

According with the pH values, arsenic in the vent fluid is mostly present as As(III) (up to 98.6%). Manganese and iron are both in reduced form. Oxidation of these elements to form the observed Fe-oxyhydroxides and Mn-oxides could occur by mediation of microorganisms. This way, oxidation products could adsorb arsenic and prevent its release from the hydrothermal fluid into the sea water.

Conclusions

Mn-oxides and Fe-oxyhydroxides play an important role in arsenic mobility discharged in the Bahía Concepción vent fluid.

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B, Li and Sr isotopes as tracers of seawater-serpentinite interaction at MAR, ODP leg 209

F. VILS¹, S. TONARINI², H.-M. SEITZ³, A. KALT¹ AND L. PELLETIER¹

¹University of Neuchâtel, Switzerland (flurin.vils@unine.ch)

²IGGI, C.N.R. Pisa, Italy

³J. W. Goethe University, Frankfurt a.M., Germany

The samples presented in this study are altered spinel harzburgites from ODP Leg 209 (sites 1272A and 1274A) at the Mid-Atlantic Ridge (MAR) between 14°N and 16°N. The degree of serpentinisation varies between 70 and 100% in site 1272A and from 50 to 97% in site 1274A. Despite the high degree of serpentinisation, some relics of primary phases are still preserved (olivine \geq orthopyroxene \gg clinopyroxene). In our previous study of the light element concentration in minerals of these samples we could show that boron is enriched in these rocks by reaction with seawater, and that the same process probably leaches lithium. Here, we present the results of strontium-, lithium- and boron-isotope analysis of these samples.

$\delta^7\text{Li}$ varies between -28.46 and +7.17, $\delta^{11}\text{B}$ ranges from +29.6 to +40.52. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (average 0.708726) are close to seawater values. Using the water-rock-ratio equation of McCulloch *et al* (1980), we obtain a low water-rock ratio (average 38.9).

Using the fractionation factors of Liu and Tossell (2005) for boron, we can model the compositional evolution of seawater to an evolved fluid (up to $\delta^{11}\text{B} + 70$ in solution, corresponding to $\delta^{11}\text{B} + 40$ in the rock) in the course of its passage through the oceanic mantle rocks.

Our results show that at ODP leg 209, B, Li and Sr isotopes can successfully be used to quantify reactions between seawater and very young oceanic mantle rocks. Low water-rock ratios lead to extremely high $\delta^{11}\text{B}$ values. This signature could potentially be transported into subduction zones. In general, however, the B, Li and Sr isotopic composition of altered oceanic mantle should be highly variable depending on water-rock ratios and on age.

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Dynamic of pedogenic carbonates in a climatic gradient: The Kabini river basin, Deccan Plateau, South India

A. VIOLETTE¹, J. RIOTTE^{1,2}, J.J. BRAUN^{1,2}, L. BARBIÉRO^{1,2}, L. RUIZ², P. OLIVA¹, M. SEKCHAR², M.S. MOHAN KUMAR², S. SUBRAMANIAN² AND B. DUPRÉ¹

¹LMTG OMP-UMR 5563, 14, avenue E.Belin, 31400

Toulouse, France. (violette@lmtg.obs-mip.fr)

²Indo-French Cell for Water Sciences (IRD/IISc Joint

Laboratory), IISc, 560 012 Bangalore, India.

(braun@civil.iisc.ernet.in)

The chemical weathering of silicate rocks consumes atmospheric CO₂. This has an impact on the long-term carbon cycle. In arid and semi-arid climatic conditions, the precipitation of pedogenic carbonates in soil, developed on silicate bedrock, is a potential carbon sink.

The West-East climatic gradient of the Deccan plateau, South Peninsular India, has induced various pedogenic carbonate occurrences, calcretes and nodules in the semi-arid zone and only nodules in the transition zone. The transition zone appears to be particularly sensitive to climatic changes and thus well designed for assessing the impact of climate change on the dynamic of pedogenic carbonates. In order to constraint the carbon sequestration in pedogenic carbonates, (1) the origin of Ca, (2) their age (U/Th dating) and (3) their current behavior (precipitation or dissolution), have to be determined.

Different types of nodules were sampled according to the structural study of the soil cover, in two representative watersheds of the transition zone. Soils, developed on a gneissic basement, show carbonate nodules either at the top of saprolite or within black soils (vertisols).

