

## Carbonic fluid production during regional and contact metamorphism in the Black Hills, USA

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### Introduction

Graphitic metapelites constitute significant portions of collisional orogens. If graphite gets consumed during metamorphism, there is potential for release of massive amounts of carbonic fluids into the atmosphere. We investigated consumption of graphite and production of carbonic fluids in Black Hills metapelites that were regionally metamorphosed and later intruded by the Harney Peak Granite during the Proterozoic Trans-Hudson orogeny. Regional metamorphic grade ranges from greenschist facies to lower amphibolite facies. The contact-metamorphic overprint heated the rocks to the second-sillimanite conditions.

### Composition of graphite and fluid inclusions

Crystallinity of graphite, as revealed by X-ray spectra, is the same at all metamorphic grades. However,  $\delta^{13}\text{C}$  values range from  $-30.4\%$  to  $-21.3\%$ . Although there is a weak correlation of increasing values with grade, there is greater amount of correlation with the amount of graphite in the rocks, where rocks with most graphite tend to have the lowest  $\delta^{13}\text{C}$  values. Whereas most lowest-grade metapelites have abundant graphite, rocks in the aureole of the Harney Peak granite have little graphite, mostly as inclusions in regional garnets. In the contact aureole, graphite has been mostly consumed from the matrix. The aureole has also elevated Li concentrations, which can be attributed to metasomatism by infiltrating magmatic fluids from the granite and its pegmatite aureole [1].

Fluid inclusions in syn-metamorphic quartz veins, as revealed by microthermometry and Raman spectroscopy, are complex mixtures of  $\text{H}_2\text{O}-\text{CO}_2-\text{CH}_4-\text{N}_2$  and other species. Many samples are dominated by  $\text{H}_2\text{O}-\text{CH}_4$  mixtures, suggesting that methane may have been the dominate carbonic species evolved and its production caused increase in  $\delta^{13}\text{C}$  of the graphite. The apparent dominance of methane contrasts with the predicted composition of fluid in equilibrium with graphite, which should have equimolar  $\text{CO}_2$  and  $\text{CH}_4$  concentrations [2].

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## Structure and diversity of microbial communities at two methane seep sites (Gulf of Guinea)

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During the French oceanographic cruises Biozaire 1 (January 2001) and Biozaire 2 (November 2001) in the Gulf of Guinea two methane seeps, lately discovered by the geologists of Ifremer (DRO/GM), have been investigated. Sampling of animals and sediments have been done with a Remote Operated Vehicule (Victor 6000). Sediment cores have been taken on bacterial mat and close to animals known as organisms depending on chemoautotrophic nutrition (*Bivalvia Mytilidae* and *Vesicomomyidae*, *Pogonophora*). Measurements of physico-chemical parameters (temperature, methane, dissolved oxygen, sulfides and pH) have been carried out.

In sediments, microbial aggregations of methane-oxidising archae (ANME2) and sulfate-reducing bacteria (*Desulfosarcinales*) have been observed using fluorescent *in situ* hybridisation (FISH). These aggregates are known to be involved in the anaerobic oxidation of methane (AOM).

This study compares the number and the repartition of microbial aggregates in sediments for different places of the methane seep (close to mussels, close to clams, beneath a microbial mat ...). The results are interpreted in relation with methane and sulfide concentrations.

Bacterial symbionts in mussels and clams have been identified by 16S rDNA. The presence of both methanotrophic and thioautotrophic symbionts in mussel gills, and only thioautotrophic symbiont in clam gills is discussed in function of methane concentrations and repartition of microbial aggregates involved in AOM.

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## Chemical diversity of chondrule melt and its origin

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### Introduction

Common chondrules, Ca-Al-rich chondrules, and CAIs show compositional diversities, and their genetic relationships are not fully understood, although bulk chemical and isotopic compositions of type B1 CAIs are interpreted to be the results of condensation and subsequent evaporation (Richter et al., 2002). The diversity of chondrule melts was investigated in the present study with the special interest in evaporation in a simple system.

### Experimental

Evaporation vector (direction and magnitude of compositional change) of liquid by evaporation was experimentally and theoretically investigated for wide ranges of melt compositions and temperatures in the system CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. Equilibrium vapor pressure and the gas composition were calculated at temperatures ranging from 1000K to 2000K on the basis of thermodynamic model and parameters after Berman (1983) and Berman and Brown (1984). The compositions of type IA chondrules and Ca-Al-rich chondrules, equilibrium condensation path and evaporation path from the literature are compared with evaporation vectors.

### Results and discussion

Bulk chemical compositions of type IA chondrules are located on the equilibrium condensation-evaporation path of the CI composition, which is saturated with forsterite at about 2100K. It can be formed from the precursor with the CI composition, heated to temperature about 2100K, began to crystallize forsterite at the temperature due to selective loss of SiO<sub>2</sub>-rich component. The composition of the mesostasis suggests cooling down to about 1500-1600K. The pressure at the highest temperature is about several Pa. Ca-Al-rich chondrules, which are plotted at the locations rich in SiO<sub>2</sub>, CaO, and Al<sub>2</sub>O<sub>3</sub> were formed by mild heating at temperatures about 1300K to get much SiO<sub>2</sub>- and (Al<sub>2</sub>O<sub>3</sub>+CaO)-rich composition. The present results show that the diversity of type IA and Ca and Al-rich chondrules were formed from precursor of CI composition through melting, partial evaporation, and crystallization due to evaporation.

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## Noble gases of Antarctic lunar meteorite Yamato 981031

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Yamato(Y) 981031 lunar meteorite has been collected by the meteorite search party of the 39th Japanese Antarctic Research Expedition, and is suspected to be paired with Y793274 lunar meteorite based on the texture, mineralogy and bulk composition (Kaiden and Kojima, 2002). Mineralogical study on the Y981031 suggests source-crater pairing of Y981031, Y793274 and QUE94281, which are brecciated mare basalts with some highland components (e.g., Arai et al., 2002). We measured noble gases of the Y981031 to confirm the predicted pairing with Y793274 and to obtain noble gas signatures characteristic for materials derived from the lunar surface.

Noble gases were extracted from two chips weighing 0.1851g and 0.0579g by stepwise heating, and then measured on a modified-VG5400 (MS-II). The temperatures were 400, 600, 800, 900, 1000, 1100, 1200, 1300, 1400, 1600 and 1800°C, though the experiment was accidentally stopped at 1300°C on the sample 0.1851g due to leakage of vacuum of purification line.

Noble gas elemental and isotopic compositions are characterized by solar composition with small contributions of cosmogenic gases. Huge amounts of He ( $1 \times 10^{-3} \text{cc}^4\text{He}$ ) and Ne ( $2 \times 10^{-4} \text{cc}^{20}\text{Ne}$ ) were released in the temperature range of 800-1000°C, while heavier noble gases Ar, Kr and Xe released at higher temperatures of 1100-1300°C. The noble gas concentrations and those of cosmogenic <sup>21</sup>Ne and <sup>38</sup>Ar, 314 and 520  $\times 10^{-9} \text{cc/g}$  respectively, agree well with the reported values for Y793274, indicating a long duration (ca. 500Ma) of irradiation by galactic cosmic-rays as well as solar wind particles on the lunar surface as described for Y793274 by Eugster et al. (1991) and Takaoka and Yoshida (1992). Trapped <sup>40</sup>Ar/<sup>36</sup>Ar=2.4, which is an antiquity indicator of regolith breccia, is also similar to 2.3 for Y793274 (Eugster et al., 1991). All the noble gas signatures determined for Y981031 support the pairing with Y793274 lunar meteorite.

Noble gas release patterns show sharp increases at the extraction temperatures of 800°C for He and Ne and 1200°C for Ar, Kr and Xe. <sup>20</sup>Ne/<sup>22</sup>Ne ratio was as high as 12.5 at the lower temperatures, and then decreased approaching to a mixing line between cosmogenic and SEP-like Ne components. These data indicate that most of low energy solar particles have been lost before arrival to the earth, probably due to gas loss by shock heating on the lunar surface.

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## Double spikes: the gourmets' choice

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Recent advances in isotope ratio mass spectrometry, namely multiple collector ICP-MS and refined TIMS techniques, will significantly enhance the ability to measure heavy stable isotope fractionation, which will lead to the development of a wide array of process-identifying (bio)-geochemical tools. MC-ICP-MS is the most versatile technique in this respect. The major problems are the analytical mass bias produced, which largely exceeds natural fractionation, and the problem of elemental and molecular isobaric interferences. Different methods to account for the analytical mass bias are in use.

Particular features of the double spike technique are: A) As with element doping (using isotopes of another element), variations of the analytical mass bias are accounted for within analyses. Thus unsystematic variations on different time scales are resolved, as well as matrix effects that change the instrumental fractionation between sample and standard. B) As with bracketing standards (standards measured before and after each sample), the mass range is restricted to the isotopes of the target element. This is favourable for static measurements, in particular when mass dispersion is large. Also, problems effecting the isotope ratio of a doping element (e.g. isobaric interferences, matrix dependent influence on the effective fractionation behaviour) are avoided.

Thus the double spike technique combines the advantages of bracketing standards and element doping and demagnifies worries about matrix effects. In addition, it provides precise concentrations from the very same aliquot. Correction for analytical mass fractionation is extended to chemical separation, provided the spike is added beforehand. Thus purification can be optimised, further reducing matrix and interference problems.

The main limitation of the double spike technique is the requirement of four or more stable isotopes. This condition however is given for ca 2/3 of elements suitable for heavy stable isotope studies (polyisotopic elements with masses >39). Notwithstanding a persistent myth, a simple double spike calibration procedure for MC-ICP-MS was given by Siebert et al. (2001). The consistency of TIMS results between different laboratories could recently be shown (Hippler et al. 2002). On line-three dimensional data reduction is straightforward and enables error assessment without propagation procedures. The choice of method and the set up of procedures will be exemplified on Ca (TIMS) and Mo (MC-ICP-MS) isotope analytics.

