

## Remote sensing on volcanoes from stable isotopic compositions in the plume

Ururu Tsunogai<sup>1\*</sup>, Daisuke Komatsu<sup>2</sup>, Fumiko Nakagawa<sup>2</sup>

<sup>1</sup>Graduate School of Environmental Studies, Nagoya University, <sup>2</sup>Faculty of Science, Hokkaido University

Molecular hydrogen ( $H_2$ ) in a high-temperature volcanic fumarole ( $> 400$  degreeC) reach to the hydrogen isotope exchange equilibrium with coexisting fumarolic  $H_2O$  under the outlet temperature of the fumarole. In this study, we applied this hydrogen isotope exchange equilibrium of fumarolic  $H_2$  as a tracer for the remote temperature sensing on volcanic fumaroles, by deducing the hydrogen isotopic composition of fumarolic  $H_2$  remotely from those in volcanic plume. To verify this new remote temperature sensing actually works or not, we determined both concentrations and hydrogen isotopic compositions of  $H_2$  in the volcanic plume emitted from the summit crater of Satsuma-Iwojima volcano, Japan, where the fumaroles exhibited various temperatures from 100 degreeC to more than 800 degreeC. The remote temperature sensing using hydrogen isotopes (HIReTS) developed in this study can be applicable to obtain the highest fumarolic temperature in many volcanoes.

Keywords: fumarolic gases, volcanic plume, molecular hydrogen, stable isotopes, isotope exchange equilibrium, remote temperature sensing

## Clean sampling technique for analysis of trace metals in seawater

Hajime Obata<sup>1\*</sup>, Taejin Kim<sup>1</sup>, Toshitaka Gamo<sup>1</sup>, Jun Nishioka<sup>2</sup>

<sup>1</sup>Atmosphere and Ocean Research Institute, University of Tokyo, <sup>2</sup>Institute of Low Temperature Science, Hokkaido University

### Introduction

Some trace metals, like iron, copper and zinc, in seawater are now known to be essential nutrients for phytoplankton growth in the ocean. The roles of trace metals in marine ecosystem have been recognized, but their biogeochemical cycles have not been understood fully yet. Recent progress of analytical chemistry enables us to reveal the isotopic composition and speciation of the trace metals in seawater, which will provide us with strong tools for the biogeochemical studies of trace metals in seawater. To apply the state-of-the-art analytical techniques for the trace metals in seawater, we need to collect the samples without any contamination. Especially for contamination-prone trace metals, such as iron and zinc, we must be very careful during seawater samplings. We have examined some sampling methods in Japanese GEOTRACES programs to establish the clean sampling technique for trace metals in seawater.

### Methods

**Research cruise:** This study was carried out during the KH-12-4 research cruise (23 August to 5 October, 2012) of R. V. Hakuho-maru under Japanese GEOTRACES program. We occupied at the sampling stations in the western and central subarctic North Pacific.

**Sampling methods:** Seawater samples were collected with Teflon-coated Niskin-X samplers. The samplers were deployed onto CTD-CMS, which was connected to titanium-armored cable. The samplers were also attached to titanium wire and Kevlar wire. After recovering the samplers, seawater was filtered with 0.2 micrometer-pore size capsule filter directly from the sampler. The filtered samples were collected in each sample bottle in class-100 air space in the laboratory of R.V. Hakuho-maru.

**Onboard analytical methods:** Seawater samples were acidified with hydrochloric acid to < pH 1.8. Zinc was determined with cathodic stripping voltammetry (van den Berg, 1984) by using ammonium-pyrrolidine dithiocarbamate (ADPC) onboard the clean laboratory of Hakuho-maru. For the voltammetric analyses, interfering organic substances in the samples were decomposed by UV-irradiation. The samples were readjusted to pH 7.0 with aqueous ammonia and buffer solution, and then analyzed. The detection limit was 0.03 nM. Iron was determined with chelating resin preconcentration and chemiluminescence detection method (Obata et al., 1993) in the same laboratory. The samples were readjusted to pH 3.2 with aqueous ammonia and buffer solution, and then analyzed. The detection limit was 0.03 nM. All the analyses were performed in the No. 4 clean laboratory of R. V. Hakuho-maru.