The $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios show that 2/3 of Sr in the carbonates originate from the parent rock and 1/3 from atmospheric inputs. This means that Ca mainly originates from the parent rock.

Preliminary U-Th ages of the well-developed nodules from the saprolite and black soils range from 15 to 23 ky while ages of soft tiny nodules from black soils would be less than 2 ky. Both populations of ages correspond to periods of weakness of the South West monsoon (drier climate). In this context, the pedogenic carbonates could be considered as paleo-climate proxies.

The current stability of the nodules was assessed by the stream chemistry of the watersheds. It indicates that the nodules are dissolving in the transition zone. The nodules dissolution significantly contributes to the output fluxes of Ca, Mg, U and REEs. However, the nodules trapped in the clayey matrix of the black soils seem to be protected from present-day chemical weathering.

Seasonal dynamics of molybdenum in a permanently anoxic lake

E. VIOLLIER¹, A. THIAM¹, P. ALBERIC²,
I. CIGLENECKI-JUSIC AND D. JEZEQUEL¹

¹IPGP & Université Paris Diderot, (viollier@ipgp.jussieu.fr)

²IST Orléans, (patrick.alberic@univ-orleans.fr)

³IRB Zagreb, (irena@irb.hr)

Mo is an essential enzyme cofactor in nitrogenase and nitrate reductase, necessary to nitrogen assimilation by phytoplankton (cyanobacteria and microalgae respectively). Mo is also considered in sediment records as a proxy of anoxic paleo-environments where sulphide builds up and precipitate molybdenum. In order to understand dissolved Mo removal mechanisms in freshwater bodies we investigated the lake Pavin water column (Puy-de-Dôme, France).

Lake Pavin is meromictic and at the bottom, about 30 meters out of 91 meters remain permanently anoxic and constitutes a natural “test tube”. The anoxic bottom layer overlaps a large density gradient layer (mesolimnion) where maximum reduced sulphur species concentrations are observed, and a more homogeneous layer where reduced compounds accumulate (monimolimnion).

The Mo size fraction was studied in the meso- and monimolimnion and compared to dissolved organic carbon (DOC) behaviour. Previous studies showed clearly Mo removal within the monimolimnion and chemical association of dissolved Mo with DOC. In this work, we demonstrate that this association is effective with large reactive organic polymers (> 1kD).

Monthly sampling of rivers input, water column solutions and solid samples (sediment traps) allowed to quantify Mo and nitrogen lake annual budget. Seasonal evolution of vertical profiles for dissolved Mo, nitrate, ammonium, sulphate and sulfide are compared and related to nitrate assimilation in the epilimnion and iron sulphide formation in the mesolimnion.

Li isotopic signature of the Reunion plume inferred from Li-Pb isotope systematic of Piton de la Fournaise historic lavas

I. VLASTELIC¹, P. TELOUK² AND T. STAUDACHER³

¹Laboratoire Magmas et Volcans, Observatoire de Physique du Globe de Clermont-Ferrand, Clermont-Ferrand France (I.Vlastelic@opgc.univ-bp.clermont.fr)

²Laboratoire des Sciences de la Terre, Ecole Normale Supérieure de Lyon, Lyon, France

³Observatoire Volcanologique du Piton de la Fournaise, Institut de Physique du Globe de Paris, La Reunion

We have investigated short-term variations of ${}^7\text{Li}/{}^6\text{Li}$ at Piton de la Fournaise volcano in order to better constrain the signature of the Reunion plume source and contribution of shallow-level processes. $\zeta^7\text{Li}$ (with reference to the IRMM-016 standard) determined in 30 lava samples erupted between 1927 and 2006 (including basalts and oceanites) ranges from +3.4‰ to +4.9‰. $\zeta^7\text{Li}$ does not correlate with the abundance of olivine xenocrysts (whose mass fraction reaches 50% in oceanites) ruling out diffusive fractionation of Li isotopes between olivine and melt as the main cause of ${}^7\text{Li}/{}^6\text{Li}$ variability. However, the heaviest compositions ($\zeta^7\text{Li} > +4.2\text{‰}$) are found in oceanites. Contrasting with global scale systematics, $\zeta^7\text{Li}$ correlates negatively with ${}^{206}\text{Pb}/{}^{204}\text{Pb}$. More precisely, three distinct arrays converge toward a unique composition, suggesting mixing between a single plume component (with $\zeta^7\text{Li} = +3.4\text{‰}$ and ${}^{206}\text{Pb}/{}^{204}\text{Pb} = 18.90$) and distinct contaminants. The dominant array may reflect interaction of plume melts with altered oceanic crust having unradiogenic Pb and heavy Li signature.

