

Origins of Deviations From Transition-State Theory: Affects of Ion-Exchange Kinetics in Glass

J. P. ICENHOWER¹, B. P. MCGRAIL¹, A. LÜTTGE²

¹Pacific Northwest National Laboratory, K6-81, Richland, WA, USA 99352 (jonathan.icenhower@pnl.gov; pete.mcgrail@pnl.gov)

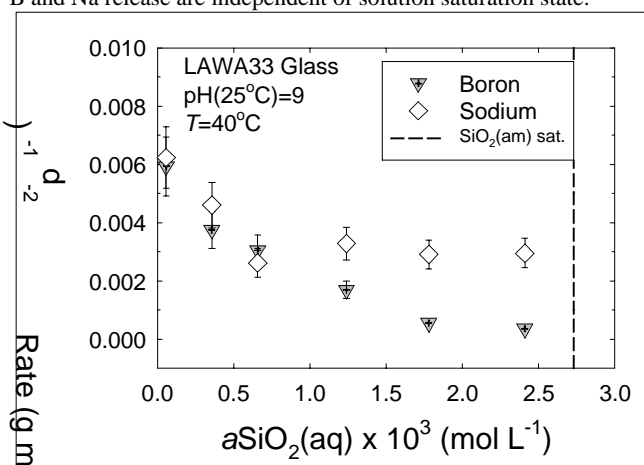
²Rice University, Geol. And Geophys., MS 126, Houston, TX, USA 77251 (aluttge@rice.edu)

Introduction

Experimental investigations of glass dissolution kinetics have highlighted deviations from Transition-State Theory (1) (TST) as solution compositions approach equilibrium with rate-limiting secondary solids. These deviations from expectations are especially prominent in alkali borosilicate glass compositions that are proposed matrices for radioactive waste disposal. To date, a satisfactory explanation for such deviations has not been advanced.

Experimental Results

Single-Pass Flow-Through (SPFT) experiments were conducted to evaluate the reaction kinetics of sodium aluminoborosilicate glasses. Solutions were doped in dissolved Si up to saturation with respect to amorphous silica. For glasses containing molar $\text{Na} > (\text{Al} + \text{B})$, the results are illustrated in below. Rates of boron and sodium release become independent of solution composition at high activities of $\text{SiO}_2(\text{aq})$, which is not predicted by TST-based models (2). The ion exchange (IEX) reaction, $\text{Na}^+ = \text{H}_3\text{O}^+$, explains not only the relatively fast release of sodium compared to boron, but the catalysis of Si—O rupture as well. Therefore, rates of B and Na release are independent of solution saturation state.



Conclusions

Our experiments indicate the importance of IEX reactions in exerting a governing influence on element release in solutions approaching saturation. Therefore, TST models must be modified to accommodate the existing database.

References

1. P. Aagaard, H. C. Helgeson, *Am. J. Sci.* **282**, 237-285 (1982).
2. B. E. Grambow, *Mat. Res. Soc. Symp. Proc.* **44**, 15-27 (1985).

Kinetics of silica nanocolloid formation from supersaturated solutions

G.A. ICOPINI¹, S.L. BRANTLEY², AND P.J. HEANEY³

¹Department of Geosciences, Pennsylvania State University, University Park, PA 16802, gicopini@geosc.psu.edu]

[²brantley@geosc.psu.edu] [³heaney@geosc.psu.edu]

The mechanisms by which silica colloids grow and precipitate are critical to understanding a host of geological and industrial processes, including silica diagenesis, fossilization by silicification, and the deposition of silica scale during the extraction of geothermal energy. However, rate laws reported for the precipitation of silica in natural environments are often contradictory, and the kinetics of monosilicic acid condensation are poorly understood. Here we examine the evolution of silica colloids in simulated brine solutions (ionic strength = 0.25 M) ranging in pH from 3 to 7.

Changes in monosilicic acid, nanocolloidal silica (<0.1 μm effective diameter), and silica precipitate concentrations were monitored in batch reactions. The experiments were conducted with initial silica concentrations of 750 and 1250 mg/L. Monosilicic acid concentrations were measured using the colorimetric silicomolybdate assay. We analysed the total dissolved silica [SiO_2] in 0.1 μm -filtered solutions using ICP-AES and calculated nanocolloid concentrations by difference. The precipitate produced in a given run was defined as the difference between the starting silica concentration and [SiO_2] measured in the 0.1 μm -filtered solutions.