### Results and Discussion

We have determined iron and zinc in seawaters collected with the three different sampling methods. Iron concentrations in the seawater samples collected with three different methods were identical. On the other hand, we obtained higher zinc concentrations in seawater samples collected with Niskin-X attached to Kevlar wire than those with other methods. Because we used the same Niskin-X bottles during titanium wire and Kevlar wire samplings, the contamination was caused during the sampling operation. Many sacrifice Zn anodes were used in the research vessel, especially around the propellers of the Hakuho-maru. By minimizing the influence from the propellers, we obtained the identical Zn concentrations from the seawater samples collected with three different methods. To collect the seawater samples without contamination, we need to know the detailed structure of the research vessel.

Keywords: ocean, trace metal, clean technique, sampling technique

## Molecular-level characterization of dissolved organic matter in inland waters using FT-ICR MS

Yuko Sugiyama<sup>1\*</sup>, TAKAHASHI, Katsutoshi<sup>2</sup>, HATCHER, Patrick G.<sup>3</sup>

<sup>1</sup>School of Human science and Environment, University of Hyogo, <sup>2</sup>The National Institute of Advanced Industrial Science and Technology, <sup>3</sup>Old Dominion University

Ultrahigh resolution mass spectrometry, i.e., Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) is currently the only mass spectrometry technique capable of achieving the resolution and mass accuracy required to determine molecular formulae of Dissolved Organic Matter (DOM), and has recently contributed substantially to the molecular understanding of DOM. DOM from various water sources has been examined extensively for its molecular characteristics. Numerous approaches were used to define the chemical composition of the DOM, and these include elemental ratios of O/C and H/C, double bond equivalents (DBE), functional group series identification determined by Kendrick mass defect (KMD) analysis, average molecular weights, etc.

We examined variety of inland waters including river, lake, rain, soil waters using FT-ICR MS, and tried to characterize them by determining their molecular constituents.

Keywords: Fourier Transform Ion Cyclotron Resonance Mass Spectrometry, Dissolved Organic Matter, Characterization

## Isotope fractionations of molybdenum and chromium at the water/metal oxide interfaces by DFT calculation

Daisuke Ariga<sup>1\*</sup>, Masato Tanaka<sup>1</sup>, Teruhiko Kashiwabara<sup>2</sup>, Yoshio Takahashi<sup>1</sup>

<sup>1</sup>Graduate School of Science, Hiroshima University, <sup>2</sup>JAMSTEC

The adsorption reaction to ferromanganese oxides is one of the most important processes that considerably influence the behaviors of trace elements in modern oxic seawater. In particular, understanding of the adsorption reaction is needed to consider the concentration and isotopic composition of molybdenum (Mo) and chromium (Cr) in seawater, since ferromanganese oxides can be important sink of these oxyanions. For Mo, large isotopic fractionation has been suggested between seawater and ferromanganese oxides where the lighter isotopes of Mo were preferentially adsorbed on ferromanganese oxides ( $d^{97/95}\text{Mo} = -2.2\text{‰}$ ). However, the mechanism of this striking isotopic fractionation of Mo during adsorption to ferromanganese oxides is unclear. Recently, it is reported that this large Mo isotope fractionation is caused by the structural change during adsorption based on the experimental evidences (Kashiwabara et al., 2011). On the other hand, theoretical explanations of this large isotopic fractionation have not been established yet although there are many studies performing quantum chemical calculations. Previous studies using quantum chemical calculations only took into account the dissolved chemical species without considering the interaction with the adsorbent surface. In this study, density functional theory (DFT) calculations are conducted to reveal the large isotopic fractionation of Mo during the adsorption, by which we discussed the relationship between adsorption reaction and isotope fractionation.

DFT calculations were performed with the GAUSSIAN 09 program. Structures (inner- or outer-sphere complex) of molybdate and chromate adsorbed on manganese and iron oxides, which cluster used to consider the interaction with the adsorbent surface directly, were determined through the optimization by DFT calculations with a hybrid functional, B3LYP. After this procedure, molybdate or chromate with clusters of the metal oxide clusters at the surface was taken out from the optimized cluster. For this cluster including molybdate or chromate, vibrational analysis was conducted by single point calculation. Finally, isotope fractionation between hydrated molybdate or chromate and those adsorbed on manganese or iron oxides were calculated from vibrational frequencies.

For molybdate, the largest isotopic fractionation factor ( $d^{97/95}\text{Mo} = -1.89\text{‰}$ ) was obtained when Mo formed inner-sphere complex with octahedral coordination. On the other hand, inner-sphere complex with tetrahedral coordination and outer-sphere complex did not show significant isotopic fractionation. These results support Kashiwabara et al. (2011) which suggested that the isotopic fractionation of Mo during the adsorption on ferromanganese oxide is controlled by the change of symmetry around Mo ion. This study suggested that taking into account of the adsorbent in DFT calculation is needed to estimate the isotope fractionation at the water/solid interface. Similar study on chromate adsorption will be also given in the presentation.