The Li isotopic signature of Reunion plume, as inferred from Li-Pb isotope relationships, is lighter than that of the Hawaiian plume and plumes sampling EM2 and HIMU mantle components, and is similar to that of DM and EM1 mantle components, as sampled by depleted MORB and Pitcairn lavas, respectively (Chan *et al.*, 2006).

In agreement with previous inferences (Vlastelic *et al.*, 2006) Li isotopes require little, or not at all, recycling of isotopically light continental sediments or isotopically heavy altered oceanic crust into the Reunion plume source.

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Non-skeletal carbonate precipitates: Indicators of Molybdenum isotopic seawater composition?

A. R. VOEGELIN¹, T. F. NÄGLER¹, E. SAMANKASSOU²,
J. R. BAHAMONDE³ AND I. M. VILLA

¹Institute of Geological Sciences, University of Bern,
Baltzerstrasse 1+3, 3012 Bern, Switzerland

²Département de Géosciences, Université de Fribourg,
Chemin du Musée 6, 1700 Fribourg, Switzerland

³Departamento de Geología, Universidad de Oviedo, Jesus
Arias de Velasco, s/n, 33005 Oviedo, Spain

Studies on black shales and oxic manganese crusts indicate that the Mo isotopic signature is a suitable proxy for the detection and interpretation of changes in past ocean redox conditions (Siebert *et al.*, 2003, Arnold *et al.*, 2004, Barling *et al.*, 2001). Carbonate rocks are a reservoir not yet investigated with respect to their Mo isotopic composition. Due to their occurrence during most of Earth's history and in a wide variety of geological settings, their Mo isotopic signature has the potential to provide a continuous record of ocean redox chemistry.

We present Mo isotopic data obtained from modern ooid sands from the Bahamas and the Persian Gulf. Their isotopic composition approximates modern seawater signature, while modern skeletal material has a significantly lighter value. Also, our data from chemically precipitated marine cements from the Carboniferous of Spain and China exhibit a heavy isotopic composition similar to today's ocean water and a distinct offset from their surrounding isotopically lighter sediment material. This has led us to hypothesize that the Mo budget of non-skeletal marine carbonates is controlled by seawater and may serve as an archive of ocean water Mo isotopic composition. As a pilot study we analyzed a transgressive carbonate sequence of Mid-Cambrian age. The already well defined Mo isotopic seawater composition of the early Cambrian (Lehmann *et al.*, 2007) serves us as a reference for the interpretation of the isotopic signal of the section. Our results indicate that Mid-Cambrian non-skeletal carbonates differ from their Carboniferous counterparts, which indicates that Early Paleozoic oxygen levels had not yet risen to Late Paleozoic and present-day concentrations.

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Colloid formation in aerated Fe(II) and As(III) containing water: Effect of phosphate, silicate and Ca on local coordination by XAFS spectroscopy

A. VOEGELIN¹, R. KÄGI², D. VANTELON³, S. J. HUG⁴

¹ETH Zurich, Switzerland (voegelin@env.ethz.ch)

²Eawag, Dübendorf, Switzerland (ralf.kaegi@eawag.ch)

³Synchrotron SOLEIL, France (vantelon@psi.ch)

⁴Eawag, Dübendorf, Switzerland (hug@eawag.ch)

Colloid formation due to iron oxidation and hydrolysis affects the cycling of nutrients and contaminants in environmental and technical systems. The extent of As oxidation and uptake by colloids and the composition and colloidal stability of the resulting colloids are major factors controlling the removal of As from As-rich anoxic drinking water. We investigated Fe(III)-colloid formation and concomitant As(III) oxidation and removal in synthetic carbonate-buffered groundwater (pH 7, 2-30 mg/L Fe(II), 0.5 mg/L As(III)) as influenced by phosphate (2-20 mg/L P), silicate (2-20 mg/L Si), and Ca (2.5 mM Ca- and 1.5 mM Mg- versus 8 mM Na-bicarbonate). The oxidation state of As and the local coordination of As, Fe, P, Si, and Ca in colloids collected after 4 hours of oxidation were investigated by X-ray absorption fine structure (XAFS) spectroscopy.