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## Mass fractionation of tin in ancient bronze

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We report isotopic fractionation of tin in bronze probably caused by evaporation. Provenance studies of bronze have been conducted by using lead isotopic tracers. Budd et al. (1995) suggested the possibility that tin isotopic ratios in bronze may have been fractionated by evaporation and they suggested that the isotopic ratio of tin may become a good tracer for recycling and mixing processes of ancient metal. Precise isotopic analyses of tin of cassiterite by McNaughton and Rosman (1991) reported that the mineral showed little fractionation irrespective of their ages. Gale (1997) analysed isotopic compositions of tin in the ancient metal and bronze and reported that the mass fractionation was less than 0.1% for the ratio of <sup>122</sup>Sn/<sup>116</sup>Sn. The reported data, however, were mass fractionation corrected, which may have erased mass fractionation by evaporation.

We used a MC-ICP-MS (IsoProbe, Micromass) for isotopic measurements of tin. Sample analyses were bracketed by the analyses of a in-house standard solution in order to normalize isotopic composition of a sample. Measurements of standard solutions of tin from four chemical companies showed isotopic fractionations, as large as 1.0 ‰ in <sup>116</sup>Sn/<sup>120</sup>Sn, probably introduced during purification. External precision of <sup>116</sup>Sn/<sup>120</sup>Sn measurements was about 0.1‰ (2σ). Six samples of bronze and a slag unearthed from China were analysed. Tin was purified using the method described by Yi et al. (1995). Isotopic fractionation during the purification was about 1 ‰. The extent of mass fractionation in <sup>116</sup>Sn/<sup>120</sup>Sn was about 4 ‰. If we follow the model of Mulliken and Harkins (1922) that described mass fractionation by evaporation, 20% loss of tin is required to explain the observed mass fractionation.

We also conducted an evaporation experiment using synthesized bronze in inductive heater under argon flow. About one percent of bronze was lost by evaporation. We found that the condensate was enriched in light isotopes, 2 ‰ in <sup>116</sup>Sn/<sup>120</sup>Sn, compared with the starting material. In summary, the results of this study have revealed isotopic fractionation of tin in bronze. In addition, we reproduced mass fractionation, although the extent seemed to be too large for the extent of evaporation loss.

## Seasonal variability of biomarkers in sinking particles in the Japan Sea

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### Sediment trap experiment

The purpose of this study is to determine seasonal variation of biomarker flux in sinking particles collected by a time-series sediment trap at the northern Japan Sea for one year on 1998-99. Sterols, alkenones as well as stable carbon and nitrogen isotopes were measured by conventional chemical procedures.

### Results and discussion

In this area, usually blooming has observed two times in winter and early summer based on chlorophyll variation detected by Satellite studies (e.g. Kim *et al.*, 2000). Sinking fluxes of TOC and dry materials were consistent with such seasonal change, suggesting that the sediment trap even deployed in 1000 m depth successfully indicates seasonal change of primary production in euphotic layer.

Biomarkers for diatom and dinoflagellate (24-methylcholesta-5,24(28)-dien-3 $\beta$ -ol, 24-methylcholest-5-en-3 $\beta$ -ol and dinosterol) showed temporal peaks in early winter and early summer. Two factors might be related to this. Nutrient supply would be enhanced by increase of vertical mixing in winter. The low  $\delta^{15}\text{N}$  values in autumn to spring evidenced this interpretation. Increase of solar radiance in early summer might also lead increase of production.

The increase of cholesterol was found slightly later than the phytoplankton markers. We estimated that the population of zooplankton increased after phytoplankton bloom.

Unexpectedly,  $\text{C}_{37}$  alkenones (haptophyte origin) showed also maximum flux in two seasons, winter and summer. Furthermore,  $\text{C}_{37}$  alkenone unsaturation index ( $\text{U}_{37}^k$ ) showed relatively less variation compared with seasonal change of sea surface temperature. We considered several reasons; change of haptophyte species and changing water depth for haptophyte habitat, etc. It might be an important clue to interpret unusual  $\text{U}_{37}^k$  temperature profiles in LGM found in piston core samples in the Japan Sea (Ishiwatari *et al.*, 2001).

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## $\delta\text{D}$ of individual PAHs from the Murchison and an Antarctic carbonaceous chondrite

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Polycyclic aromatic hydrocarbons (PAHs) have been reported from carbonaceous chondrites and interplanetary dust particles, and also suggested to be present in interstellar medium. PAHs may be among the most ubiquitous organic compounds in the universe. Naraoka et al (2000) proposed two reaction pathways ("pyrene series" and "fluoranthene series") of extraterrestrial PAH formation based on  $\delta^{13}\text{C}$  values of individual PAH from an Antarctic CM2 carbonaceous chondrite (A881458). In this study, we have measured  $\delta\text{D}$  values of fluoranthene and pyrene from the Murchison and A881458 by gas chromatography-pyrolysis-isotope ratio mass spectrometry.

Preliminary compound-specific  $\delta\text{D}$  and  $\delta^{13}\text{C}$  values of pyrene and fluoranthene are shown in Table 1 as averaged values based on replicate injections. Standard deviations were generally less than 10‰ for  $\delta\text{D}$  and 0.5‰ for  $\delta^{13}\text{C}$ .  $\delta\text{D}$  value of individual PAHs is quite different from  $\delta\text{D}$  value of the reported bulk PAH fraction (~+500‰) from the Murchison. Fluoranthene is more depleted in D than pyrene, although pyrene and fluoranthene are structural isomers ( $\text{C}_{16}\text{H}_{10}$ ) each other. This  $\delta\text{D}$  signature may also suggest two distinctive reaction pathways for the extraterrestrial PAH formation. However, the  $\delta\text{D}$  trend is opposite to  $\delta^{13}\text{C}$  trend (fluoranthene more enriched in  $^{13}\text{C}$  than pyrene). In addition,  $\delta^{13}\text{C}$  values of PAHs are similar between the Murchison and A-881458, while the  $\delta\text{D}$  values are quite different (250-340‰). This isotopic difference may indicate a different aqueous history between the Murchison and A-881458.

**Table 1.**  $\delta\text{D}$  and  $\delta^{13}\text{C}$  values of fluoranthene and pyrene from the Murchison and A881458 meteorite

	Murchison	A881458
<b><math>\delta\text{D}</math> (vs. SMOW)</b>		
Fluoranthene	-560	-219
Pyrene	-421	-168
<b><math>\delta^{13}\text{C}</math> (vs. PDB)</b>		
Fluoranthene	-7.5	-8.3
Pyrene	-15.6	-15.8

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## Ore-Forming Fluids of Au-Hg Deposits

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Despite the similarity of mineral composition (gold, pyrite, arsenopyrite, cinnabar, realgar, stibnite, Tl-minerals, barite, etc.) and geochemical features of ores (Au, Hg, As, Sb, Tl, Ba, etc.), the gold-mercury deposits are similar formations which formed by different ore-forming systems: volcanogenic-hydrothermal and plutogenic-hydrothermal.

The fluid inclusion study carried out at 22 gold-mercury deposits of Russia and Mongolia showed that all these deposits formed at low temperatures (<280°C) and on the whole they are close to the Sb-Hg deposits, but fluids of volcanogenic-hydrothermal deposits are characterise by low salinity (0.5 – 10 wt. %) and chloride or chloride-bicarbonate-sodium composition with low-dense (N, CO<sub>2</sub>, ±CH<sub>4</sub>) gas phase. The lower temperature deposits (<150-170°C) have fluids of lower salinity (0.5-7 wt. %). For a number of higher temperature deposits heterogenization of fluids with separation of gas phases (H<sub>2</sub>O>>CO<sub>2</sub>>N<sub>2</sub>) is observed. Plutogenic-hydrothermal deposits are distinguished by wider variations in salinity of ore-forming fluids (0.2-25 wt. %), more complex composition (NaCl, CaCl<sub>2</sub>, FeCl<sub>2</sub>, KCl etc.), and essentially carbon dioxide gas phase (CO<sub>2</sub>> N<sub>2</sub> > H<sub>2</sub>O). In fluid inclusions of these deposits the liquid carbon dioxide occurs, testifying to higher pressure of hydrothermal fluids (up to 510 bar).

However gold-mercury deposits significantly differ from the other types of gold deposits such as gold-sulfide-quartz, gold-silver, gold-antimony which are higher temperature formations. The specific feature of fluid composition of Au-Hg deposits is mainly determined by the participation of various types of exogenous waters (meteoric water, oil water, chloride brines, etc.). This is manifested in the specifics of their composition for particular regions, distinguished by paleohydrogeological environment of formation of gold-mercury deposits under the near-surface condition. During formation of Au-Hg mineralization one of the main factors responsible for the deposition of Au and Hg is a process of heterogenization of ore – forming fluids and decrease of temperature and pressure.

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## Sr-Pb isotopic evidence for plume-ridge interaction along the Central Indian Ridge

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The Central Indian Ridge (CIR) between 18° and 20°S shows characteristics of hotspot-ridge interaction such as increased crustal thickness and the presence of off axis ridges (Rodrigues, Three Magis and Gasitao ridges [1]). We present triple spike Pb isotope [2] and Sr isotope data for on and off-axis MORB samples from this region to determine whether such interaction is taking place.