Keywords: molybdenum, isotope, DFT calculation, adsorption

## Reevaluation of highly siderophile element concentrations and Re-Os isotopes in geological reference materials

Akira Ishikawa<sup>1\*</sup>, Ryoko Senda<sup>2</sup>, Katsuhiko Suzuki<sup>2</sup>

<sup>1</sup>Graduate School of Arts and Sciences, The University of Tokyo, <sup>2</sup>Institute for Research on Earth and Evolution, Japan Agency for Marine-Earth Science and Technology

Highly siderophile elements (HSEs: Re, Au, Ir, Os, Ru, Rh, Pt and Pd) and the Pt-Re-Os isotope systems embedded within these elements are recognized as important tracers for understanding the origin and evolution of the Earth, complementary to the more commonly used lithophile elements and isotopes. Current database on HSE concentrations and Os isotopes in meteorological/geological samples are dominated by data from isotope dilution-mass spectrometry (ID-MS), which is expected to yield high quality data (excepting monoisotopic Rh and Au) regardless of chemical recovery. In most cases, ID-MS is coupled with sample digestion using inverse aqua regia in closed glass vessels under high pressure (~130 bars) and temperature (220-320°C) such as a Carius tube (CT) and high-pressure asher system (HPA). These acid digestion techniques are now apparently preferred over traditional flux fusion techniques such as NiS fire assay (NiS-FA) because of (1) much lower procedural blank levels; (2) less chance of incomplete spike/sample equilibration; and (3) capability of Re-Os determinations on the same sample aliquot. By contrast, two major issues have been associated with the limitation of acid digestion procedure. First, typical CT and HPA techniques, which can only process 1-2 g portions of samples, are vulnerable to the so-called nugget effect because most HSEs in rocks are generally concentrated in minor accessory phases such as base metal sulfides and platinum-group minerals. The second issue concerns the incomplete digestion if aqua regia cannot leach out any of the HSEs hosted in silicates and other acid-resistant phases such as spinel and HSE alloys. In order to overcome these potential drawbacks, considerable efforts have been devoted to obtaining better accuracy and precision by modifying CA and HPA digestion techniques.

We describe in this presentation a renewed analytical protocol that is suitable for small amount of samples (<2 g), with the aim of obtaining accurate <sup>187</sup>Os/<sup>188</sup>Os ratios and HSE concentrations (except for mono-isotopic Rh and Au) from a single aliquot of geological samples by using ID-ICP-MS and ID-N-TIMS. The optimum digestion method adopted after intensive tests with varying methodologies (i.e. Carius tube or microwave), conditions (i.e. temperature and duration) and protocol (i.e. HF desilicification before or after aqua regia attack) includes the regular inverse aqua regia attack in Carius tubes followed by a desilicification step with HF in order to liberate HSEs contained in residual silicates. Although the method has already been introduced for determining Ir, Ru, Pt and Pd concentrations of mid-oceanic ridge basalt (MORB) glasses by Bezos et al. (2005) and Tongan arc basalts by Dale et al. (2012), we extend the application to the Re-Os isotope systems which are not fully evaluated in previous studies. The importance of the desilicification step for different sample type was examined by comparing the results of replicate analyses of basaltic (TDB-1 and BIR-1), ultramafic (UB-N and JP-1) and sedimentary (SCO-1 and SDO-1) rock reference materials digested with and without HF. Resultant analytical values for the reference materials, which are compared to literature values, support the previous notion that HF treatment is necessary for some basaltic materials but not for typical ultramafic and sedimentary samples.

Keywords: highly siderophile elements, Re-Os isotopes, isotope dilution analysis, ICP-MS, N-TIMS

## Development of highly precise and accurate molybdenum isotope analysis using N-TIMS in meteorites

Yuichiro Nagai<sup>1\*</sup>, Tetsuya Yokoyama<sup>1</sup>

<sup>1</sup>Dept. of Earth and Planet. Sci., Tokyo Tech

Recent developments of mass spectrometry have made it possible to detect isotope anomalies of some heavy elements present in a variety of meteorites. Some of the anomalies are only marginal with <10 ppm deviations from terrestrial samples. To make highly precise and accurate isotope analysis, it is essential to develop the following techniques: 1) Completely dissolve terrestrial and extraterrestrial materials. 2) Separate target elements in the materials with high recovery. 3) Develop isotope analysis of the elements using state-of-the-art mass spectrometer. These points are very important not only to preserve precious meteorites but also to detect the isotopic compositions in tiny materials.