Previous experiments have shown that in solutions supersaturated with respect to amorphous silica, monomeric silica first condenses to nanoscale colloids with particle sizes of ~ 3 nm. This population persists metastably until the nanocolloids coalesce and precipitate as silica gel. In this study, we explored the first step of this reaction in a simulated brine solution. Our analysis of the reaction kinetics that govern the initial stages of transformation from monosilicic acid to nanocolloids reveals that the rate of decrease of dissolved monomeric silica with time, R , has a fourth order rate dependence: $R = k [\text{SiO}_2]^4$. Here, k ($\text{mM}^{-1} \text{sec}^{-1}$), the rate constant, varies with pH according to $k = k_o [H^+]^{0.89}$, and k_o is the rate constant at pH 0 (Figure 1). Data at lower concentrations and ionic strength currently are being fit to a similar fourth order model.

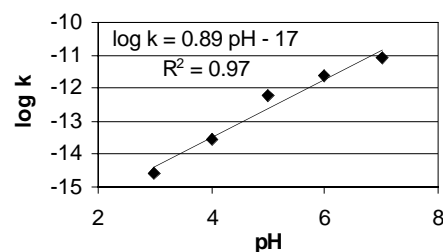


Figure 1. pH dependence of the transformation from monosilicic acid to nanocolloids.

Composition of sound producing sand in Japan

CHIAKI IGARASHI AND NAOTASTU SHIKAZONO

Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama, Japan

The sound producing sand is well known as musical sand or booming sand. It has been reported for over the centuries how and why the sand makes sound from the physical point of view but still the mystery is surround. This study is performed to characterize samples geologically and mineralogically. About 150 samples, including both silent and sound producing sand, are collected from beaches in Japan. Both the sound producing sand and the silent sand are perfectly dried and are analyzed with XRD, XRF and ICP-MS.

The major and minor minerals are analyzed with XRD: quartz and feldspar as major, and clay and biotite as minor. XRF study has indicated that SiO₂ and CaO content negatively correlate with Al₂O₃, suggesting the beach sand is mostly composed of quartz and montmorillonite. The most major elements (Na and Ca) are positively correlated with SiO₂ content. Minor elements and REE are observed with a positive correlation of Al₂O₃. Heavy REE, particularly Er, are enriched in beach sand compared with averaged standard granitic rock of Geological survey in Japan. REE of beach sand are controlled by fine particles of clay minerals and other secondary minerals. The distinct difference between the major, minor and REE content of both sound producing sand and silent sand is not obvious. However, each area has its own characteristics of the sand and is controlled by the secondary particles.

Seasonal trace element and isotope variations in freshwater tufas: potentials and limitations for climate reconstruction

C. IHLENFELD¹, R. MAAS¹, M. K. GAGAN², M. D. NORMAN² AND G. M. HENDERSON³

¹ Dept. of Earth Sciences, La Trobe University, Melbourne, Vic. 3086, Australia (C.Ihlenfeld@latrobe.edu.au)

² Research School of Earth Sciences, The Australian National University, Canberra, A.C.T. 0200, Australia

³ Dept. of Earth Sciences, Oxford University, Parks Road, Oxford OX1 3PR, UK

Extracting useful climate information from annual trace element and isotope variations in terrestrial carbonates has proven to be difficult in most cases. Nevertheless, qualitative or even quantitative inter-pretation of the proxy data may be possible if the geochemical processes acting at a specific site are thoroughly understood.

To this end, we analysed trace element (e.g. Mg, Sr, Ba, U) concentrations and isotope ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $^{234}\text{U}/^{238}\text{U}$) compositions along a continuous ~14-year-long (1985-1999) profile of a modern freshwater tufa from NE Australia (Ihlenfeld et al., 2001). An accurate chronology for the tufa profile was developed based on the temperature dependence of the $\delta^{18}\text{O}$ signal, which allowed us to compare the geochemical data sets with available meteorological observations. Temperatures calculated from Mg concentrations in the tufa provide close approximations of annual water temperature variations. Furthermore, temporal changes in $\text{Mg}/\text{Ca}_{\text{water}}$ can be estimated from $\text{Sr}/\text{Ba}_{\text{tufa}}$ using an empirically derived equation, which may improve the potential of Mg as a useful thermometer in fossil tufas from the area. Variations in Sr, Ba, $\delta^{13}\text{C}$ and U along the profile provide semi-quantitative measures of effective wet season rainfall. While sympathetic variations in Sr, Ba and $\delta^{13}\text{C}$ can be explained by variable amounts of calcite precipitation within the vadose zone of the karst aquifer, the pronounced variability of U records changes in the U flux from the soil to the water table.

Data will also be presented for a 52 ka tufa from the same river. However, despite our understanding of the modern system a straightforward interpretation of *some* of the proxy records from this fossil tufa is hampered because different geochemical processes appear to have dominated.

In summary, our work highlights both the potentials and limitations of seasonal trace element and isotope variations in freshwater tufas for high-resolution climate reconstruction.

References

Ihlenfeld et al., *Geochim. Cosmochim. Acta*, in review.