The isotope data show the existence of two distinct groups, consistent with those defined from major and trace elements variations [3]. The first one, composed by MORB produced on the CIR-axis, is characterized by lower Sr and Pb isotope ratios (<sup>206</sup>Pb/<sup>204</sup>Pb = 18.304-18.703; <sup>207</sup>Pb/<sup>204</sup>Pb = 15.502-15.571; <sup>208</sup>Pb/<sup>204</sup>Pb = 38.182-38.737 and <sup>87</sup>Sr/<sup>86</sup>Sr = 0.7031-0.7038) than the Gasitao group (<sup>206</sup>Pb/<sup>204</sup>Pb = 18.583-18.792; <sup>206</sup>Pb/<sup>204</sup>Pb = 15.551-15.579; <sup>208</sup>Pb/<sup>204</sup>Pb = 38.532-38.730 and <sup>87</sup>Sr/<sup>86</sup>Sr=0.7035-0.7039). These two groups form two distinct arrays in <sup>207</sup>Pb/<sup>204</sup>Pb-<sup>206</sup>Pb/<sup>204</sup>Pb space with different slopes. The Gasitao group data are displaced toward higher Pb and Sr isotope ratios, and trend towards the field of the Réunion hotspot [4]. There is also a North-South decrease in Pb isotope ratios along the CIR axis, similar to that found using trace elements [3].

We interpret the along-axis variations as reflecting the influence of the fossil Réunion hotspot track, which is cut by the CIR at around 15°S. At this latitude, both Pb and Sr isotope ratios of CIR MORB display a clear increase, consistent with such an interpretation. The Gasitao group can be explained in terms of mixing between a CIR component and a present-day Réunion plume component. Despite the close spacing of the samples, there are significant isotopic differences between the two groups, suggesting the presence of a boundary between two different mantle domains.

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## Direct Calorimetric Measurements of Surface Energies and Phase Stability of Nanophase Oxides

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High temperature oxide melt solution calorimetry is used to measure the energetics of oxide phases as a function of surface area. The effects of polymorphism, surface area, and hydration must be separated. Crossovers in thermodynamic stability of polymorphs at the nanoscale has been confirmed for alumina (alpha and gamma) and titania (rutile, brookite, and anatase). Oxyhydroxides generally have smaller surface energies than anhydrous oxides; thus fine particle size may increase the P-T stability field of hydrous phases. Systematic trends in surface and transformation energies of oxides of Al, Fe, Ti, Zr, and Si are discussed.

## Rare Earth Elements and Neodymium Isotopic Systematic in the groundwaters of French Guiana

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The current use by the population of French Guiana of untreated river water for drinking purposes has important impacts on public health. Consequently, groundwater is of major importance as a possible alternative drinking-water supply to reduce these impacts. The present study is part of a program dedicated to the knowledge of French Guiana aquifers: hard rock fractured and littoral deposits, in order to improve both their prospecting and management. French Guiana covers 10% of the Guyana Shield, which forms the northern extension of the Amazonian Platform. The Guyana Shield mainly comprises granite-gneiss and volcano-sedimentary rocks of Archean to Middle Proterozoic age. An extensive Holocene sandy-argillaceous terrane, borders the Atlantic Ocean.

We report Rare Earth elements (REE) contents as well as the isotopic composition of Nd in groundwaters and surface waters. Groundwater samples were collected from (i) shallow drill holes in this coastal area, which is the only densely populated area in French Guiana, and (ii) deeper wells in the basement around Cayenne and along the Maroni River from which groundwater is pumped from bedrock fractures. Surface water samples were collected from two coastal streams (Yiyi and Kourou) and from one small inland river (Eau Claire).

The determination of REE contents by inductively coupled plasma mass spectrometry and of Nd isotopic ratios by multiple collector mass spectrometer was described in Négrel et al. (2000). The Nd isotope ratios are used to complement the degree of water-rock interaction and clarify mixing processes within the groundwaters.

The contents of individual dissolved REEs and total dissolved REEs in the investigated waters, vary over several order of magnitude and fall within the range observed by several authors either in surface or groundwaters. The values appear broadly independent of other parameters such as total dissolved solids and pH but organic matter seems play a significant role in controlling the dissolved REE contents in waters. REE crustal normalised patterns exhibited relatively uniform patterns with enrichment in heavy REEs.

The isotopic composition of Nd in the waters from French Guiana ranges from  $^{143}\text{Nd}/^{144}\text{Nd} = 0.511377 \pm 9$  to  $0.512162 \pm 8$  associated with a  $^{147}\text{Sm}/^{144}\text{Nd}$  in the range 0.085-0.150, clearly intermediate between that of the parent rocks and that of suspended matter from the Amazon Basin.

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## The role of dissolved water in the compositional evolution of anorogenic magmas

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Phase equilibrium “fractionation” experiments were conducted on natural rocks from the three hy-normative (silica-saturated) suite-types found in hotspot and early continental rift regimes that contain units ranging from basalts to rhyolites (or their plutonic equivalents). The Nandewar suite of NSW Australia was chosen to represent the hawaiite through rhyolite and comendite of the alkalic series. Fine-grained samples from the Laramie Anorthosite Suite and the Snake River plain volcanic province were used to represent the potassic, Fe-, Ti-, and P-rich units of the “continental tholeiitic series”. Samples from Pinzon and Alcedo, Galapagos represented the ocean island series. This investigation focused on (a) determination of possible conditions under which the units of each suite-type can be produced by fractionation (b) investigation of the possibility of a common tholeiitic parent for the three suite-types.

### Experimental results

The hy-normative alkalic trend was replicated at 9 kbar at water contents of 0.4 wt% and higher. Early clinopyroxene domination induces the typical alkali enrichment at constant silica content. Kaersutite dominates the intermediate stages of evolution leading to sodic rhyolite.

The Fe-Ti-P enrichment and early silica depletion of ferrodiorites (jotunites) of the anorthosite massifs and the ferrobasalts of the Snake River Plain are produced in a tholeiitic gabbro at 9 kbar at < 0.4 wt% H<sub>2</sub>O. For bulk water contents slightly below this, the silica-depletion trend reverses shortly after this water content is attained by the melt. At pressures of 4.kbar and water contents >0.4 wt%, tholeiitic gabbro produces the typical potassic granite of the anorthosite/rapakivi-type granite complexes. Experiments at 0kbar confirm the tholeiitic ocean island trend.

Investigation of the possibility that these three suite-types could arise from a similar parent but with different water contents and different pressures of crystallisation was accomplished by “cross-over” experiments. Jotunite has been produced from sodic alkalic rocks by reducing the water content below 0.4 wt%. The ocean island tholeiitic trend has been produced from alkalic rocks at low pressure. Intermediate pressures fractionation of sodic hawaiite above 0.4 wt% H<sub>2</sub>O produces potassic granite.

Within each specific range of bulk water content above and below this critical value the liquid compositions that can coexist with an aqueous fluid are now well constrained and can be used to facilitate understanding of the hydrothermal stage of evolution.

## Hadean Earth crust: microanalytical investigation of 4.4 to 4.0 Ga zircons from Western Australia

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The oldest identified Earth remnants are 4.4 to 4.0 Ga zircons found within c. 3.0 Ga sediments (Froude et al., 1983; Compston and Pidgeon, 1986; Wilde et al., 2001; Nelson, 2002) and c. 2.7 Ga orthogneisses (Nelson et al., 2000) of the Yilgarn Craton. Their source rocks have not been identified but their trace-element patterns, euhedral zoning and siliceous inclusions suggest crystallization within granitic *sensu lato* melts. Combined SHRIMP U–Th–Pb isotopic, EMA trace-element microanalysis and BSE/CL imaging indicate a range of <sup>207</sup>Pb/<sup>206</sup>Pb dates within each mineral; the oldest provide a minimum age for zircon crystallization, with younger dates not accounted for by zircon rims attributable to radiogenic-Pb loss from μm-scale domains within each grain. Concurrence in <sup>207</sup>Pb/<sup>206</sup>Pb dates within and between zircons favors episodic loss of radiogenic Pb during 4404, 4350, 4276, 4185, 4150, 4005, 3978, 3945 and 3874 Ma events rather than continuous loss during a ≤3750 Ma event. As significant Pb diffusion from zircon will only occur at >900°C, these times may correspond to high-grade thermal metamorphic events related to mantle upwelling or convective overturn episodes.

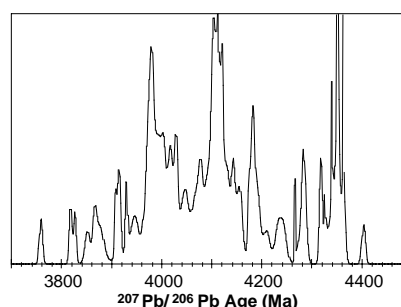


Figure 1. Gaussian probability plot for ≥95% concordant SHRIMP <sup>207</sup>Pb/<sup>206</sup>Pb dates obtained from ≥4.0 Ga zircons (refs. given below).

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## Nd-Sr-Hf-Pb Isotope Correlations in lavas from Lanai, Hawaii

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The extremes of Nd-Sr-Hf-Pb isotope compositions of shield-stage Hawaiian volcanoes are well documented in Koolau (relatively enriched isotopic signature) and Mauna Kea (relatively depleted isotopic signature). Koolau has much greater intravolcano isotopic variability than Mauna Kea. Based on an expanded data set for West Maui (Gaffney et al., this volume) and Lanai we show that this contrast in variability also holds for other volcanoes dominated by either the Koolau or Kea component.

We sampled several areas of Lanai to encompass the stratigraphically lowest and highest exposed flows. In three places we were able to collect short stratigraphic sections. Sample compositions span a significant part of the isotopic range of shield to late-shield lavas exposed in Hawaii.  $\epsilon_{Nd}$  and  $\epsilon_{Hf}$  range from -0.2 to +4.2 and +4.6 to +9.8, respectively, with no compositional gaps. The data are remarkably strongly correlated, with 18 of 20 samples within analytical error of the best-fit line. This correlation also holds for Nd-Sr isotope variation in which 21 of 24 acid-leached samples (including those of West et al., 1987) are within analytical error of a linear correlation.

$^{206}Pb/^{204}Pb$  (17.85 – 18.06) also correlates with Hf and Nd compositions. Although TIMS (Seattle) and MC-ICP-MS (Lyon) data for the same samples overlap within analytical precision, correlated variation with  $^{207}Pb/^{204}Pb$  is resolvable only by the higher precision data. In addition, when grouped by the stratigraphic section from which each sample was collected, each section describes just resolvable, subparallel linear trends in Pb isotope space.