Molybdenum is one of the promising elements for the study of isotopic anomalies in meteorites. It has seven stable isotopes that were synthesized from three different nucleosynthetic processes (s-, r- and p- process). A recent study using MC-ICP-MS reported variable Mo isotope anomalies in some meteorites [1], but there still remains an unsolved question regarding the origin of the anomalies because Mo isotopic compositions in meteorites have been reported only in limited studies. As a preliminary stage to produce a new comprehensive dataset of highly precise and accurate Mo isotopes in bulk meteorites and their components, here we have developed a new chemical separation method for Mo, W and HFSE from meteorite sample. We also developed highly precise and accurate isotope analysis of Mo using N-TIMS.

The separation method consists of a two-stage column chemistry using anion exchange resin (Eichrom 1X8, 200-400 mesh). We have evaluated the performance of our technique by using powdered terrestrial rock samples (JB-3 and JLk-1) and meteorites (Charcas and Allende). A quadrupole-type ICP-MS (X SERIES II, Tokyo Tech) was used to determine the elution profiles as well as recovery yields of Mo, W and HFSE. Recovery yields of these elements were near 100%.

Molybdenum isotope analysis was carried out using N-TIMS (TRITON plus, Tokyo Tech) equipped with nine moveable Faraday cups. Molybdenum dissolved in HNO<sub>3</sub>-HCl solution was loaded on degassed Re filament, and it was covered with Gd, La and Ca as emitter. The filament was heated to 1230-1280 degrees C for stable analysis of Mo isotopic compositions. The isotopes were measured as MoO<sub>3</sub><sup>-</sup> ion. No interferences from Zr and Ru isotopes were observed. The precision of isotope analysis was determined by repeated analysis of a standard Mo solution (Kanto Chem.) and some terrestrial rock samples. The accuracy of isotope analysis was evaluated by measuring multiple in-house Mo isotope standards that were gravimetrically prepared by mixing the Mo standard solution with <sup>97</sup>Mo enriched and <sup>100</sup>Mo enriched spikes in different proportions.

References: [1] Burkhardt C. et al. (2011) EPSL, 312, 390-400.

Keywords: molybdenum, meteorite, TIMS, isotope, analysis



## $^{142}\text{Nd}$ isotope anomaly in chondrite revisited

Tetsuya Yokoyama<sup>1\*</sup>, Hirokazu Takahashi<sup>1</sup>, Hiroshi Yamazaki<sup>1</sup>

<sup>1</sup>Department of Earth and Planetary Sciences, Tokyo Institute of Technology

A variety of isotope anomalies have been documented in chondrites and differentiated meteorites for some elements such as Cr, Ti, Mo and Ru, suggesting heterogeneous isotope distribution in the early Solar System. For Nd, chondrites are known to have  $^{142}\text{Nd}/^{144}\text{Nd}$  ratios 20 ppm lower than terrestrial materials. The finding most likely suggests the occurrence of large scale silicate differentiation that fractionated Sm-Nd in early history of the Earth when short-lived  $^{146}\text{Sm}$  existed. However, most of the Nd isotope data in chondrites were determined by incomplete sample digestion which could not dissolve acid resistant, isotopically anomalous presolar grains. Thus, the origin of  $^{142}\text{Nd}/^{144}\text{Nd}$  anomalies in chondrites is still debated.

To resolve this issue, we have developed a new method for determining Nd isotope ratios in meteorites with ultra-high precision using thermal ionization mass spectrometry (TIMS: TRITON plus at Tokyo Tech), coupled with complete sample decomposition technique using a pressure digestion system (DAB-2, Berghof, Germany). Meteorite samples were put in Teflon inserts together with a mixture of HF, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. The insert was placed in a stainless jacket, tightly sealed and heated at 240 °C for 12 hours under high pressure. The existence of H<sub>2</sub>SO<sub>4</sub> facilitates digestion of acid resistant presolar SiC. Subsequently, the insert was opened and dried at 120 °C for 12 hours to evaporate HF and HNO<sub>3</sub>. Then the solution was transferred to a quartz glass beaker and completely dried at 300 °C. The dried sample was dissolved in 1M HCl and passed through cation exchange resin and Ln spec to isolate Nd. The separation efficiency was Ce/Nd < 2.1x10<sup>-4</sup> and Sm/Nd < 1.0x10<sup>-9</sup>, respectively. In the TIMS analysis, we have modified three points; chemical form of sample loaded on filament, temperature control of filaments and determination of Ce interference. The improved method increased  $^{142}\text{Nd}^+$  beam intensity from 2 V to 20 V, resulting in an excellent analytical precision of  $^{142}\text{Nd}/^{144}\text{Nd}$  (2 ppm, 2SD) for repeated analysis of JNdi-1.