Simultaneous determinations of U-Pb age and REE abundances for zircons using Laser Ablation-ICPMS

T. IIZUKA AND T. HIRATA

Laboratory for Planetary Sciences, Tokyo Institute of Technology, O-okayama 2-12-1, Meguro, Tokyo 152-8551, Japan (tiiduka@geo.titech.ac.jp)

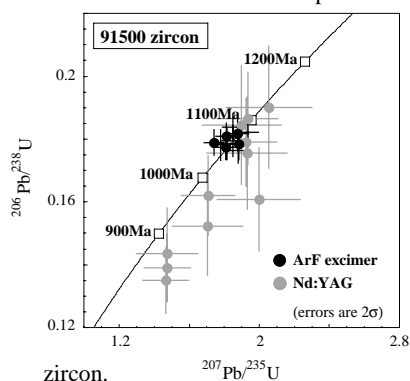
Introduction

Laser ablation-ICP-MS (LA-ICP-MS) has been recently shown to be a potentially valuable alternative to U-Pb dating (Hirata and Nesbitt, 1995) and has the potential to detect sub-ppm level REE in situ. In this study, we have developed a new procedure for simultaneous determinations of U-Pb age and REE abundances from ~20 μm ablation pits of single zircon grains using ArF excimer LA-ICP-MS equipped with a chicane ion lens system.

Experimental

An ArF excimer laser ablation system provides stable and reproducible signal intensity with smaller elemental fractionation effect compared with a Nd-YAG wavelength. With the chicane ion lens applied to quadrupole based-ICP-MS instruments, higher elemental sensitivity (x4 for Pb and U) and lower background count (<5 cps for Pb and <2 cps for U) could be achieved.

Coupling of ArF excimer laser ablation system and the chicane ion lens system provided us much precise U-Pb age data and REE abundances on single ablation pit. The results of U-Pb age and REE abundances for Nancy 91500 standard zircon show good agreement with those for literature values [Wiedenbeck et al., 1995, Sano et al., 2001]. Fig.1 shows the U-Pb data obtained here for Nancy 91500 standard zircon with those obtained by the conventional Nd-YAG system, indicative of remarkable improvement in analytical precision.



Details of the analytical technique and U-Pb age and REE abundances data for other samples will be discussed in this talk.

Figure 1: Concordia diagram for 91500 zircon.

References

- Hirata T. and Nesbitt R. W., (1995), *Geochim. Cosmochim. Acta.* 59, 2491-2500.
 Sano Y., Terada K. and Fukuoka T., (2002), *Chem. Geol.* 184, 217-230.
 Wiedenbeck, M., Alle, P., Corfu, F., Griffin, W. L., Meier, M., Ober, F., Von Quant, A., Roddick, J.C. and Spiegel, J., (1995), *Geostand. Newsl.* 19, 1-23.

Geochemical characteristics of cretaceous collision-related plutonism in Turkey

N. ILBEYLI¹ AND J.A. PEARCE²

¹ Mustafa Kemal University, Faculty of Engineering, Hatay, 31024, Turkey (nurilbeyli@yahoo.com)

² Cardiff University, Dept. of Earth Sciences, PO Box 914, CF10 3YE, Cardiff, UK (pearceja@cf.ac.uk)

Turkey is one of the important segments of the Tethyan orogenic collage and it is the product of mainly two major collision zones. The more recent is the Eocene continent-Pontide arc collision after which large volumes of post-collisional magmas were erupted in eastern Anatolia. The earlier episode, subject of this study, is the Cretaceous continent-island arc collision. Here, the Central Anatolian Massif contains Paleozoic-Mesozoic metamorphic rocks overthrust by Upper Cretaceous ophiolitic units and intruded by a number of post-collisional plutons (about 79.5 to 66.6 Ma). The Massif exhibits good examples of calc-alkaline to alkaline magmatism of similar age in a collision-related tectonic setting. In the Massif, three different rock types have been recognised on the basis of their petrographical, mineralogical and geochemical characteristics: (i) calc-alkaline (Behrekdag, Cefalikdag, Celebi, Kösefakili); (ii) transitional (Baranadag); and (iii) alkaline (Hamit). The calc-alkaline and transitional rocks are metaluminous, I-type, ranging from monzodiorite through monzonite to granite. The alkaline rocks are alkaline-potassic, predominantly peralkaline and A-type ranging from monzosyenite through syenite to quartz syenite. All intrusive rocks exhibit enrichment in large ion lithophile elements (LILE) and light rare earth elements (LREE) relative to high field strength elements (HFSE) and have high ⁸⁷Sr/⁸⁶Sr (0.70804-0.70964) and low ¹⁴³Nd/¹⁴⁴Nd (0.512206-0.512303) ratios. These characteristics indicate a mantle lithospheric source region(s) carrying a subduction component inherited from a pre-collision subduction event. The Rb versus (Y+Nb) and the Th/Yb versus Ta/Yb diagrams show that the calc-alkaline, transitional and alkaline intrusive rocks have been affected by crustal assimilation combined with fractional crystallization (AFC) process. Coexistence of calc-alkaline and alkaline magmatism in the Massif has been attributed to mantle source heterogeneity pre-collision. Perturbation of metasomatized-lithosphere by either delamination of the thermal boundary layer or slab detachment is the likely mechanism for the initiation of the post-collision magmatism in the Central Anatolian Massif.