The linear Hf-Nd trend implies little difference in endmember Hf/Nd ratios and simple binary mixing of two homogeneous sources. Linear extrapolation of the trend from  $\epsilon_{Hf}$  of +9.8 (the most radiogenic Lanai sample) to +12.2 (the homogeneous average composition of Mauna Kea and West Maui) predicts a Nd isotope composition only 1  $\epsilon$ -unit lower than observed for Mauna Kea and West Maui. As observed in Mauna Kea (Abouchami et al., 2000), Lanai lavas also define multiple mixing lines in Pb isotope space that require binary mixing among more than just two components. Unlike Mauna Kea, however, mixing pairs may be associated with a stratigraphically discrete sequence of lavas.

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## U-Pb SHRIMP dating of opals

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The applicability of U-Pb dating to uraniumiferous opal has been known for at least two decades (Ludwig *et al.*, 1980), but only recently has this technique been increasingly used in constraining the timing of surface processes (Neymark and Paces, 2000; Neymark et al, 2000; Ludwig and Paces, 2002). These studies revealed significant micro-scale variations of both U-Pb and U-series ages within the opal, emphasising a need for high spatial resolution analysis and driving subsequent attempts to use micro-analytical techniques for opal dating. Paces et al. (2000) presented results of the first successful application of SHRIMP for U-series analysis of opal. The aim of our study is to extend their work and develop analytical protocol for the U-Pb SHRIMP dating of opals.

U-series analysis of opal is relatively simple. Th/U ratios for unknowns are corrected using a ~2.2 Ma opal standard (Amelin and Neymark, 1999). This contains 800-1000 ppm of U, and has both  $^{230}Th/^{238}U$  and  $^{234}U/^{238}U$ -activity ratios equal to one. Longer integration times (30-40 sec for less abundant isotopes and the background) and larger primary beams (15 to 50 nA) were used for these analyses, as compared to a standard zircon SHRIMP analysis, to improve the counting statistics. This had no visible effect on observed Th/U ratios; however, the longer sputtering using a stronger primary beam severely affected U/Pb ratios. It resulted in partial loss of conductivity at the end of a run and consequent drift of U/Pb ratios, which was unsupported by a change in UO/U ratios. To combat this problem intermediate run times and smaller primary beam currents (10-15 nA) were adopted.

Our U-Pb results for opals from both USA and Australia are comparable with the TIMS ages of these samples and support the potential for SHRIMP dating of opal.

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## Quantitative molecular techniques to study the abundance and activity of microorganisms in the marine deep subsurface

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The Ocean Drilling Program Leg 201 Peru Biosphere, dedicated to studying deep sub-surface marine microbiota, focused on the abundance and activity of microorganisms in marine deep sediments of the Peru Continental Margin and the Equatorial Pacific down to 400 m below seafloor. Currently, we are applying fluorescence in situ hybridization (FISH) and real-time Polymerase Chain Reaction (rt-PCR) to quantify bacteria and their activity in ODP Leg 201 samples. The rt-PCR approach for quantification of microorganisms promises to be more sensitive than FISH or MPN under subsurface conditions. Experimental design of rt-PCR permits the quantification of phylogenetic groups or single species of microorganisms by amplification of 16S rDNA(rRNA) molecules. The metabolic state of microorganisms can be determined by the quantification of mRNA of functional genes. We have studied the detection limits, reproducibility, and applications of the method, measuring the expression of 16S rRNA and dissimilatory (bi)sulfite reductase (DSR) mRNA in *Desulfobacterium autotrophicum* during in vitro growth. Using DSR as phylogenetic and activity marker, we will study the *in situ* activity of sulfate reducing bacteria in the sub-seafloor biosphere.

## Activity coefficient and polymerization of aqueous silica based on high-PT solubility measurements

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We have made high-PT solubility measurements on several mineral assemblages which buffer aqueous SiO<sub>2</sub> at a wide range of concentrations, in order to define more closely the activity-concentration relations. Solution equilibria at 800 °C and 12 kbar were determined on zircon (ZrSiO<sub>4</sub>, ZRC)-baddeleyite (ZrO<sub>2</sub>, BDY), enstatite (MgSiO<sub>3</sub>, EN)-forsterite (Mg<sub>2</sub>SiO<sub>4</sub>, FO), and kyanite (Al<sub>2</sub>SiO<sub>5</sub>, KY)-corundum (Al<sub>2</sub>O<sub>3</sub>, COR) assemblages from both the SiO<sub>2</sub>-undersaturated and -oversaturated directions on synthetic crystalline materials. The NaCl-graphite piston-cylinder apparatus was used with welded Pt capsules containing H<sub>2</sub>O+initial SiO<sub>2</sub> and a perforated inner Pt capsule containing the mineral assemblages. Solubilities were determined by weight changes of the inner capsule after a run (solubilities of components other than SiO<sub>2</sub> were below detection). The SiO<sub>2</sub>-buffering reactions, higher and lower bounds on the equilibrium SiO<sub>2</sub> molality ( $m_h$  and  $m_l$ ), and the mean SiO<sub>2</sub> activity coefficient ( $\gamma_s$ ) derived from the Zotov and Keppeler (Chem. Geol., 2002) dimerization model, are given in the table below.

Reaction	$\Delta G^\circ$ kJ/mol	$m_h$ molal	$m_l$ molal	$\gamma_s$
ZRC=BDY+SiO <sub>2</sub>	16.31	0.0632	0.060	1.090
2 EN=FO+SiO <sub>2</sub>	9.17	0.285	0.267	0.527
KY=COR+SiO <sub>2</sub>	2.05	1.027	0.940	0.333
QTZ=SiO <sub>2</sub>	0	1.500		0.277

$\Delta G^\circ$  at 800 °C and 12 kbar of each reaction (with quartz: Holland and Powell, J. Meta. Geol., 1998) and quartz solubility (Manning, Geochim. Cosmochim. Acta, 1994) are necessary inputs.

The equilibrium constant controlling dimer (d) formation from monomers (m) at constant  $T$  and  $P$  is:

$$K = (X_d/X_m^2) \cdot a_{\text{H}_2\text{O}}^{\Delta n}$$

where  $a_{\text{H}_2\text{O}}$  is the activity of H<sub>2</sub>O and  $\Delta n$  is the net change in hydration number. This model with  $\Delta n=1$  fits all of our solubility brackets very well with  $K=169$ , except for the ZRC-BDY assemblage, whose very low SiO<sub>2</sub> solubility gives an impossible negative  $K$  and  $\gamma_s > 1$ . This may indicate a different solution behavior at very low SiO<sub>2</sub> concentration.

## Extreme U-Th-Pb fractionation among hydrogenic fracture-coating minerals in felsic tuffs at Yucca Mountain, Nevada, USA: Implications for geochronology

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Extreme fractionation of U, Th, and Pb among the fracture-coating calcite, silica, fluorite, and Mn oxides from hydrologically unsaturated Miocene-age welded tuffs at Yucca Mountain, Nevada, is the basis for the use of U-series and U-Pb dating methods to establish the paleohydrologic history of the site

Concentrations of U, Th, and Pb in hydrogenic fracture-coating minerals vary by 6-7 orders of magnitude (Figure).

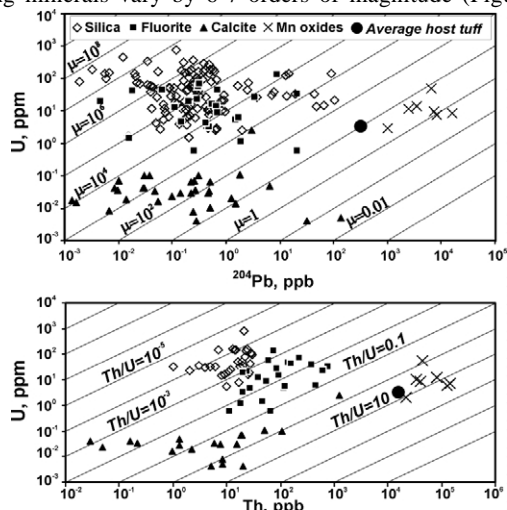


Figure: Concentrations of U (ppm), Th (ppb), and <sup>204</sup>Pb (ppb) in hydrogenic fracture-coating minerals and an average host tuff at Yucca Mountain.

Calcite is depleted in all three elements relative to the host tuffs, whereas other minerals are commonly enriched in U. Concentrations of Th and common Pb are high in Mn-oxides and low in most silica and fluorite samples, which indicates that Mn oxides may behave as sinks for Th and Pb carried by water percolating down through the fracture. Silica, calcite, and fluorite, which are typically younger than Mn oxides, have elevated U/Th and <sup>238</sup>U/<sup>204</sup>Pb ( $\mu$ ) ratios and are suitable minerals for U-series and U-Pb dating. Previous studies have shown that Yucca Mountain opal and calcite can be dated successfully by the U-series techniques. The initial excess of intermediate decay products of <sup>238</sup>U complicates the application of U-Pb geochronology to low-U calcite. <sup>206</sup>Pb/<sup>238</sup>U dating of silica is complicated by initial excess of <sup>234</sup>U, inherited from fracture water, but <sup>207</sup>Pb/<sup>235</sup>U ages are reliable and consistent with the microstratigraphy of the coatings. Preliminary data indicate that the U-Pb method can be used to date high- $\mu$  fluorite at Yucca Mountain.

## A possible magmatic origin of Bayan Obo Fe-Nb-REE deposit, China

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The Fe-Nb-REE deposit at Bayan Obo, Inner Mongolia, China, is the world's largest REE resource. It occurred in dolomite, and has been interpreted as being formed by multiple episodes of hydrothermal activity. Here we present some new data on the fluid(melt) geochemistry to suggest that a possible magmatic process may have been involved in the deposit formation.