Using the techniques, we determined Nd isotope compositions in four chondrites; Murchison (CM2), Saratov (L4), Chergach (H5) and NWA4814 (R4), as well as terrestrial samples. These chondrites have  $^{142}\text{Nd}/^{144}\text{Nd}$  ratios of 23 +/- 3ppm lower than the terrestrial samples, although the  $^{145}\text{Nd}/^{144}\text{Nd}$ ,  $^{148}\text{Nd}/^{144}\text{Nd}$  and  $^{150}\text{Nd}/^{144}\text{Nd}$  ratios were not resolvable from the terrestrial. This indicates that Nd isotopes were homogeneously distributed in the early Solar System, and the deficit of  $^{142}\text{Nd}/^{144}\text{Nd}$  is the result of the  $^{146}\text{Sm}$  decay in the depleted mantle produced by silicate differentiation in the early Earth. Our result supports the existence of enriched hidden reservoir whose chemical composition is complementary with depleted mantle that formed early history of the Earth while  $^{146}\text{Sm}$  existed.

Keywords: chondrite, isotope anomaly,  $^{142}\text{Nd}$ , presolar grain, complete sample decomposition

## Mossbauer microspectroscopy for geosciences

Keiji SHINODA<sup>1\*</sup>, KOBAYASHI, Yasuhiro<sup>2</sup>, SOEJIMA, Hiroyoshi<sup>3</sup>

<sup>1</sup>Osaka City Univ. Department of Geosciences, <sup>2</sup>Kyoto Univ. Research Reactor Institute, <sup>3</sup>Applied Science Lab.

Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio in minerals is an important geosciences' information, because the ratio suggests oxygen fugacities of the mineral formation, high or low temperature oxidation after crystallization, and weathering. Mossbauer spectroscopy is a major method to detect Fe<sup>2+</sup> and Fe<sup>3+</sup> in minerals without chemically decomposing analyses. Mossbauer spectroscopy is a recoil-less atomic nuclear gamma ray resonance. Although Mossbauer spectroscopy is a very useful method, it was not applied to microspectroscopy. This is because there was no way to focus gamma ray. Recently, multi-capillary X-ray lens (MCX) to focus X-ray was developed and applied to Mossbauer microspectroscopy (Yoshida and Soejima, 2010). The author also started to construct Mossbauer microspectrometer using MCX for the applications to geosciences. In this report, we introduce newly developed Mossbauer microspectrometer and gamma ray beam examination. Although Mossbauer spectrum of Fe foil at 0.5mm was confirmed to be measured by this Mossbauer microspectrometer, the following problem remains. The gamma ray of 121 keV due to a transition from the second to the first excited states radiates from the gamma ray source <sup>57</sup>Co in addition to the 14.4 keV due to the transition from the first to the ground states. The 121 keV gamma ray straightly transmits the MCX and activates a sample at the focus of MCX and cause X-ray fluorescence. The X-ray fluorescence results in background of gamma ray spectra. To cut of the 121 keV as possible, a pinhole plate of Pb needs to be placed at the focus of MCX. S/N ratio can be improved by the Pb pinhole. However, Pb-L fluorescence of 10.6 keV is added to gamma ray spectra. The 10.6 keV Pb-L line is closed to 14.4 keV and makes S/N worse. To solve S/N problem, we are optimizing optical paths of gamma ray of this Mossbauer microspectrometer.

Keywords: Mossbauer spectroscopy, microspectroscopy



## Trace-element analysis of single fluid inclusions by PIXE

Masanori Kurosawa<sup>1\*</sup>, SASA, Kimikazu<sup>2</sup>, ISHII, Satoshi<sup>3</sup>

<sup>1</sup>Univ. Tsukuba, Life and Environ. Sci., <sup>2</sup>Univ. Tsukuba, Pure and Applied Sci., <sup>3</sup>Univ. Tsukuba, Tandem Accelerator Complex

A fluid inclusion is a minute "fossil" of Earth's fluid trapped in a crystal during crystallization or recrystallization. Elemental composition of the fluid inclusions is so important because it can provide direct information about the generation and behavior of fluids and element transport by fluids. Fluid inclusions are commonly small, typically <30  $\mu\text{m}$ ; a single mineral grain contains many inclusions, possibly generated by multiple distinct mechanisms and of different compositions. Therefore, microanalyses of individual fluid inclusions are required to decode the changes in fluid activity and geological conditions recorded in single minerals. Owing to its high spatial resolution, non-destructive character and high sensitivity for almost element ( $Z > 17$ ), proton-induced X-ray emission (PIXE) is a reliable technique for quantitative element analysis of single fluid inclusions. In this paper, we report the quantification methods for trace elements in fluid inclusion by PIXE and chemistries of fluid inclusions in quartz from island arc granite.