Seasonal variations in a “greenhouse” Earth: Cretaceous coastal sea-surface temperatures inferred from $^{18}\text{O}/^{16}\text{O}$, Mg/Ca and $^{44}\text{Ca}/^{40}\text{Ca}$ ratios

A. IMMENHAUSER¹, TH. F. NÄGLER², TH. STEUBER³ AND D. HIPPLER²

¹ Department of Earth Sciences, Vrije Universiteit, Amsterdam, The Netherlands (imma@geo.vu.nl)

² Isotope Geology, Institute of Geological Sciences, University of Bern, Switzerland (naegler@geo.unibe.ch) (hippler@geo.unibe.ch)

³ Ruhr-Universität Bochum, Institut für Geologie, Mineralogie und Geophysik, Germany (thomas.steuber@ruhr-uni-bochum.de)

The last major episode of global greenhouse conditions began in the middle Cretaceous time and extended into the early Tertiary (~110-50 Ma). Well-constrained seasonality data for such periods, essential for climate modelling and prediction, are scarce. Temperature records of the Cretaceous sea-surface waters are mainly based on oxygen-isotope ratios from biogenic carbonate materials. The oxygen isotope proxy, however, is also sensitive to changes in freshwater input, carbonate system effects and diagenetic alteration. Thus, additional information from independent systems is needed. Here we report a combined application of $^{18}\text{O}/^{16}\text{O}$, calcium ($^{44}\text{Ca}/^{40}\text{Ca}$) and magnesium/calcium (Mg/Ca) ratios to low-Mg calcite of Late Cretaceous rudist shells. All three palaeotemperature proxies monitor seasonal variations in Cretaceous sea-surface temperatures (SST). The observed anti-correlation of $\delta^{18}\text{O}$ and $\delta^{44}\text{Ca}$ is expected for temperature dependent fractionation processes. The high degree of correlation ($R=0.82$) is at odds with the assumption of a significant diagenetic overprint. Yet, $\delta^{18}\text{O}$ and Mg/Ca proxies suggest high temperature seasonality (average values = 7°C and 8.5°C respectively), with $\delta^{18}\text{O}$ suggesting high and Mg/Ca rather low absolute temperatures. The $^{44}\text{Ca}/^{40}\text{Ca}$ data exhibit clear dependence on seasonal variations, demonstrating the potential of this new SST proxy. A first order calculation produces a reasonable temperature range (4.5°) for the $^{44}\text{Ca}/^{40}\text{Ca}$ proxy, pending further calibration.

With three different temperature proxies consistently indicating significant seasonal temperature changes, our data provide a detailed geochemical support for the existence of seasonal fluctuations of SST during the Late Cretaceous. Results presented here indicate that $\delta^{44}\text{Ca}$ bears the potential to become an essential tool for palaeoclimatic reconstructions. The multi-proxy approach provides improved palaeotemperature estimates and, in future, may shed light on the widely debated controversy surrounding Late Cretaceous and Early Palaeogene tropical sea-surface temperatures.

Endolithic genetic record of ancient microbes in Cretaceous black shale

F. INAGAKI¹, H. OKADA², A. I. TSAPIN³, K. H. NEALSON^{1,3}, K. HORIKOSHI¹

¹Subground Animalcule Retrieval (SUGAR) Project, Frontier Research System for Extremophiles, Japan Marine Science and Technology Center (JAMSTEC), Yokosuka 237-0061, Japan (inagaki@jamstec.go.jp)

²Division of Earth and Planetary Sciences, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan (oka@ep.sci.hokudai.ac.jp)

³Astrobiology Research Element, NASA Jet Propulsion Laboratory, Pasadena MS183-301, CA 91109, USA (knealson@mail1.jpl.nasa.gov)