The removal of As from solution by uptake into settling colloids depends on a range of coupled processes such as the enhanced As(III) oxidation in presence of Fe(II), the competition of phosphate, silicate, and As for sorption sites on Fe(III)-colloids, and the effect of phosphate, silicate and Ca on molecular-scale colloid structure and colloid aggregation. While higher Fe(II) concentrations promote As(III) oxidation in solution, the associated increase of sorption sites on Fe(III)-colloids reduces anion competition, resulting in a higher fraction of colloidal As(III) (relative to total colloidal As). Increasing P/Fe ratios promote the formation of basic Fe-phosphates and increasing Si/Fe ratios the formation of ferrihydrite at the expense of lepidocrocite (which forms in the absence of P and Si). In the presence of P and Si, the P/Fe and Si/Fe ratios determine the extent to which basic Fe(III)-phosphate- and ferrihydrite-type colloids form. In the absence of Ca, colloids formed at low Fe concentration and high P/Fe ratio are colloidal stable, resulting in reduced As removal from solution. The presence of Ca promotes colloid coagulation by diminishing electrostatic colloid repulsion. Especially at high P/Fe ratios, we find that Ca is also directly incorporated into the colloid structure, suggesting the formation of mixed basic Ca-Fe(III)-phosphates. Spectroscopic data further suggest that also As(V) may be incorporated into these phosphates.

Molecular $\delta^{13}\text{C}$ values of leaf wax components from plants growing in different tropical habitats

A. VOGTS, H. MOOSSEN, F. ROMMERSKIRCHEN AND J. RULLKÖTTER

Institute of Chemistry and Biology of the Marine Environment (ICBM), Carl von Ossietzky University of Oldenburg, P.O. Box 2503, D-26111 Oldenburg, Germany (a.vogts@icbm.de)

Long-chain leaf wax components from tropical C_3 plants were analysed for their carbon isotopic composition. Averaged $\delta^{13}\text{C}$ values for alkanes (weighted mean average of the $n\text{-C}_{27}$ to $n\text{-C}_{35}$ alkanes) were $-33.5 \pm 2.8\text{‰}$ for savanna plants and $-36.9 \pm 2.5\text{‰}$ for rain forest plants. The difference of 3.4‰ originates mainly from (1) the different isotopic composition of the source CO_2 caused by recycling effects in the closed canopy of the rain forest, and (2) the stronger discrimination of the heavier carbon isotope due to slower assimilation of CO_2 in the shady rainforest. Similar differences (3.3 to 3.8‰) were found by Ehleringer *et al.* (1987) for leaf tissue material of shrubs, trees, ferns and grass from open and closed canopy habitats.

In general, tropical vegetation changes from rain forests over savannas and finally to arid grasslands due to climatic conditions. Woody C_3 plant contribution decreases with an increase of grassy C_4 plants. The $\delta^{13}\text{C}$ values of the $n\text{-C}_{27}$ to $n\text{-C}_{35}$ alkanes increase in the course of this vegetation change (Fig. 1). The C_4 grasses of the savanna have the highest values due to their different metabolic pathway.

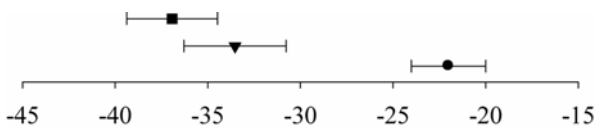


Figure 1. Averaged $\delta^{13}\text{C}$ values of $n\text{-C}_{27}$ to $n\text{-C}_{35}$ alkanes (weighted mean average) from leaf wax of C_4 grasses (circle, Rommerskirchen *et al.*, 2006, $n = 34$), savanna C_3 plants (triangle, $n = 24$) and rain forest C_3 plants (square, $n = 18$).

These results give a clearer look at key data for studies estimating the variation of land plant biomarker contribution to dust, soils and sediments in tropical regions. Until now such research projects often only distinguished between the molecular carbon isotopic signatures of C_3 and C_4 plants. Our study provides data about a significant difference in the molecular $\delta^{13}\text{C}$ values of C_3 plants from savannas and rain forests. This has to be taken into consideration, e.g., in palaeoclimatic studies.