PIXE is effective for nondestructive trace-element analyses of minerals and the technique is also useful for trace-element analyses of single fluid inclusions buried in a mineral matrix because of the large penetration of the high-energy ion beam. In quantification of natural fluid-inclusion analyses, analytical errors of 8% relative for most elements and 14% relative for Cl. The major source of error in the quantification was the uncertainty in the determination of the inclusion depth. Detection limits of 15 to 40 ppm for elements with mass numbers 25-38 were achieved in analyses of ellipsoidal fluid inclusions (size, 50  $\mu\text{m}$  x 30  $\mu\text{m}$  x 30  $\mu\text{m}$ ; depth, 10  $\mu\text{m}$ ; bubble size, 15  $\mu\text{m}$ ; and NaCl solution, 10 wt. %) in quartz, at an integrated charge of 1.0  $\mu\text{C}$ . The detection limits are improved by the analyses with long-time measurements.

Trace metal compositions of single fluid inclusions in quartz from two granite bodies were also analyzed by PIXE to elucidate chemistries and behaviors of hydrothermal fluids derived from calc-alkaline granite at island arc. Quartz samples were collected from miarolitic cavities, simple quartz veins, and hydrothermal ore veins in two Miocene granite bodies at Kofu, Yamanashi, and Uchiyama, Nagasaki, Japan. These veins and cavities are genetically related to the granite bodies and contained five types of fluid inclusions; two-phase, polyphase, vapor, liquid, and CO<sub>2</sub> fluid inclusions. The predominant fluid inclusions were two-phase, polyphase, and vapor inclusions, so that trace elements in the three types of inclusions were analyzed. As the results, polyphase inclusions from the veins and cavities demonstrate lower contents of K and Rb and higher Ge contents than those from alkaline granites at the continental area. Trace-element contents in the polyphase, vapor, and two-phase inclusions were positively correlated with Cl contents (salinities), indicating behaviors as chloride complexes of these elements in the hydrothermal fluids. The Br/Cl ratios by weight of the two-phase and vapor-rich inclusions were nearly constant and were almost lower than the Br/Cl ratio of seawater. Those of the polyphase inclusions demonstrated higher ratios, and there were distinct trends of the variations for each of the three geological settings sampled. The characteristics of the polyphase inclusions can be explained mainly by P-T dependences of the partitioning of Cl and Br between fluid and magma during fluid segregation and between brine and vapor during boiling.

Keywords: Fluid inclusion, trace element, X-ray analysis, granite, PIXE, ion beam

## Material Identification of single particle using magnetic volume force

Chiaki Uyeda<sup>1\*</sup>, Keiji Hisayoshi<sup>1</sup>

<sup>1</sup>Chiaki Uyeda

The efficiency to observe translation and rotation of a sub-millimeter sized sample induced at low field intensity has increased by improving an apparatus that is operated in a short micro-G condition. From the period of rotational oscillation induced in a homogeneous field of 0.2T, paramagnetic anisotropy was newly detected on a sub-millimeter sized crystal, namely for hydroxyl-apatite. From velocity of a diamagnetic grain that is ejected in the direction of monotonously decreasing field ( $B_{\max}=0.5T$ ), diamagnetic susceptibility is detected for a single grain. From the compiled experimental data, mass independent property of translation was confirmed on a metal material, namely bismuth. The obtained techniques to observe field-induced motions of sub-millimeter sized samples is a step forward to detect susceptibility and its anisotropy of a weak magnetic particle at micron- and nm level, which is expected to provide information on the relationship between lattice deformation and size reduction.