### New Data of Immiscible REE-rich melt in melt Inclusion of Host Dolomite

Some melt inclusions in host dolomite which was not overprinted by later hydrothermal event were identified first time. Within them, some typical features of coexisting of two immiscible melt can be determined, one of them enriched in REE, and the other is poor in REE. A lot of microthermometry, SEM-EDS and Laser Raman analysis works have been done on these melt inclusions.

### Conclusions and Discussions

Recognizing first time of melt inclusions and immiscibility process in host dolomite of Bayan Obo Fe-Nb-REE deposit gives two following possibilities: 1. The host dolomite is possibly carbonatitic origin. Which is consistent with recent work done by Le Bas et al. (1997). 2. REE-rich melt could unmix from primary carbonatitic magma during the magmatic differentiation process, and cause REE concentration in Bayan Obo. The present study suggests that carbonatitic magma could play an important role in REE enrichment, and a possible magmatic origin may have been involved in the formation of Bayan Obo Fe-Nb-REE deposit.

### Acknowledgment

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## Uranium Retention by Biogenic Magnetite

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### Introduction

Uranium mobility, and therefore its potential hazard, is highly dependent on its chemical speciation and redox state. Recently there has been great interest in the possibility of remediation of uranium contaminated sites through uranium immobilization via *in situ* reduction of U(VI) to U(IV) by dissimilatory metal reducing bacteria. A variety of organisms, including *Shewanella Putrafaciens* (CN32), have been shown to reduce both Fe(III) to Fe(II) and U(VI) to U(IV). Additionally, batch studies have shown that CN32 will simultaneously reduce both Fe(III), as ferrihydrite, and aqueous U(VI) at significant rates.

Previous investigations of microbial induced ferrihydrite reduction under dynamic flow conditions have shown significant soluble Fe(II) production that in turn drives extensive down gradient ferrihydrite to magnetite conversion.

The current study examines uranium dynamics in the presence of both CN32 and ferrihydrite under flow conditions. Uranium (U(VI)) in a synthetic groundwater medium was introduced in to a column packed with ferrihydrite coated sand that was inoculated with *Shewanella Putrafaciens* (CN32).

### Results

As anticipated from previous studies, significant reductive dissolution of ferrihydrite and subsequent magnetite formation occurred. Although migration of the U(VI) through the column was greatly retarded, no appreciable uranium reduction was observed, as determined by XANES spectroscopy. Instead, the uranium appears to be primarily associated with the secondary magnetite.

After 21 days (~60 pore volumes) substantial uranium breakthrough was observed. At this point the synthetic groundwater medium was changed to "contaminant free" groundwater to investigate the uranium release rate. After another 21 days less than 15% of the uranium had been released from the system, indicating a relatively strong uranium sorption complex. EXAFS spectroscopy was utilized to elucidate the bonding environment of the sorbed uranium.

### Conclusions

Despite no significant microbial reduction of the U(VI) was observed, microbial activity within the column had profound effects on the uranium transport through the production of new biogenic mineral phases.

## Sediment subduction and magma genesis in the central Aleutian arc

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Recent investigations of arc volcanism have suggested that Hf isotopic signatures may vary with the amount of sediment being subducted (e.g., Marini et al., 2000; Woodhead et al., 2001). Oblique subduction of the Pacific plate beneath the central and eastern Aleutian arc results in the lateral movement of subducting fracture zones with time. High Sr and Pb isotopic ratios in lavas from Seguam Island led Singer et al. (1996) to propose that the Amlia fracture zone introduced anomalously high amounts of sediment into the magma source beneath Seguam. The Amlia fracture zone was subducted beneath Yunaska Island several million years prior to its subduction beneath Seguam and has not yet been subducted beneath Atka Island. New Hf, Sr, Nd, and Pb isotope data test the idea that this "point source" delivered anomalous amounts of sediment and that this has influenced the Hf isotopic signatures of different volcanoes along the arc.

<sup>176</sup>Hf/<sup>177</sup>Hf ratios for Seguam (n=4) and Yunaska (n=7) samples fall between 0.283125 and 0.283177, whereas samples for Atka (n=4) range consistently higher (<sup>176</sup>Hf/<sup>177</sup>Hf = 0.283192-0.283228±12 e-6, avg. 2σ error). Hafnium isotopic compositions from a single island show some variation outside of error, but the most striking difference is the markedly higher Hf isotopic signature of Atka relative to Seguam and Yunaska. This Hf isotopic signature correlates inversely with Sr and Pb isotopic ratios corroborating the influence of subducted sediments upon Hf. However, these same lavas have moderately high Ba/La (36-60), a signal that has been interpreted to reflect a slab-derived component, perhaps produced during dewatering of subducted oceanic crust. Correlations between isotopic ratios, Ba/La, and distance along the arc suggests that the chemical contribution of the fracture zone sediments to the source is superimposed upon a more robustly expressed slab component.

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## Improving the distinction of cosmogenic $^{21}\text{Ne}$ from other neon components in quartz

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The accuracy of surface exposure dating based on cosmogenic  $^{21}\text{Ne}$  depends critically on our ability to discriminate against non-cosmogenic Ne components, such as nucleogenic Ne produced by ( $\alpha, n$ ) reactions on  $^{18}\text{O}$  and  $^{19}\text{F}$  or non-atmospheric trapped Ne. In quartz, the mineral most widely used for cosmogenic nuclides studies today, the abundance and significance of such components is obviously related to the type of host rock, its age and its metamorphic history. For example, quartz from granitic rocks may carry a lot of nucleogenic Ne produced in U/Th-rich inclusions or by implantation of  $\alpha$  particles into the quartz. On the other hand, vein quartz may contain a lot of trapped gases in fluid inclusions, with isotopic compositions differing from those in the atmosphere. Recent work in the Potsdam lab has provided some new insights applying to  $^{21}\text{Ne}$  surface exposure dating.

In quartz from granitic rocks exposed by giant landslides in the Puna region (Argentina), a considerable reduction of the nucleogenic Ne contribution was achieved by adopting the integral quartz separation procedure of Kohl and Nishiizumi (1992) and reducing the average grain size to  $<50\mu\text{m}$ , instead of applying a simple HCl treatment followed by hand-picking. A test is currently underway to investigate whether a better purity of quartz resulting from HF/ $\text{HNO}_3$  etching or the opening of fluid inclusions is the primary reason for the reduced abundance of nucleogenic Ne. In the case of vein quartz containing noble gases derived from crustal fluids, grinding to small grain size is an obvious method to get rid of a major part of these trapped components. The distinction of cosmogenic Ne from crustal Ne is thus facilitated by larger relative  $^{21}\text{Ne}$  excesses. Adsorption of atmosphere-derived Ne on fresh grain surfaces, as indicated for the heavier noble gases Ar and Xe, is insignificant.

According to earlier studies, cosmogenic Ne in quartz degasses predominantly below a temperature of  $600^\circ\text{C}$ . Our data confirm a release at low temperatures, but indicate some variation among samples suggesting that  $800^\circ\text{C}$  is a safer general limit. The variations are obviously related to grain size, as the release patterns of samples crushed to  $<50\mu\text{m}$  are shifted towards lower temperatures. In one case,  $\sim 95\%$  of cosmogenic  $^{21}\text{Ne}$  was degassed below  $400^\circ\text{C}$ , raising the question whether such fine-grained quartz may lose part of its cosmogenic Ne already during grinding or by pre-heating at  $100^\circ\text{C}$  in the sample storage section of the extraction line. Such a possibility, which would require precautions not to crush quartz too finely, is currently investigated.

Kohl C.P. and Nishiizumi K. (1992) *Geochim. Cosmochim. Acta* **56**, 3583-3587.

## Isotopic compositions and concentrations of estuarine thallium

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A recent study has revealed significant fractionations of Tl stable isotope compositions in the marine environment (Rehkämper et al., 2002).  $\epsilon^{205}\text{Tl}$  varies between  $-6$  for seawater and  $+15$  for ferromanganese crusts (where  $\epsilon^{205}\text{Tl} = 10^4 * ((^{205}\text{Tl}/^{203}\text{Tl})_{\text{sample}} - (^{205}\text{Tl}/^{203}\text{Tl})_{\text{NIST 997}}) / (^{205}\text{Tl}/^{203}\text{Tl})_{\text{NIST 997}}$ ). Therefore, it appears that Tl isotopic variations, combined with concentration data, can be used for a detailed characterisation of the distribution and behaviour of Tl in the oceans.

In this study, we analysed Tl in water samples covering the entire salinity gradient of the Amazon estuary. All measurements were conducted by MC-ICPMS; concentrations were determined using isotope-dilution. The analytical reproducibility for in-house river and seawater standards was better than  $\pm 1 \epsilon^{205}\text{Tl}$  (2sd) for the isotopic compositions and better than 3% (2sd) for the concentrations.

The results demonstrate that Tl does not behave conservatively in the Amazon estuary. The riverine endmember has a significantly lower Tl concentration ( $\sim 4$  ppt) than seawater ( $\sim 11$  ppt). The highest Tl abundances ( $\sim 18$  ppt) are observed at mid-salinities (15‰), after which they decline rapidly to seawater values at 25‰ salinity. In contrast, the Tl isotope compositions are observed to be almost constant at  $\epsilon^{205}\text{Tl} \approx -3.5$ . Only the seawater endmember is slightly lighter at  $\epsilon^{205}\text{Tl} \approx -4.5$ . The negative  $\epsilon^{205}\text{Tl}$  of the river water probably reflects fractionation during weathering because igneous rocks in general have  $\epsilon^{205}\text{Tl} > -3$ . Weathering processes are thus inferred to generate dissolved Tl with low  $\epsilon^{205}\text{Tl}$  values and a residue with higher  $\epsilon^{205}\text{Tl}$ .