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Surface water freshening and high-latitude river discharge in the Eocene North Sea

SILKE VOIGT¹, ANNE ZACKE², MICHAEL JOACHIMSKI³ AND ANDY S. GALE⁴

¹IfM-Geomar Kiel, (svoigt@ifm-geomar.de)

²University of Cologne, (anne.zacke@uni-koeln.de)

³University of Erlangen, (joachimski@geol.uni-erlangen.de)

⁴University of Portsmouth, (asg@nhm.ac.uk)

A fish-teeth derived $\delta^{18}\text{O}_\text{p}$ record of the early Palaeogene North Sea mirrors the global oceanic temperature evolution, except of a 2-4 Myr period across the Palaeocene-Eocene transition, when unusually light $\delta^{18}\text{O}_\text{p}$ values in teeth of surface dwelling sharks indicate substantial surface water freshening. The $\delta^{18}\text{O}_\text{p}$ decrease with a magnitude of 6.3 ‰ commenced during the Palaeocene-Eocene thermal maximum (PETM), and prevailed until the early Ypresian. Coeval occurring bottom dwelling sharks indicate normal marine conditions and strong water column stratification in the early Ypresian North Sea. The magnitude of the negative $\delta^{18}\text{O}_\text{p}$ excursion suggests a depletion of surface water $\delta^{18}\text{O}$ by 3.6 ‰ relative to Eocene mean ocean water. This value is lower than that of coeval freshwater lakes and indicates that large rivers sourced by strongly fractionated precipitation drained into the North Sea. The investigated odontaspid and lamnid sharks are fully marine organisms and do not live in waters with salinities lower than 20 ppt today. We consider this value as the lower salinity tolerance limit for large predators. The construction of a mixing line between marine and brackish waters and their corresponding oxygen isotopic compositions in the Eocene results in $\delta^{18}\text{O}$ values of -10 to -13 ‰ for river waters. These values are in a good agreement with the isotopic composition of Arctic precipitation, recently estimated from hydrogen isotopes in terrestrial plant-derived n-alkanes (Pagani *et al.* 2006), and suggest a high-latitude source of the river discharge into the North Sea. The commencement and duration of brackish surface-water conditions in the North Sea coincide with the main phase of effusive basaltic volcanism and associated tectonic uplift in the North Atlantic region. As a result, the North Sea probably became temporarily isolated and the fluvial catchment areas extended into the high latitudes. The marginal North Sea became reconnected with the North Atlantic Ocean during the transgression at 54 Myr, when normal marine conditions returned indicated by $\delta^{18}\text{O}_\text{p}$ in teeth from surface and bottom dwelling sharks.

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The rheological behavior of samples from Tungurahua volcano, Ecuador

F. W. VON AULOCK, Y. LAVALLEE, D. RICHARD,
K-U. HESS AND D. B. DINGWELL

Department of Earth and Environmental Sciences, Section of Mineralogy, Petrology and Geochemistry, Ludwig-Maximilians Universität München (LMU), Theresienstrasse 41/III, 80333 München, Germany (Felix.von.aulock@googlemail.com)

For a better understanding of eruption mechanisms it is important to investigate the rheological behaviour of the magma during its ascent in the conduit. We can reveal this information by measuring the physico-chemical properties of volcanic ejecta. Between 16th and 18th of August 2006 a large eruption occurred on Tungurahua volcano including fire fountains, ash-, rock- and pumice falls and lava flows, as well as several pyroclastic flows. Shortly after this, we collected five different rock samples from the pyroclastic flow deposit which represent the most of the mass of rocks of the pyroclastic flows produced in this eruption. The rocks of the pyroclastic flows are:

- ~5% of dome material with a low porosity of about 15%;
- ~90% of bread crust bombs which have a higher porosity of about 30-50%.

A reconnaissance study of the rheological properties of our samples obtained via glass transition temperature (T_g) determinations was performed. To this end we have employed an advanced dilatometric method, newly developed by Helo *et al.* (2006).

By detecting the dilatometric softening temperature (T_{gsoft}) in successive runs with the same sample at constant heating and cooling rates, we observed a shift of T_{gsoft} with increasing run number, presumably due to degassing of the supercooled liquid phase. The measured T_{gsoft} for the dome material were 974 °C for the first run and 1030 °C for the 10th run, and ~1060 °C up to ~1100 °C for the bombs. The increase of T_{gsoft} in successive runs was higher for the dome material than for the bread crust bombs.