Field-induced rotation and translation was commonly observed in a diffuse micro-g condition for a single sized diamagnetic particle by applying a static magnetic field below 1T. The motions are independent to mass of grain because they are induced by magnetic volume forces which derive from individual atoms composing grains. Field-induced motions of ordinary solid, free of spontaneous moment, has not been recognized previously at such low field. By using the above-mentioned apparatus, the reproduction of various elemental (rotational and translational) processes of dust particles that are expected in space and planetary science becomes possible in an ordinary laboratory. The result of above-mentioned field-induced translation is applicable in identifying the micron-sized grains or regolith collected at the surface of asteroids, planets and satellites. The observations are desired as well on the elemental processes assumed in other models on dust alignment. The motions were observable by introducing a short drop-shaft (micro-g duration  $> 0.5$  s), which was realized by adopting a pair of small Nd-Fe-B plates (3 x 1 x 0.5cm) as a field generator. The present technique established for sub-mm sized crystal is a step to detect the movement of micron-sized grains.

[1]C.Uyeda et al(2010)J. Phys. Soc. Jpn,79, 064709.

[2]K Hisayoshi et al(2011)J. Phys.: Conf. Ser. 327 012058

Keywords: magnetic ejection, magnetic oscillation, material identification, diamagnetic anisotropy, magnetic alignment, dust alignment

## Development on analysis of planetary materials by using negative muon cap-ture

Kentaro Terada<sup>1\*</sup>, Kazuhiko Ninomiya<sup>1</sup>, Takahito Osawa<sup>2</sup>, Shogo Tachibana<sup>3</sup>, Yasuhiro Miyake<sup>4</sup>, Kenya Kubo<sup>5</sup>, Naritoshi Kawamura<sup>4</sup>, Wataru Higemoto<sup>2</sup>, Masayuki Uesugi<sup>6</sup>, Akira Tsuchiyama<sup>7</sup>, Mitsuru Ebihara<sup>8</sup>

<sup>1</sup>Osaka University, <sup>2</sup>Japan Atomic Energy Agency (JAEA), <sup>3</sup>Hokkaido University, <sup>4</sup>KEK, <sup>5</sup>International Christian University, <sup>6</sup>JAXA, <sup>7</sup>Kyoto University, <sup>8</sup>Tokyo Metropolitan University

Recently, the intense pulsed muon source, J-PARC/MUSE has been constructed (Miyake et al. 2009), providing the potential of the 3-D elemental map from the near surface to the interior of the planetary materials. Last year, we successfully demonstrated the depth profile analysis of the four layered sample that consists of SiO<sub>2</sub>, C (graphite), BN (boron nitride) and SiO<sub>2</sub> changing the Muon's momentum from 32.5MeV to 57.5MeV/c. Here, we report on Muonic X-ray from carbonaceous chondrites.

Keywords: Muon analysis, J-PARC, Non-destructive measurement, meteorite, chemical composition

## Spectroscopic measurements on dissolution mechanism of quartz in C-O-H fluid under high pressure and temperature.

Ayako Shinozaki<sup>1\*</sup>, Hiroyuki Kagi<sup>1</sup>, Naoki Noguchi<sup>1</sup>, Hisako Hirai<sup>2</sup>, Hiroaki Ohfuji<sup>2</sup>, Taku Okada<sup>4</sup>, Satoshi Nakano<sup>3</sup>, Takehiko Yagi<sup>2</sup>

<sup>1</sup>Geochimical Research Center, Graduate School of Science, The university of Tokyo, <sup>2</sup>Geodynamics Research Center, Ehime university, <sup>3</sup>NIMS, <sup>4</sup>Institute for Solid State Physics, The university of Tokyo

C-O-H fluids affect the phase relation and melting of silicate minerals in the Earth's mantle. The mantle is expected to become progressively reduced with increasing depth, so that H<sub>2</sub> fluid is considered to exist in the deep mantle with H<sub>2</sub>O fluids. Influence of H<sub>2</sub>O fluids to stability and dissolution of silicate minerals have been reported. SiO<sub>2</sub> components dissolved into H<sub>2</sub>O fluid as SiOH groups under high pressure and temperature. On the other hand, dissolution mechanism of SiO<sub>2</sub> components in H<sub>2</sub> fluid is still unknown. In this study, stability and dissolution mechanism of quartz in presence of H<sub>2</sub> fluid was examined using a laser heated diamond anvil cell. Dissolution of quartz was observed after heating at 1500 K to 1700 K and 1.7 GPa to 3.0 GPa by SEM observation of the recovered sample. In situ Raman and infrared absorption spectra under high pressure and room temperature indicates that SiO<sub>2</sub> components dissolved in H<sub>2</sub> fluid as Si-H group. The dissolution mechanism in H<sub>2</sub> fluid is differ from that was observed in SiO<sub>2</sub>-H<sub>2</sub>O system, in which SiO<sub>2</sub> components dissolved in H<sub>2</sub>O fluid to form Si-OH groups.