A record of the history of the planet Earth is hidden in the subsurface biosphere, like the annual rings of an old tree. From limited evidences retrieved from underground, one can infer the geographical, geological and biological events that occurred throughout Earth's history. We report here the successful recovery of genetic record of ancient microbial community in mid-Cretaceous black shale. We drilled the black shale core sample from the continental margin at Serre des Castets, the southern part of France. The core contained one phosphate-accumulated strata, defined as a part of the mid-Cretaceous OAE (Oceanic Anoxic Events). Nanofossil analysis suggested that the OAE stratum was formed at 108 million years ago. Endolithic DNA was extracted from the several axis parts of the core, then bacterial ribosomal RNA genes (rDNA) was amplified by PCR. The molecular approaches such as the terminal-restriction fragment length polymorphism (T-RFLP) fingerprinting analysis, phylotype similarity analysis of rDNA clone libraries and the phylogenetic analysis of representative rDNA sequences revealed that recovered rDNA sequences were phylogenetically similar to microbial components in deep-sea sediments. T-RFLP and rDNA phylotypes analysis indicated that the rDNA structures were obviously associated with lithology. At the phosphate rich OAE stratum, the delta-subclass (sulfate reducing bacteria) of Proteobacteria class was predominantly detected, while at other sections gamma-Proteobacteria such as genera *Shewanella*, *Moritera*, and *Psychromonas* were predominant microbial components. In addition, porosity data and X-ray scanning analysis strongly supported that the extant microorganisms could not infiltrate physically into the examined black shale materials. These genetic rDNA signatures probably associated with the past microbial habitats occurring at 108 million years ago, serves as potential geomicrobiological evidence reflecting novel records of extinct life in the seafloor paleoenvironment.

Biogeochemistry of trace metals during a coastal bloom in the Baltic Sea

JOHAN INGRI¹, JENNY LARSSON², SUSANNA NORDLING², ÖRJAN GUSTAFSSON², JENNY RÖNNEGÅRD^{1,2} AND PER ANDERSSON³

¹ Division of Applied Geology, Luleå University of Technology, 971 87 Luleå, Sweden (Johan.Ingri.@sb.luth.se)

² Institute of Applied Environmental Research (ITM), Stockholm University, 106 91 Stockholm, Sweden

³ Laboratory for Isotope Geology, Swedish Museum of Natural History, Box 50007, 104 05 Stockholm, Sweden

Ultrafiltration was performed before and during spring-bloom, using filters with six different cut-offs (1kD, 3kD, 5kD, 10kD, 100 kD and 0.22µm).

By early May, phytoplankton production was the important source of particulate carbon. POC to chlorophyll-a decreased from 200 to 50, $\delta^{13}\text{C}$ -POC increased from -30‰ to -22‰, and TEP (Transparent Exopolymeric Particles, reflecting sugar-rich exudates from mainly diatoms) increased around 8 times. COC (1kD-0.22µm) was around 30% and POC 5% of TOC before plankton production started. During bloom COC increased to about 45% and POC up to 10% of TOC.

The unfiltered Cu, Ni and Co concentrations remained relatively stable throughout the sampling period (around 30, 34 and 1.5 nM, respectively). Furthermore, the colloidal fractions remained relatively constant for these three elements. Approximately 60% of colloidal Cu was found in the 5-10kD fraction and around 25% in the 1-5kD fraction, both before and during bloom. However, a distinct decrease in the solution (<1kd)/colloidal ratio was observed during bloom.

The Fe data showed that the LMW fraction was reduced from 50nM down below 7nM during bloom, in spite of the fact that the total Fe concentration was around 600 nM. This slow transfer may induce iron-stressed conditions for certain plankton species during bloom.

Data indicate a slow transfer of low molecular trace metals (directly bioavailable) from particulate and colloidal phases. Most of the decrease in the solution fraction (LMW fraction) reflects uptake in the particulate fraction.

Three different mechanisms could explain this phase change. Active uptake of LMW trace metals by living plankton, uptake by TEP and scavenging by Mn-rich particles (which were formed during bloom).

About 75% of the unfiltered Al concentration was retained by the 0.22 µm filter before bloom and 90% during bloom. The LMW/colloidal ratio decreased from 8 down to 1 during the sampling period. These data indicate an uptake of LMW Al into the particulate fraction during plankton bloom. Active uptake of Al by plankton appears to be a less likely explanation for this phase change. Association of LMW Al with TEP is a more reasonable explanation.

Modelling of catalytic abiogenic synthesis of the hydrocarbons in the Earth's crust

K. G. IONE

Scientific-Engineering Center "Zeosit" SB RAS, Novosibirsk, Russia (zeosit@batman.sm.nsc.ru)

The problems of the hydrocarbon deposits origin are being considered for a long period of time. The most conventional models imply biogenic mechanisms of oil-gas lenses formation in the Earth's crust.

The present paper summarizes the research results of the lab-scale and pilot synthesis of hydrocarbons from CO, C_2 and C_2 over bifunctional metal-containing catalysts (covering Fe, Ni, Co, Mo etc.) mixed with clays, SiO_2 , Al_2O_3 and zeolites. The compositions of the synthesised hydrocarbon mixtures are compared with those of the natural gas-condensate deposits.

The conclusion was made that the modern technologies of abiogenic hydrocarbon synthesis on bifunctional catalysts allow obtaining the natural variations of hydrocarbon mixtures – from predominantly methane to the liquid hydrocarbon mixtures (up to C_{20+}) with various contents of olefins, n-alkanes, iso-paraffins, and aromatic hydrocarbons.