The increase of the Tl concentrations at intermediate salinities can be explained by the release of Tl from particulate matter. It is unlikely that this Tl comes from detrital particles. If such particles indeed have high  $\epsilon^{205}\text{Tl}$ , the release of Tl must be accompanied by isotope fractionation. Thus, only a small fraction of the Tl could be released without changing the isotope composition of the dissolved Tl. Alternatively, there may be significant Tl that is not held within detrital phases and is in isotopic equilibrium with the estuarine water. If the Tl isotopic composition of these particles is different relative to the dissolved Tl, release of Tl by desorption must be accompanied by isotope fractionation. Mass balance then requires that only a small fraction of the Tl is released. The scenario becomes much simpler if the readily released particulate Tl and the dissolved Tl have the same isotope composition. In this case, there is no restriction on the extent of Tl-release from particulates.

## Sediments in the Peruvian upwelling region: Organic matter composition and sulfate reduction rates

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The sediments in the Peruvian upwelling region reflect the high productivity in the surface waters. During RV SONNE cruise 147 in June 2000 several sediment cores underlying bottom waters with varying oxygen contents were sampled.

Exceptionally high concentrations of organic carbon (up to 17%) were found in sediments from the center of the oxygen minimum zone. Highest sulfate reduction rates (SRR) however, were measured in shallower waters. In general SRR show a correlation with water depth rather than with organic carbon concentrations and appear to depend on the quality of the organic matter. We analysed the sediments for selected compound classes of the labile fraction, mainly lipids, chlorins, and amino sugars to assess the freshness of the organic material and to get information on its origin.

Lipid compositions,  $\delta^{13}\text{C}$ -values and C/N-ratios indicate a predominating marine source of the organic material. Chlorin concentrations and the Chlorin-Index (a parameter assessing the freshness of phytodetritus) can in part explain the distribution of SRR. Amino sugars comprise an important part of the labile fraction of organic matter in marine sediments. Muramic acid derives exclusively from bacterial cell walls and may therefore provide a measure of bacterially derived organic matter. We compared the amino sugar composition of sediments deposited under different oxygen conditions at the sediment surface and in the overlying water column.

## Petrology of parental melts of Sao Miguel and Pico, Azores islands: Magmatic inclusions study

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The Azores volcanic chain is frequently attributed to melting of an underlying hotspot. We have made a melt inclusion study of two islands in the Azores, Sao Miguel and Pico to investigate the compositions, origin and evolution conditions of their parental melts.

There are significant major element differences between lavas of Sao Miguel and Pico. At the same MgO, Sao Miguel lavas are richer in  $\text{TiO}_2$ ,  $\text{FeO}^*$ ,  $\text{MnO}$ ,  $\text{K}_2\text{O}$ ,  $\text{Ca/Al}$  and poorer in  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$  relative to Pico. These differences are possibly compatible with different degrees of melting, the involvement of different sources or melting conditions beneath the two islands. To address these questions we present preliminary data of mineralogy and parental melt petrology for Sao Miguel and Pico islands lavas.

Crystallisation temperatures and melt compositions determined from homogenisation and quenching experiments of melt inclusions in olivine phenocrysts Fo 89.5-77 for Sao Miguel and Fo 86-74 for Pico range from 1330° to 1125°C (MgO=15-5wt. %) and from 1230° to 1100°C (MgO=8.5 - 3.5 wt. %), respectively. In contrast to Sao Miguel, observed decreasing CaO in olivine and melt, and decreasing Cr# in spinel imply clinopyroxene as dominant liquidus phase during early crystallization of Pico parental melt (<Fo 86). Also, crystallisation of Pico melt occurred under more oxidised condition (+0.5 NNO) compare the Sao Miguel melt (QFM-NNO). Parental melt compositions of Sao Miguel and Pico demonstrate the same difference observable from lava compositions. Modeling shows that cooler and more differentiated parental melt of Pico could not result from olivine or clinopyroxene crystallisation from Sao Miguel parental melts. This suggests that differences in source compositions beneath the islands, not greatly evident in isotopic compositions, strongly influence the composition of melts produced.

"Primary" melts of Sao Miguel and Pico (equilibrium with  $\text{Fo}_{90}$ ) were used to estimate the minimum pressure of the last equilibrium of these melts with peridotite mantle source. The pressure of primary magmas origin ranging from 25 to 32 kbar for Sao Miguel and from 18 to 22 kbar for Pico. Temperature of primary melts segregation under these pressures are 1430+/-50°C for Sao Miguel and 1360+/-20°C for Pico.

## Analyses of proteins in natural carbonates: Recent aragonitic ooids, Great Bahama Bank

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### Introduction

Amino acids have previously been identified in a variety of non-skeletal carbonates. However, the methods used for identification do not distinguish between amino acids that are free in solution versus amino acids that are covalently linked into a peptide or protein. Proteins cannot be easily formed abiotically and, thus, the identification of a protein in a carbonate would signify that the carbonate is either skeletal in nature or contains a remnant of a deceased organism from the vicinity.

### Results

Three proteins were identified in aragonite ooids from the Bahamas Bank using gel electrophoresis. The proteins have apparent molecular weights larger than 55,000 g/mol. The first fifteen amino acids of the most abundant protein was sequenced by N-terminal sequencing. The sequence, however, did not match any protein in the current protein databases. This indicates that the proteins are not a result of human contamination (since the sequences of human skin and hair keratin are in the database) and the protein has either not been entered into the database, has not yet been identified, or the protein has been degraded beyond recognition. Two species of *Halimeda*, a prolific organism in the Bahamas platform, were compared to the ooid sample. *Halimeda* extracts contain proteins of molecular weights similar to the ooids and may be the source of the proteinaceous material.

### Conclusions

These results indicate that not only free amino acids but intact proteins may be incorporated into non-skeletal carbonates. The proteins may even serve as a template for deposition and, therefore, facilitate the process.

## Li isotopic systematics of volcanic rocks in marginal basins

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Li isotopic data may provide useful information on material behaviours through the subduction process. The Li isotopic compositions of volcanic rocks from the convergent plate margins differ from those of the divergent boundaries: the  $\delta^7\text{Li}$  values ( $\delta^7\text{Li}$  (‰) =  $([^7\text{Li}/^6\text{Li}]_{\text{sample}}/[^7\text{Li}/^6\text{Li}]_{\text{L-SVEC standard}} - 1) \times 1000$ ) of many magmatic arc lavas range between those of fresh MORB (ca. +4‰) and those of subducted components ( $\delta^7\text{Li} > +10\%$ ) such as altered oceanic crusts and marine sediments, which may be explained by the mixing of these two components [1]. Chan et al. [1] has reported that the  $\delta^7\text{Li}$  values of several lavas from the Central American volcanic arc range  $> -3\%$ , which are significantly lower than the fresh MORB value (ca. +4‰). In addition, Chan et al. [1] has reported that the  $\delta^7\text{Li}$  value of back-arc basin basalts (BABB) from Lau basin are +1.7‰ and +0.5‰, which are slightly lower than the fresh MORB value (ca. +4‰). Such low  $\delta^7\text{Li}$  values cannot be explained by above-mentioned simple mixing model. To resolve the origin of negative  $\delta^7\text{Li}$  source, we have analyzed Li isotopic ratios of volcanic rocks in several marginal basins, with Sr, Nd, He, Ar, C and N isotopic ratios.

Li isotopic ratios of volcanic samples have been analyzed using the second-generation multiple-collector ICP mass spectrometry [2]: The analytical error of our  $\delta^7\text{Li}$  values is within  $\pm 0.82\%$  ( $2\sigma$ ). Analyzed fresh quenched glasses were recovered from three Pacific back-arc basins (North Fiji basin, Manus basin, and Mariana Trough).

There were correlations between the  $\delta^7\text{Li}$  values and the  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{143}\text{Nd}/^{144}\text{Nd}$ , and La/Sm ratios. These results show that the N-MORB-like depleted BABB glasses (low- $^{87}\text{Sr}/^{86}\text{Sr}$ , high- $^{143}\text{Nd}/^{144}\text{Nd}$ , and low-La/Sm ratios) have low- $\delta^7\text{Li}$  values, in comparison with enriched back-arc volcanic glasses (high- $^{87}\text{Sr}/^{86}\text{Sr}$ , low- $^{143}\text{Nd}/^{144}\text{Nd}$ , and high-La/Sm ratios). The  $\delta^7\text{Li}$  values of N-MORB-like BABBs, whose chondrite normalized La/Sm ratios are less than 1, are  $+2.3 \pm 0.4\%$  ( $1\sigma$ ,  $n=10$ ). To estimate the  $\delta^7\text{Li}$  value of N-MORB, we have also measured fresh MORB glasses that were recovered from Mid-Atlantic and Indian Ocean. The results show that  $\delta^7\text{Li}$  values of N-MORBs, whose chondrite normalized La/Sm ratios are less than 1, are  $+3.2 \pm 0.7\%$  ( $1\sigma$ ,  $n=8$ ). Accordingly,  $\delta^7\text{Li}$  value of the mantle end-member source (most uncontaminated by the recycled components) in mantle wedge is lower than those of the upper mantle.

[1] Chan et al. (1999), Chem. Geol. 160, 255-280.

[2] Nishio & Nakai (2002), Anal. Chim. Acta 456, 271-281

## Variational formulation of the steady diffusion model of a reaction zone

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This paper reformulate the steady diffusion model originally formulated by Fisher (1973) and Joesten (1978), to include coupling effects among diffusive flows and to describe properly the movement of the interstitial fluid. Variational principle for the condition of minimum entropy production rate is employed to define the steady state where non-fixed thermodynamic force and its conjugate flux will disappear. The variational formulation with volume-fixed (constant porosity) reference frame shows that cross coefficients  $L_{ij}$ s ( $i \neq j$ ) are not independent of proper coefficients  $L_{ii}$ s. This results in a simple form of the flux-ratio equation in terms of the ratio of partial molar volumes of diffusing components. Thus the parameter controlling the stability of the layer sequence in a reaction zone is not  $L$ -ratios but partial molar volume ratios. Because partial molar volume ratios have definite values at given temperature and pressure, only one layer sequence is stable.