This was unexpected as the dome material is believed to be more degassed and should therefore have a higher T_{gsoft} than bombs which had less time for degassing. But the results show the opposite trend: higher T_{gsoft} and a faster rise in T_{gsoft} for the porous bomb material. The results of this study will be discussed in terms of the relative degassing histories and kinetics of the dome versus bomb rocks as well as their crystalline textures.

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How fast do the Alps erode? A cosmogenic nuclide study on Central Alpine river basins

F. VON BLANCKENBURG¹, H. WITTMANN,
T. KRUESMANN, K.P. NORTON AND P.W. KUBIK

¹Institute for Mineralogy, Leibniz University of Hannover, Callinstrasse 3, D-30167 Hannover, Germany

²Institute for Particle Physics, Paul Scherrer Institute / ETH Zürich, CH-8093 Zürich, Switzerland

Cosmogenic ¹⁰Be, measured in river-borne quartz now routinely provides denudation rates at the river basin spatial scale and at the temporal scale of a few kiloyears (von Blanckenburg 2005). A north-south traverse through the Swiss Central Alps reveals that denudation rates correlate with recent rock uplift rates in both magnitude and spatial distribution. As a prerequisite, we took care to investigate the potential influence of shielding from cosmic rays due to snow, glaciers, and topographic obstructions, to calculate a possible memory from LGM glaciation, and to identify a watershed size that is appropriate for systematic sampling. Mean denudation rates are 0.27 ± 0.14 mm*yr⁻¹ for the Alpine foreland, and 0.9 ± 0.3 mm*yr⁻¹ for the crystalline Central Alps. The measured cosmogenic nuclide-derived denudation rates are in good agreement with post-LGM lake infill rates and about twice as high as denudation rates from apatite fission track ages that record denudation from 9-5 Myr. Cosmogenic nuclides now provide the ability to decipher correlations between denudation rate and geomorphic parameters. For example, the rates correlate with hill slope in the Mittelland catchments, but they are independent of angle in the high Alps. We interpret this to mean that high Alpine landscapes are at threshold hillslope, where slopes cannot increase any further before failure occurs. In general, denudation rates are high in areas of high relief and high altitude. Levelling measurements show that the Central Alps are uplifting today with 0.5-1.6 mm yr⁻¹ (Kahle *et al.* 1997). The similarity in the spatial distribution and magnitude of denudation rates and those of rock uplift rates can be interpreted in several ways: (i) postglacial rebound or climate change has introduced a transient change in which both uplift and denudation follow each other with a short lag time; (ii) the amplitude of glacial to interglacial changes in both is small and is contained in the scatter of the data; (iii) both are driven by ongoing convergence where their similarity might hint at some form of long-term quasi steady state; (iv) enhanced continuous Quaternary erosion and isostatic compensation of the mass removed accounts for the distribution of present-day rock uplift.

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A new U/Pb-spike ($^{233-235}\text{U}/^{202-205}\text{Pb}$) for high precision zircon dating: First results of standard zircons, precision and accuracy

A. VON QUADT¹, S. GEORGIEV¹ AND I. PEYTICHEVA^{1,2}

¹ETH Zurich, IGMR, (georgiev@erdw.ethz.ch; vonquadt@erdw.ethz.ch)

²CLMK, BAS, Sofia 1000, (peytcheva@erdw.ethz.ch)

For high precision U/Pb zircon, xenotime and monazite analyses there is a new U/Pb spike ($^{233-235}\text{U}/^{202-205}\text{Pb}$) produced at ETH Zurich. The enrichment for the ^{205}Pb isotope is greater than 99.95 and for the ^{202}Pb isotope greater than 99.73. Important ratios of this new mixed double U/Pb spike are: $^{206}\text{Pb}/^{205}\text{Pb} - (0.001132)$, $^{204}\text{Pb}/^{202}\text{Pb} - (7.7351\text{E-}05)$, $^{206}\text{Pb}/^{204}\text{Pb} - (10.0025)$ and $^{233}\text{U}/^{235}\text{U} - (0.969945)$. The new U/Pb spike was calibrated against a highly pure metal solution based on NBS 982 and NBS 960. One of the aims to produce the new double lead and uranium spike ($^{233-235}\text{U}/^{202-205}\text{Pb}$) was to avoid the usage of external mass-fractionation, and to improve precision and accuracy of U-Pb measurements. In the past the instrumental mass-fractionation was estimated by repeated measurements of NBS 982 or NBS 981 material as well as of U 500 standard material.