The supposition is analysed that the processes of hydrocarbons synthesis from C_2 , C_4 and C_2 mixtures over inorganic catalysts may simulate the macro-geochemical processes having proceeded in the Earth's crust at different stages of its geochemical history.

The possible geochemical schemes for the abiogenic synthesis of hydrocarbon mixtures are proposed.

It was taken into account that the biogenic version of hydrocarbon synthesis has a low thermodynamic probability: the carbon dioxide and water bonding reactions proceed in the endothermic way, requiring an energy source. Their intensity in the oxygen-free atmosphere would be negligible. However in case of the abiogenic hydrocarbon syntheses the reactions proceed with a considerable heat release and thermodynamically are very highly probable. The intensity and probability of these processes under the primary atmosphere conditions must have been quite high.

References

- Chang C.D. and Scott Han, (1994), *Kirk-Othmer Encyclopedia of Chemical Technology* **12**, Fuel synthesis (liquid).
 Udaya V., Rao S. and Cormley R.J., (1990), *Catal. Today* **6**, 207-234.
 Mysov V.M., Stepanov V.G. and Ione K.G., (1997), *Stud. Surf. Sci. Catal.* **105**, 1381-1392.
 Ione K.G., Mysov V.M., Stepanov V.G. and Parmon V.N., (2001), *Chemistry for Sustainable Development* **9**, 129-143.
 Ione K.G., Mysov V.M., Stepanov V.G. and Parmon V.N., (2001), *Neftekhimia* **41**, 178-184.

Hf-Nd-Sr isotope relationships in spinel and garnet facies peridotite xenoliths: inferences for the age and evolution of the lithospheric mantle

DMITRI IONOV & DOMINIQUE WEIS

Department of Earth and Environmental Sciences, CP 160/02,
Université Libre de Bruxelles, 1050 Brussels, Belgium
(dionov@ulb.ac.be; dweis@ulb.ac.be)

We report Hf-Nd-Sr isotopic compositions of cpx, garnet and amphibole separated from >30 spinel and garnet peridotite xenoliths in volcanic rocks from Siberia and Mongolia. Hf-isotope compositions were determined on a Nu Plasma MC-ICPMS instrument at the University of Brussels. The new data are considered together with results earlier reported for xenoliths from central and NE Asia [Baikal region and SE Siberian craton; Ionov et al. (2001); Blichert-Toft et al. (2000)]. The $^{176}/^{177}\text{Hf}$ values in off-cratonic peridotites range from 0.2830 to 0.2842 and are negatively correlated with Hf abundances. The Hf-Nd-Sr isotope relationships define 3 major fields. (1) Depleted, poorly metasomatised peridotites have $^{176}/^{177}\text{Hf}$ and $^{143}/^{144}\text{Nd}$ similar to those in the N-MORB or higher. (2) Some metasomatised peridotites plot within the terrestrial Hf-Nd-Sr isotope array defined by MORB and OIB indicating uniform mixing between the depleted and enriched sources. (3) LREE-Sr-enriched peridotites with negative Hf anomalies plot above the Hf-Nd and Hf-Sr arrays. Some of the latter retain Lu-Hf relationships and Hf-isotope compositions imposed by the early depletion events and (as well as the depleted peridotites) yield Precambrian Lu-Hf model ages (>1Ga). The Hf-isotope compositions in those rocks are much less affected by metasomatism than those of Sr and Nd, either because Hf is more compatible (higher cpx/melt and garnet/melt partition coefficients) or because the metasomatic media are poor in Hf (i.e. have negative HFSE anomalies). Lu-Hf data for those rocks can, together with Re-Os isotope data, be used to infer depletion ages and the timing of the lithospheric formation. The Lu-Hf ages for coexisting cpx-garnet and cpx-amphibole pairs are either close to the eruption age of host volcanic rocks or indicate pre-eruption events or incomplete isotopic equilibration.

References

- Ionov D., Weis D., Shirey S., Prikhod'ko V. and Chazot G., (2001), *EOS, Abstr. AGU 2001 Fall Meeting*.
Ionov D., Chazot G., Prikhod'ko V. and Weis D. (2001), *J. Conf. Abs.* **6**, EUG XI.

Tracer Test with As(III) and As(V) at the Cape Cod Site

M. ISENBECK-SCHRÖTER¹, R. HÖHN¹, S. STADLER¹, S. JANN¹, J. DAVIS², D. KENT², V. NIEDAN¹, C. SCHOLZ¹, A. TRETNER¹ AND R. JAKOBSEN³

¹Institute of Environmental Geochemistry, Heidelberg, Germany (mischroe@ugc.uni-heidelberg.de)

²Geological Survey, Menlo Park, CA, USA

³Danish Technical University, Lyngby, Denmark

In spring and summer 2000, transport experiments with As(III) and As(V) were run in close cooperation with scientists of the USGS at the Cape Cod Site near Boston. The project was funded by the DFG and supported by the USGS Toxic Substances Program. The Cape Cod Site is a famous hydrogeological test site of the USGS. Following longterm contamination by sewage waters, a vertical redox zonation occurs in the aquifer due to the degradation of organic substance. Whereas the upper 3-4 meters are oxic, a suboxic zone and in 20 meters depth also an anoxic zone have developed.