### Application

Consider an enstatite layer between forsterite and quartz at a given temperature and pressure. The layer is assumed to be polycrystalline with intergranular water. The entropy production  $\sigma$  by diffusion can be written as

$$T\sigma = J_{H_2O}X_{H_2O} + J_{MgO}X_{MgO} + J_{SiO_2}X_{SiO_2},$$

where  $T$  denotes temperature,  $J_i$  diffusive flux of  $i$ , and  $X_i$  stands for thermodynamic force conjugate to  $J_i$ . Variational principle for the steady state requires

$$\partial T\sigma / \partial X_{H_2O} = 0. \quad (\text{eq.1})$$

Combining eq.1 and the Gibbs - Duhem relation for enstatite  $X_{MgO} + X_{SiO_2} = 0$  together with a volume - fixed reference frame:

$$V_{H_2O}J_{H_2O} + V_{MgO}J_{MgO} + V_{SiO_2}J_{SiO_2} = 0,$$

we get the following formula for the cross coefficients:

$$L_{MgOSiO_2} = L_{SiO_2MgO} = (V_{MgO}L_{MgOMgO} - V_{SiO_2}L_{SiO_2SiO_2}) / (V_{MgO} - V_{SiO_2}),$$

where  $V_i$  denotes a partial molar volume of diffusing species  $i$ .

Finally we get the flux ratio equations:

$$J_{MgO} / J_{SiO_2} = (L_{MgOMgO} - L_{MgOSiO_2}) / (L_{MgOSiO_2} - L_{SiO_2SiO_2}) \\ = - V_{SiO_2} / V_{MgO} \equiv - \alpha$$

Using this relation, the total reaction can be written as



This paper also discuss an application to quartz - dolomite system, which is discussed by Joesten(1991), to show that Qtz/Talc/Talc+Calcite/Dolomite is an only possible layer sequence.

## Selected Microbial Interactions with Actinide

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Microorganisms can interact with actinides by both direct interaction (biosorption, bioaccumulation, oxidation and reduction reactions) and indirect interaction (change of pH and redox potential). They may play an important role in the immobilization and mobilization of actinides in aquifers and subsurface environments.

This talk will present several detailed examples of the interaction of aerobic soil bacteria (*Pseudomonas*, *Bacillus* and *Deinococcus* strains) with uranium and plutonium. Details of the nature of the bacterial functional groups involved in the interfacial actinide interaction process will be reported. Based on time-resolved laser-induced fluorescence spectroscopy (TRLFS) and synchrotron X-ray absorption spectroscopy (XANES and EXAFS) studies, molecular-level mechanistic details of the different interaction processes will be discussed. Areas of this emerging field in actinide research will be outlined where additional information and integrated interdisciplinary research is required.

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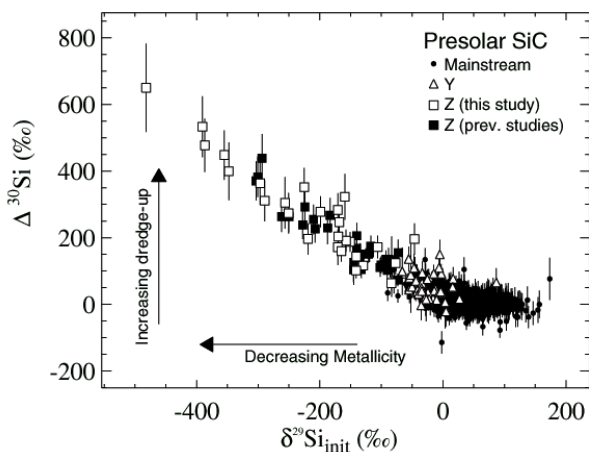
## Towards a unified understanding of presolar SiC grains from AGB stars

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Presolar SiC grains of type mainstream (~90%), Y (2%), and Z (2%) are believed to originate in asymptotic giant branch (AGB) stars, with the metallicity of the parent stars decreasing in the order mainstream->Y->Z. Here, a new large database of presolar SiC grains from the Murchison meteorite [1] is used to investigate the relationships between mainstream, Y and Z grains and the evolution of AGB stars as a function of metallicity.

Silicon isotopic compositions of AGB SiC grains are believed to reflect mixing of initial compositions determined by galactic chemical evolution (GCE) and material dredged-up to the parent stars' surfaces during the AGB phase. Following [2,3], we have projected grain Si compositions onto an assumed GCE line to deconvolve the two components. Shown in the Figure are inferred  $\Delta^{30}\text{Si}$  values (shifts in  $^{30}\text{Si}/^{28}\text{Si}$  from the GCE line) plotted versus inferred initial  $\delta^{29}\text{Si}$  ratios for ~1,300 new SiC grains, and for 27 Z grains from previous studies [2]. For grains with  $\delta^{29}\text{Si}_{\text{init}} < 0$ , there is a striking linear correlation between  $\Delta^{30}\text{Si}$  and  $\delta^{29}\text{Si}_{\text{init}}$ , which flattens out for higher  $\delta^{29}\text{Si}_{\text{init}}$  values. Qualitatively this is consistent with theoretical predictions [eg, 3], but the calculations do not appear to predict such a tight trend. Moreover, Z grains have a similar C-isotopic distribution to mainstream grains, but models predict higher  $^{12}\text{C}/^{13}\text{C}$  ratios for larger  $\Delta^{30}\text{Si}$  values. The smooth trend from mainstream to Z grains suggests that typical low-metallicity AGB stars do not have high  $^{12}\text{C}/^{13}\text{C}$  ratios, perhaps requiring cool bottom processing during the AGB phase. In this regard, it is intriguing that Y grains ( $^{12}\text{C}/^{13}\text{C} > 100$ ) have a relatively limited range of  $\delta^{29}\text{Si}_{\text{init}}$  values.



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## Production of selected cosmogenic radionuclides by muons

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Targets of  $\text{C}_9\text{H}_{12}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , S, Ar,  $\text{K}_2\text{SO}_4$ ,  $\text{CaCO}_3$ , Fe, Ni, Cu, Gd, Yb and Tl were irradiated with slow negative muons at the Paul Scherrer Institute in Villigen and with 100 and 190 GeV muons at CERN in Geneva. Short- and long-lived radionuclides were measured by  $\gamma$ -spectroscopy and AMS, respectively. Channel probabilities for the production of radionuclides after nuclear  $\mu^-$  capture and cross sections of fast muon induced production reactions to radionuclides were determined. The investigated long lived radionuclides were  $^{10}\text{Be}$ ,  $^{14}\text{C}$ ,  $^{26}\text{Al}$ ,  $^{36}\text{Cl}$  and  $^{53}\text{Mn}$ . Calculations of cosmic-ray muon fluxes and muon energies were carried out in the lithosphere as function of depth. With the help of the measured channel probabilities and cross sections calculations of the cosmic-ray muon induced production of radionuclides in the lithosphere were performed. Production of radionuclides by the nucleonic component of the cosmic rays and production by neutron capture reactions were also considered where the neutrons originate from the nucleonic component, negative muon capture, fast muon induced reactions and from decays of U and Th. The relevance of the measurements and calculations for geological applications as e.g. determinations of erosion and ablation rates and of surface exposure ages, for low-level counting experiments as e.g. solar neutrino measurements and dark matter searches, and for neutron fluence measurements in Hiroshima and Nagasaki is pointed out.

## New $^{40}\text{Ar}/^{39}\text{Ar}$ ages for Central Atlantic Magmatic Province in French Guyana: a younger volcanism?

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This study presents new  $^{40}\text{Ar}/^{39}\text{Ar}$  ages on French Guyana's dykes related to the earliest Jurassic Central Atlantic Magmatic Province (CAMP). To limit the spurious effects of younger K-rich alteration phases we have carefully selected 150 to 250  $\mu\text{m}$  unaltered plagioclases. Multigrain samples (10 mg to 30 mg) were heated incrementally with a  $\text{CO}_2$  laser and in a induction furnace. All spectra are characterized by saddle-shaped spectra which are due to none non- atmospheric initial (excess) argon. Four specimens yielded a flat segment comprising 6 to 8 concordant steps and 35 to 50 % of  $^{39}\text{Ar}$  released with weighted-mean ages ranging from  $195.4 \pm 1.6$  Ma to  $197.2 \pm 2.2$  Ma (FCs = 28.02Ma). One specimen seems to be less affected by excess argon and displays a very flat spectrum over more than 80% (weighted-mean age of  $196.4 \pm 0.7$  Ma). Due to the presence of excess argon our new ages are interpreted as maximum ages of the dolerites; nevertheless, these ages are younger than most of the CAMP (ca.  $199 \pm 2$  Ma) and further supports the trend of younger magmatic activity near the coastline of South America and West Africa. We propose that this younger magmatism could correspond to secondary magmatism pulses (197-194Ma) with high-Ti chemical signature (asthenospheric upwelling?) located in the center of the CAMP.

## $^{240}\text{Pu}/^{239}\text{Pu}$ isotopic ratio in the western northwest Pacific Ocean

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Plutonium is one of the long-lived anthropogenic radioelements and is a useful chemical tracer in the ocean. It has been introduced into the ocean via stratospheric fallout from nuclear tests that peaked in 1962, but it is suggested that plutonium in the Pacific Ocean has also been derived from close-in tropospheric fallout (Bowen et al., 1980). Isotopic analysis using high sensitive mass spectrometry is a powerful tool to specify these origins in the ocean. However, few studies for plutonium isotopic analysis have been made (Bartine et al., 1986; Buesseler, 1997). Here we report  $^{240}\text{Pu}/^{239}\text{Pu}$  isotopic ratio in the western northwest Pacific Ocean.