Keywords: C-O-H fluid, quartz, laser heated diamond anvil cells, Raman, IR

## Comprehensive studies to reveal the origin of diamonds using micro-FT-IR spectroscopy and noble gas mass spectrometry

Hirochika Sumino<sup>1\*</sup>, Syuya Tago<sup>1</sup>, Daichi Toyoshima<sup>1</sup>, Hiroyuki Kagi<sup>1</sup>, Keisuke Nagao<sup>1</sup>, Dmitry A. Zedgenizov<sup>2</sup>, Alexey L. Ragozin<sup>2</sup>

<sup>1</sup>GCRC, Grad. Sch. Sci., Univ. Tokyo, <sup>2</sup>Sobolev Institute of Geology and Mineralogy, SB, RAS

Chemical and isotopic compositions of volatile species in diamonds have a potential to constrain the origin of the host diamonds. Among them, noble gas isotopes can provide unique insights because they show different values between the more primordial plume source, which is possibly stored in the deep mantle, and the depleted MORB source in the convecting mantle. On the other hand, noble gases must be extracted by crushing or heating the samples, resulting in complete destruction of the sample which makes further investigation using other analytical methods impossible. Here we present comprehensive studies on various types of diamonds using non-destructive micro-spectroscopic methods and following noble gas isotope analysis to extract as much information as possible from a single diamond crystal.

Cubic diamonds from the Udachnaya kimberlite pipe, Siberia with abundant micro-inclusions [1] were investigated to clarify their origin and genetic relation to the host kimberlite. According to the distribution of inclusions traced by carbonates observable with FT-IR mapping, the samples were cut into several pieces and noble gases in each of them were extracted using in vacuo stepwise heating or crushing. The crush-released He exhibited  $^3\text{He}/^4\text{He}$  of 4-7  $R_A$ , indicating that the inclusion-hosted He has similar  $^3\text{He}/^4\text{He}$  to that of the host kimberlite magma (6  $R_A$ , [2]). A correlation between  $\text{CO}_3^{2-}$  and  $^3\text{He}$  contents suggests that mantle-derived noble gases are trapped in the carbonate-rich inclusions. In contrast, predominant release of radiogenic  $^4\text{He}$  by the heating indicates that diamond-lattice-hosted He is dominated by radiogenic  $^4\text{He}$  produced in situ from trace amounts of U and Th after the diamond formation. The crush-released inclusion-hosted Ne isotope ratios obtained by the crushing several diamond stones together, which exhibits similar volatile compositions each other based on FT-IR investigation, showed a striking similarity to that of the host kimberlite magma, indicating they have the common origin. Since their source He-Ne isotopes are explainable by a mixing between a plume-like and a radiogenic/nucleogenic components [2], the diamond-forming fluids and incipient carbonatitic fluids/melts of the kimberlite magma may originate from SCLM peridotite previously metasomatized by a plume, or HIMU plume involving recycled material.

The primary source of alluvial diamonds from a placer deposit in the northeastern Siberian Platform has not been well constrained (e.g., [3]). Because secondary minerals might have formed in abundant cracks in the diamonds, micro FT-IR analysis was applied before and after each heating step of noble gas extraction up to 1100 deg. C, to trace possible decomposition of secondary minerals. Subsequently the samples were crushed in vacuum to extract noble gases from inclusions enclosed in the host diamond. Neither change in FT-IR spectra nor noble gas release was significantly observed during the heating, indicating negligible contribution of secondary noble gases adsorbed and/or trapped in the cracks. While carbonate-rich diamonds showed He and Ne isotope ratios similar to MORB, significant radiogenic/nucleogenic contribution were observed in carbonate-poor samples, suggesting that the latter formed in a subducted slab. Although crustal noble gases in polycrystalline diamonds have been reported (e.g., [4]), it has not been well clarified whether such noble gases are hosted by the diamonds or secondary minerals. Our observation using FT-IR spectroscopy and noble gas mass spectrometry revealed that the crustal noble gas feature is intrinsic to some of the Siberian alluvial diamonds and that the origin of unknown source diamonds can be constrained by their primary noble gas signatures.

[1] Zedgenizov et al. (2004) *Mineral. Mag.* 68, 61. [2] Sumino et al. (2006) *GRL* 33, L16318. [3] Ragozin et al. (2009) *Dokl. Earth Sci.*, 425A, 436. [4] Honda et al. (2004) *Chem. Geol.* 203, 347.

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