The minimum amount of NBS Pb and U for the external fractionation correction is limited by Pb-blank, the temperature during the measurement and parameters of the ion counter system. Nevertheless, the measuring procedure needs more time for the measurement based on six Pb isotopes, three U isotopes and sometimes two additional isotope to correct interferences on the mass ^{202}Pb .

To demonstrate the advantage of the new ($^{233-235}\text{U}/^{202-205}\text{Pb}$) spike we have measured several zircon standards R33 (Black *et al.*, 2004), 91500 (Wiedenbeck *et al.*, 1995) and the PL zircon (Slama *et al.*, 2006) using a "common" $^{235}\text{U}/^{205}\text{Pb}$ and the new double U/Pb spike. First preliminary results show that the scattering of the $^{206}\text{Pb}/^{238}\text{U}$ ages and the mean error of the $^{206}\text{Pb}/^{238}\text{U}$ ages are much smaller compared to the use of the "conventional" $^{205}\text{Pb}/^{235}\text{U}$ spike.

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Identification of potential geochemical reactions in German subsurface storage sites of CO₂

HANS-DIETER VOSTEEN AND FRANZ MAY

Federal Institute for Geosciences and Natural Resources (BGR), Stilleweg 2, 30655 Hannover, Germany (Hans-Dieter.Vosteen@bgr.de)

Large scale CO₂ geological storage in Germany can be realized both in deep saline aquifers and in mature natural gas reservoirs. Some of the injected CO₂ will dissolve in the already highly mineralized Na-Ca-Cl brine to form CO₂ (aq) and carbonic acid. Such a change in brine composition can lead to dissolution or precipitation of minerals within the storage formation or the cap rock. Mineral dissolution will yield an increase in porosity. Depending on where it occurs, it can either increase the storage capacity or reduce the cap rock integrity. Mineral precipitation will either result in long term mineral storage of CO₂ or - if it occurs near to the well - it can yield technical problems during CO₂ injection. Numerical simulation of reactive transport processes and associated mineral reactions are generally used for predictions of such processes. But, reaction rates of silicates are very slow and reliable thermodynamic data obtained by experimental studies of mineral precipitation or dissolution is difficult to obtain. In many cases realistic thermodynamic data does not exist for all minerals within a rock formation. Data for lacking minerals such as mixed crystals has to be estimated. If we consider high-salinity brines, which are omnipresent in the North German Basin, the Pitzer formalism has to be used. Many simulation tools do not facilitate simulation of redox reactions or aluminosilicate reactions in combination with the Pitzer formalism. These limitations result in potentially unrealistic and therefore uncertain interpretations of geochemical simulation results. Another way to identify and quantify potential alteration reactions is to study natural analogues. For the case of CO₂ injection, natural analogues can be found in regions with CO₂-rich water, e.g. in active volcanic regions. Potential alteration reactions, identified by natural analogue studies can further be used as comparison and for qualitative calibration of numerical simulations. For the German storage formations Bunter Sandstone and Rotliegend sediments such natural analogue studies yield the dissolution of calcite and chlorite and precipitation of dolomite. Another slow alteration reaction is the dissolution of albite and the precipitation of kaolinite. By studying natural analogues of the Rhenish Massif, May (2005) found that the alteration of greywacke and shale rocks by CO₂-rich water led to the dissolution of chlorite and feldspar and to the precipitation of kaolinite, iron-bearing carbonates, quartz and bicarbonate water.

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Origin of UHP garnet lherzolite and serpentinitised harzburgites from Pohorje, Eastern Alps, Slovenia

M. VRABEC¹, J.C.M. DE HOOG² AND M. JANAK³

¹Dept. of Geology, University of Ljubljana, Ljubljana, Slovenia (mirijam.vrabec@ntfgeo.uni-lj.si)

²Dept. of Earth Sciences, University of Oxford, Oxford, UK

³Geological Institute, Slovak Academy of Sciences, Bratislava, Slovak Republic

The presence of former mantle rocks in continental crust sections from orogenic terrains may give important clues on the tectonic history of the region. The Slovenska Bistrica ultramafic complex (SBUC; Eastern Alps, Slovenia) occupies the south-eastern most part of the Pohorje mountains, which represent an extruded piece of continental crust subducted during the Cretaceous Eo-Alpine orogeny. The SBUC is the only known occurrence of ultramafic rocks within this nappe system apart from a few dismembered pieces in the near vicinity. The main body is composed of serpentinitised harzburgites with local occurrences of garnet lherzolite, and as a whole it records a complex history of melt depletion, metasomatism, subduction and exhumation.