In each redox zone a specific tracer experiment was run using bromide as ideal tracer. As(III) was injected into the oxic and the suboxic zones using a pulse injection method with high loads of As(III). The different geochemical environments lead to different transport and reaction behavior of both As species. In the oxic zone, a retardation of As(III) and a slow oxidation to As(V) could be observed. The formed As(V) was nearly immobile. In the suboxic test, As(III) was transport fast and also fast oxidation reactions occurred.

The reduction of As(V) was studied under iron reducing conditions injecting As(V) continuously into the anoxic layer of the aquifer. As(V) accumulated in the solid phase due to small amounts of injected oxygen which oxidized the ferric iron and bound the As(V). A mobilisation of As(III) could be observed when anoxic conditions reestablished. Sulfate reduction seems to submit the reduction of the arsenic and the iron, whereas specific arsenic reducing microorganisms or a significant mediation of hydrogen concentrations could not be detected.

Further studies will focus on laboratory studies of redox reactions at manganese and ironhydroxide surfaces. These studies will lead to the concepts which are necessary to obtain a transport-reaction-modell for the tracer tests.

Fluid-mantle interaction in an intra-oceanic arc: constraints from high-precision Pb isotopes

O. ISHIZUKA^{1,2}, R.N. TAYLOR¹, J.A. MILTON¹ AND R.W. NESBITT¹

¹Southampton Oceanography Centre, Empress Dock, Southampton SO14 3ZH, United Kingdom (rex@soc.soton.ac.uk)

²Institute of Geoscience, Geological Survey of Japan/AIST Central 7, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8567, Japan (o-ishizuka@aist.go.jp)

We present new isotopic and trace element data for back-arc lavas from the Izu-Bonin arc including high-precision double-spike Pb isotope measurements. Systematic along-arc isotopic variation of lavas has been identified, with coherent isotopic trends for the volcanic front and back-arc volcanoes. Sr isotopes are more radiogenic, while Pb isotopes are less radiogenic in the northern compared to the central part of the arc. This is particularly apparent in the back-arc seamounts. Decoupled variation of Pb and Sr isotopes cannot be explained by variation in the amount of single subduction component.

Almost parallel but distinct trends on Pb-Pb plots imply differing mantle sources in the northern and central sections of the arc. The decoupling of Sr and Pb isotopic variation for both volcanic front and back-arc can be explained by the presence of two mantle components; a MORB source observed in the back-arc basins of the Philippine Sea Plate (e.g. Hickey-Vargas, 1998) and a Pacific MORB-like source. Lesser contribution of Pacific MORB-type source in the northern part of the arc could consistently explain along-arc isotopic variation.

By assuming the regional mantle end-member components, volcanic front magmatism is compatible with having no direct sediment (melt) input, but having 2 to 2.5 % of a fluid derived from sediment and altered oceanic crust in a mixing ratio of about 1:100. In contrast, high $\Delta 7/4$ and low $^{143}\text{Nd}/^{144}\text{Nd}$ associated with high Th/Ce imply that subducted sediment melt is an important component in the back-arc. The magmatism in the back-arc seamounts is estimated to have 0.2 to 0.3% of sediment melt (bulk sediment) and 0.5% of fluid from altered oceanic crust added to the source for both northern and central parts of the arc.

In the arc where sediment melt is significant as a slab-derived component, slab input could become more significant towards the back-arc for the elements like Nd and Th, while it becomes less significant towards back-arc for fluid-mobile elements.

References

Hickey-Vargas R., (1998), *J. Geophys. Res.* 103. 20963-20979.

Geochemistry of ostracode calcite: Empirical calibration of 3 species from Page Pond, Ohio, U.S.A.