Large volumes of seawater samples (800~4,200 l) were collected from the Sea of Japan, Okhotsk Sea, and northwest Pacific during the KH98-3 cruise of R/V Hakuho-Maru in July-August, 1998. Plutonium was extracted from seawater using  $\text{MnO}_2$ -impregnated fibers and separated from uranium by solvent extraction.  $^{240}\text{Pu}/^{239}\text{Pu}$  isotopic ratio in the final sample solution was determined by ICP-MS (Norisuye et al., 2001).

The isotopic ratios at CM6 ( $45^\circ 25' \text{N } 145^\circ 05' \text{E}$ ), CM12 ( $41^\circ 21' \text{N } 137^\circ 20' \text{E}$ ), CM20 ( $37^\circ 44' \text{N } 135^\circ 14' \text{E}$ ) and CM22 ( $40^\circ 00' \text{N } 145^\circ 00' \text{E}$ ) were found to be in the range of 0.20-0.23, which were not so different from the average global fallout ratio of 0.18. However, these isotopic ratios and previously measured  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios in the North Pacific except for locally contaminated regions, seem to be slightly higher than the global fallout ratio, suggesting possibility of plutonium from close-in tropospheric fallout in 1950s. Determination of  $^{238}\text{Pu}$  and  $^{241}\text{Pu}$  activity by alpha spectrometry and precise measurement of  $^{240}\text{Pu}/^{239}\text{Pu}$  isotopic ratio by multi-collector (MC) ICP-MS are the further works to clarify the matter.

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## High HCl flux from Miyakejima volcano, Japan

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### Introduction

Halogen gases play an important role in gas chemistry in the atmosphere. Miyakejima volcano, Japan, started to erupt in June 2000, and after the collapse to form a big summit crater with 1300m x1400m in diameter and 450m in depth, huge amount of volcanic gas has continued to emit from the southern rim of new crater bottom. SO<sub>2</sub> flux determined by COSPEC showed an average flux to be 42000t/day (Sep-Dec 2000), 27000t/day (Jan-Jun 2001) and 16000t/day (Jul-Dec 2001) (GSJ, AIST, 2002). So roughly 10Tg (=10<sup>12</sup>g) of SO<sub>2</sub> was released for 1year Sep.2000. In this work, we determine HCl/SO<sub>2</sub> ratio of the volcanic gas to evaluate the HCl flux from Miyakejima volcano.

### Observation

HCl/SO<sub>2</sub> ratio of volcanic gas was determined using a remote FT-IR spectroscopic method, which our group has developed (Mori et al., 1993; Mori and Notsu, 1997). IR absorption spectra of volcanic gas were obtained at 4 remote sites a few km apart from the volcanic plume, in Dec.2000 and Mar.2001. In this observation, sun light scattered by cloud or plume was used as an IR light source.

### Result and Discussion

Measured HCl/SO<sub>2</sub> mole ratios were 0.05-0.08 for dense volcanic gas with white color, and 0.09-0.12 for transparent to pale-colored volcanic gas. Since the former gas is thought to be abundant in steam mist, possibly dissolving part of HCl, the original HCl/SO<sub>2</sub> ratio just after gas emission from the vent could be 0.09-0.12, which is within the range of indirect estimation; i.e. dissolved Cl/S mole ratio in alkaline solution contacting air-diluted volcanic gas (GSJ, AIST, 2002). Assuming the HCl/SO<sub>2</sub> ratio of volcanic gas was constant for 2000-2001, annual HCl flux was calculated 0.5-0.7 Tg/yr. This value is similar to HCl flux of Etna volcano in non-eruptive stage (0.6 Tg/yr), roughly 10% of the global volcanic flux (0.4-11 Tg/yr) and 20% of the global anthropogenic flux (3.0 Tg/yr) (Francis et al., 1996). Such high HCl flux from Miyakejima volcano, combined with high SO<sub>2</sub> flux, resulted in acid rain, affecting local environment. Taking into consideration that HCl emission of sea salt origin from ocean is as high as 300 Tg/yr (Symonds et al., 1988), the global effect of HCl emission from Miyakejima seems negligible.

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## Reactions of biogenic ligands in the presence of metals – what can we learn from studying anthropogenic chelating agents?

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There are many studies emphasizing the importance of chelation on *metal* bioavailability, plant uptake, toxicity, transport, adsorption, distribution and fate. Conversely, *chelating agents* are also affected by the presence of metals. The presence (and identity) of a coordinated metal ion can substantially affect chelating agent adsorption, precipitation, ligand-assisted dissolution, metal mobilization, chemical degradation, photodegradation, and biodegradation. Strong chelating agents occur in natural waters predominantly in the form of metal complexes. Therefore, a discussion of the fate of a chelating agent *always* has to address the presence of metals and how they interact with the chelating agents.

Many biogenic compounds such as siderophores, phytochelatins, and organic acids are potent chelating agents that influence mineral weathering, metal cycling and bioavailability in the environment. Based on the knowledge gained with anthropogenic chelating agents, we can expect that the reactions of the biogenic ligands in the environment will also be determined by the metals they are bound to.

The reactions of organic chelating agents of the group of the aminopolycarboxylates (e.g. EDTA) and the phosphonates in the presence of metals will be discussed. Topics will include adsorption, ligand-assisted dissolution, mobilization of metals, and chemical degradation. The results from the anthropogenic compounds will then be used to predict the potential influence of metals on the reactions of biogenic ligands such as siderophores in heterogeneous systems.

## LAM-ICP-MS and whole-rock investigations on mantle xenoliths from Chukotka, NE-Siberia

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The late Cenozoic intra-plate Bering Sea Basalt Province comprise 17 volcanic fields that occur on islands in the Bering Sea, on the west coast of Alaska and on the northeast coast of Russia. The lavas are mainly tholeiitic and alkalic olivine basalts with subordinate basanites and nephelinites. The Enmelen volcanic field in east Chukotka differs from the other volcanic fields in that the majority of the lavas are undersaturated (olivine melaneophelinites and few tephrites) and carry abundant mantle xenoliths.

Xenoliths hosted by the lavas are spinel lherzolites. Augite, diopside, orthopyroxene, olivine, ilmenite and phlogopite megacrysts up to 13 cm in diameter are also very common.

On the basis of trace element analyses of whole-rock and of their clinopyroxenes, three groups of spinel lherzolites can be distinguished. Group A shows chondrite-normalized whole-rock REE patterns with typical depletion of LREE relative to intermediate and HREE ( $La_N = 0.5 \times C1$  and  $Yb_N = 1.4 \times C1$ ). The clinopyroxene chondrite-normalized REE patterns have  $La_N$  ranging between 0.8 - 1.2 x C1 and  $Yb_N \sim 10 \times C1$  and plot almost parallel to the whole-rock REE patterns. As there is no evidence for metasomatic events, model calculations show that group A represents the residue left after 3-4% fractional melting of a primitive mantle. Group B is represented by spinel lherzolites that have whole-rock chondrite-normalized REE patterns with strongly enriched LREE relative to intermediate and HREE ( $La_N = 9 \times C1$  and  $Yb_N = 1 \times C1$ ). Their clinopyroxenes are also enriched in LREE and plot sub-parallel to the whole-rock REE patterns ( $La_N \sim 70 \times C1$  and  $Yb_N \sim 10 \times C1$ ). The lack of hydrous phases suggests that group B has experienced cryptic metasomatism in previous stage(s) of their evolution before re-equilibration. Group C is characterized by the presence of amphibole. Whole-rock chondrite normalized REE are enriched in LREE relative to intermediate and HREE ( $La_N = 5 \times C1$  and  $Yb_N = 1 \times C1$ ). Chondrite-normalized REE from the core of clinopyroxenes have patterns with depleted LREE similar to those of group A. However, their rims show, relative to the core, an increase of the LREE ( $La_N/Sm_N = 0.21$  and 2.44 for core and rim respectively). The introduction of fluids, rich in OH, LREE, Sr and Ti and the formation of amphibole must have taken place shortly prior to the incorporation of the rocks into the host lavas and before re-equilibration could be achieved.

## CO<sub>2</sub> Fluxes from the Mantle Plume in the Eifel

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### Introduction

Geodynamic phenomena in the western part of the Rhenish Massif are triggered by a mantle plume centred slightly south of the West Eifel. The mantle plume has been identified by Ritter et al (2001) as a columnar low P-velocity anomaly in the upper mantle with a lateral contrast of up to 2 %. The plume structure is about 100 km wide, it extends into the upper mantle to at least 400 km depths and corresponds to about 150-200 K excess temperature (Ritter et al 2001). Surface expressions of the mantle plume in the Eifel are not only very young volcanism and an enhanced geodynamic activity but also the presence of numerous mineral springs and gas emanations extremely enriched in carbon dioxide.

### Results and Discussion

At present the Eifel districts are among the major CO<sub>2</sub>-gas producing regions in Europe. There is an overabundance of CO<sub>2</sub>-gas rich springs, with the overall distribution of CO<sub>2</sub>-gas being much more extensive than the distribution of Tertiary and Quaternary volcanics at the surface. This is predominantly the case for the West Eifel, where to the SW and NW (the Ardennes) of the volcanic West Eifel several clusters of CO<sub>2</sub> gas discharges and CO<sub>2</sub>-gas rich springs occur. Rare gas isotopes in these waters and gases show a significant enrichment of mantle-derived volatiles (Griesshaber and Niedermann 2002), although, south of the volcanic West Eifel and in the Ardennes there is neither volcanism at the surface nor an incorporation of melts within the crust.

The central aim of this study is to present the overall distribution pattern and thus anomalies of carbon dioxide in waters and gases at the Eifel districts. From the different partial flows the surface flux of carbon dioxide has been determined for the East and West Eifel districts, the Hocheifel and the Ardennes. Herewith the amount of magmatic carbon dioxide is assessed that is added in the region of the Eifel mantle plume to the continental crust.

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