The harzburgites are highly depleted following melting within the spinel stability field, as exemplified by high whole-rock MgO, low Sc, Lu_N, and Gd_N/Yb_N, and high Cr# of Cr-spinel. Fluid-immobile trace elements (Th, Ti, Zr, Sc, V, HREE) correlate well and are consistent with a melt depletion trend. Other incompatible elements show little correlation and are probably strongly modified by the serpentinitisation process. However, comparable LREE enrichment of all samples suggests that this piece of mantle was already metasomatised by melts or fluids before serpentinitisation. In lherzolite CaO and Al₂O₃ contents were high enough to form garnet after spinel thus recording an UHP stage (4 GPa, 900°C) not visible in the harzburgites. Because of the evidence of an earlier lower pressure stage within the spinel stability field, the SBUC represents a piece of subducted mantle.

As subduction was intra-continental, the most obvious source of the SBUC is subcontinental lithosphere from the overlying continental slab, but this is in conflict with the strongly depleted nature of the rocks. Alternatively, it may have been part of the oceanic lithosphere after rifting of the N Apulia passive margin. This fits better with the geochemistry of the rocks, including negative Ce and positive Li and U anomalies - typical of weathering at the sea floor and commonly observed in abyssal peridotites. However, it is unclear how much these features are affected by serpentinitisation processes. A third possibility is that the SBUC represents subduction-modified depleted mantle from the hanging wall composed of S Apulia subcontinental mantle. A Re-Os isotope study is underway to obtain additional constraints on the origin of this piece of mantle.

Investigating the source of continental flood basalts: Insights from intra-lava flow osmium isotope variations

C.L VYE¹, A. GANNOUN^{1,2}, K.W. BURTON^{1,3}, T.L. BARRY¹, AND S. SELF¹

¹Dept. of Earth Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA. UK (cvye@open.ac.uk)

²Dept. of Earth Sciences, University of Oxford, Parks Road, Oxford, OX1 3PR. UK (mouhcine@earth.ox.ac.uk)

³LMTG, Université de Toulouse, 14 Av. E. Belin, F-31400, Toulouse, France (burton@lmtg.obs-mip.fr)

Geochemical debates over the source of continental flood basalts usually assume that individual lava flows represent compositionally uniform and rapidly erupted products of large well-mixed magma reservoirs. This study presents an examination of intra-lava flow chemical and isotopic variations in relation to eruption sequence, which provide insights into the mechanisms of flood basalt petrogenesis.

The temporal variations implicated by the pahoehoe inflation model (Self *et al.* 1997) have been applied to a flow field, formed by a single flood basalt eruption, both vertically within each sheet lobe and laterally between the constituent lobes. This framework provides insight into sequential magmatic evolution during the timescale of one eruption.

We present results from a 2,660 km³ flow field formed during a single eruption in the Columbia River Basalt Province, USA. Our findings show that small but statistically significant major and trace element intra-lobe variations were present at the time of emplacement e.g. MgO 3.09-4.55 wt%, Ni 17.5-25.6 ppm, indicative of fractional crystallisation. However, such data does not reveal other processes such as source variations and/or crustal contamination. In contrast, Re-Os isotopes indicate progressive crustal contamination of the magma over the timescale of a single flood basalt eruption. Initial ¹⁸⁷Os/¹⁸⁸Os ratios range from 0.287 (lava core) to 1.569 (lava crust) within a single 35m thick sheet lobe. These values are more radiogenic than any known enriched sources (normative mantle ~0.127, HIMU ~0.15) consistent with previous data for CRBs (Chesley and Ruiz, 1998) indicating that neither an enriched source nor the SCLM can be the cause of the radiogenic values. Preliminary data for an individual lava from the Deccan Traps indicate a similar process of contamination. These data have important implications for flood basalt genesis and the nature of their source, and indicate that uniformity of individual lavas cannot be assumed.

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