EMI ITO¹, SONIA W. BACON², ALISON J. SMITH², AND DONALD F. PALMER²

¹Limnological Research Center, University of Minnesota, Minneapolis, MN, 55455, USA (eito@umn.edu)

²Department of Geology, Kent State University, Kent, OH 44242 (asmith@kent.edu, dpalmer@kent.edu)

Ostracode life cycles, shell geochemistry, and associated hydrochemistry were studied over a period of one year in a holomictic oligohaline pond with surface and groundwater inflow in northeastern Ohio, USA. Species and water samples were collected monthly from 5 stations within the pond, including the inlet, the middle, two groundwater inflow sites, and the outlet. Adult and juvenile *Physocypria globula* and *Cipridopsis vidua*, both nektonic species, were found year round. High numbers of adult *P. globula* were found late February - late September, and juveniles were abundant during mid-summer. Large populations of juvenile and adult *C. vidua* were found late May - September. *Candona crogmaniana* adults (a benthonic species) appeared November - March with juveniles abundant March - October. *P. globula* shell chemistry is consistent with the species moulting to adult stage during the warmest month of August when the water temperature was consistently well above 15°C. *C. vidua*, on the other hand, moulted to adult stage June - October whenever the water temperature was $\geq 15^\circ\text{C}$. The shell chemistry of *C. crogmaniana* is consistent with its becoming adult during the cold months (November - March?) but reflecting its infaunal habitat within groundwater inflow sites, shows a large scatter in $\delta^{18}\text{O}$, Mg/Ca and Sr/Ca values. Thus the fossil shells of *P. globula* are a record of the hydrochemical environment that prevailed when water temperature was well above 15°C. Because *C. vidua* juveniles undergo the final moult whenever water is $\approx 15^\circ\text{C}$, the species is likely to have short life cycles during those time periods, and the individuals that become adults in October overwinter until May when the reproductive cycle resumes. Thus the fossil shells of *C. vidua* record a range of hydrochemical conditions that existed during those time periods when water temperature was $\geq 15^\circ\text{C}$. For a mid-latitude temperate locality such as northeastern Ohio those conditions occur 5 to 6 months of the year whereas in warmer climates those conditions may be met year-round. This suggests that the fossil shells of *C. vidua* (and possibly of *P. globula* as well) should only be analyzed as large pooled samples to obtain some sort of averaged paleoenvironmental information. Nektonic ostracode species are more likely than benthonic species to track overall hydrochemical conditions of the water body.

^{40}Ar - ^{39}Ar age of a fresh glassy pseudotachylite from the Fuyun fault zone, northwest China

N. IWATA¹, Y. TAKIGAMI² AND A. LIN³

¹Dept. Earth and Environmental Sciences, Yamagata Univ., Yamagata, Japan (iwata@sci.kj.yamagata-u.ac.jp)

²Kanto Gakuen Univ., Ohta-Shi, Gunma, Japan (ytakigam@kanto-gakuen.ac.jp)

³Institute of Geosciences, Shizuoka Univ., Shizuoka, Japan (slin@ipc.shizuoka.ac.jp)

The Fuyun region is located on the southwestern side of the Aertai mountains, northwest China. In the Fuyun fault zone, glassy and microlitic pseudotachylites occur in the granitic mylonites (Lin, 1994a, b).

Isotopic dating of fault-generated pseudotachylite provides geochronological information from brittle fault rocks. Thus, ^{40}Ar - ^{39}Ar datings on pseudotachylite has been tried by several investigators (e.g. Kelley, et al., 1994; Karson, et al., 1998; Sherlock and Hetzel, 2001).

We carried out ^{40}Ar - ^{39}Ar dating of the glassy and microlitic pseudotachylites and biotite separated from host granitic mylonite from the Fuyun fault zone in order to estimate the age of the fault activity.

^{40}Ar - ^{39}Ar dating experiments were performed at the University of Tokyo by the stepwise heating method. Pseudotachylites were measured as whole-rock forms.

^{40}Ar - ^{39}Ar age spectrum of the glassy pseudotachylite indicates a pattern consisting of decreasing apparent ages with increasing extraction temperature. The age spectrum does not indicate a plateau age, and yields a total age of ~500 Ma, whereas the host granitic mylonite provides a total age of ~150 Ma. Two analyses of microlitic pseudotachylites reveal relatively flat patterns in the age spectra, but do not yield plateau ages. They show total ages of ~180 Ma and ~210 Ma.

The monotonously decreasing pattern in the age spectrum for the glassy pseudotachylite resembles that of a recoiled sample. $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of ~20,000 are shown in the lower temperature steps (500, 600 degrees Celsius) of the glassy pseudotachylite analysis. These ratios imply the presence of extraneous argon in the glassy pseudotachylite.

We consider that the recoil effect and the extraneous argon that had been intruded during the glassy pseudotachylite formation caused the significantly older total age of the glassy pseudotachylite than that of the host mylonite.

References

- Karson, J.A., Brooks, C.K. Storey, M. and Pringle, M.S., (1998), *Geology*, **26**, 39-42.
- Kelley, S.P., Reddy, S.M., and Maddock, R., (1994), *Geology*, **22**, 443-446.
- Lin A., (1994a), *J. Struct. Geol.* **16**, 71-83.
- Lin A., (1994b), *J. Geol.* **102**, 317-329.
- Sherlock, S.C. and Hetzel, R., (2001), *J. Struct. Geol.*, **23**, 33-44.