Japan Geoscience Union Meeting 2013
(May 19-24 2013 at Makuhari, Chiba, Japan)

MTT38-01 Room:201A Time:May 22 14:15-14:30

Remote sensing on volcanoes from stable isotopic compositions in the plume

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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

MTT38-02 Room:201A Time:May 22 14:30-14:45

Clean sampling technique for analysis of trace metals in seawater

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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 chmiluminescence 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

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

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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

MTT38-04 Room:201A Time:May 22 15:00-15:15

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

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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 ($\mathrm{d}^{97/95}\mathrm{Mo} = -2.2\ ^{o}/_{oo}$). 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 ($\mathrm{d}^{97/95}\mathrm{Mo} = -1.89\ ^{o}/_{oo}$) 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

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MTT38-05 Room:201A Time:May 22 15:15-15:30

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

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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 meteological/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^{o}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 ^{187}Os/^{188}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

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MTT38-06 Room:201A Time:May 22 15:30-15:45

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

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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 nucleostynthetic 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_3-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_3^- 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 ^{97}Mo enriched and ^{100}Mo enriched spikes in different proportions.

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

Keywords: molybdenum, meteorite, TIMS, isotope, analysis

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MTT38-07 Room:201A Time:May 22 15:45-16:00

^{142}Nd isotope anomaly in chondrite revisited

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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}Nd/^{144}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}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}Nd/^{144}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_3 and H_2SO_4. The insert was placed in a stainless jacket, tightly sealed and heated at 240 ^oC for 12 hours under high pressure. The existence of H_2SO_4 facilitates digestion of acid resistant presolar SiC. Subsequently, the insert was opened and dried at 120 ^oC for 12 hours to evaporate HF and HNO_3. Then the solution was transferred to a quartz glass beaker and completely dried at 300 ^oC. 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^{-4} and Sm/Nd $<$ 1.0x10^{-9}, 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}Nd$^+$ beam intensity from 2 V to 20 V, resulting in an excellent analytical precision of ^{142}Nd/^{144}Nd (2 ppm, 2SD) for repeated analysis of 500 ng 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}Nd/^{144}Nd ratios of 23 +/- 3ppm lower than the terrestrial samples, although the ^{145}Nd/^{144}Nd, ^{148}Nd/^{144}Nd and ^{150}Nd/^{144}Nd ratios were not resolvable from the terrestrial. This indicates that Nd isotopes were homogenously distributed in the early Solar System, and the deficit of ^{142}Nd/^{144}Nd is the result of the ^{146}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}Sm existed.

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

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Mossbauer microspectroscopy for geosciences

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Fe^{2+}/Fe^{3+} 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^{2+} and Fe^{3+} 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 lense (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 ^{57}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

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MTT38-09 Room:201A Time:May 22 16:30-16:45

Trace-element analysis of single fluid inclusions by PIXE

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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 $<$30 um; a single mineral grain contains many inclusions, possibly generated by multiple distinct mechanisms and of different compositions. Therefore, microanalyses of individual fluid inclusions are required to decode the changes in fluid activity and geological conditions recorded in single minerals. Owing to its high spatial resolution, non-destructive character and high sensitivity for almost element ($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, 50um x 30um x 30um; depth, 10 um; bubble size, 15 um; and NaCl solution, 10 wt. %) in quartz, at an integrated charge of 1.0 uC. 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 CO2 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

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MTT38-10 Room:201A Time:May 22 16:45-17:00

Material Identification of single particle using magnetic volume force

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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 (Bmax=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 ansiotropy 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 a 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 x1x0.5cm)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 ansiotropy, magnetic alignment, dust alignment

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MTT38-11 Room:201A Time:May 22 17:00-17:15

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

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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 SiO2, C (graphite), BN (boron nitride) and SiO2 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

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

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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_2 fluid is considered to exist in the deep mantle with H_2O fluids.Influence of H_2O fluids to stability and dissolution of silicate minerals have been reported. SiO_2 components dissolved into H_2O fluid as SiOH groups under high pressure and temperature. On the other hand, dissolution mechanism of SiO_2 components in H_2 fluid is still unknown. In this study, stability and dissolution mechanism of quartz in presence of H_2 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_2 components dissolved in H_2 fluid as Si-H group. The dissolution mechanism in H_2 fluid is differ from that was observed in SiO_2-H_2O system, in which SiO_2 components dissolved in H_2O fluid to form Si-OH groups.

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

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MTT38-13 Room:201A Time:May 22 17:30-17:45

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

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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}He/^{4}He of 4-7 R_A, indicating that the inclusion-hosted He has similar ^{3}He/^{4}He to that of the host kimberlite magma (6 R_A, [2]). A correlation between $CO_3{}^{2-}$ and ^{3}He contents suggests that mantle-derived noble gases are trapped in the carbonate-rich inclusions. In contrast, predominant release of radiogenic ^{4}He by the heating indicates that diamond-lattice-hosted He is dominated by radiogenic ^{4}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 metasomatised 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.

Keywords: noble gas, micro-FTIR spectroscopy, diamond, mantle plume, subcontinental lithospheric mantle, alluvial diamond

Japan Geoscience Union Meeting 2013
(May 19-24 2013 at Makuhari, Chiba, Japan)

MTT38-P01 Room:Convention Hall Time:May 22 18:15-19:30

Carbon isotope analysis of carbon dioxide using Raman Spectroscopy: Application to fluid inclusions in mantle xenolith

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Carbon is often observed in mantle rocks, and its isotopic composition is used to discuss the carbon cycle inside the earth. Some carbon exists as fluid inclusions mainly composed of carbon dioxide in rocks. Generally carbon isotopes in rocks have been measured by mass spectroscopy analyzing gas extracted when heating or crushing. Arakawa et al. (2007, Applied Spectroscopy) suggested a possibility that micro-Raman spectroscopy is applicable for determining carbon isotopic composition of carbon dioxide.Development of this method will become easier to conduct non-destructive measurement of carbon isotopic composition for individual fluid inclusions.

In this study, we attempted to solve a problem raised by Arakawa et al. and to examine applicability of the method to natural samples. We analyzed a fluid inclusion in natural olivine by micro-Raman spectrometer installed at Department of Earth Sciences, Kanazawa University. After we carried out original peak fitting on spectrum of 1240-1514 cm^{-1} as Raman shift including a fermi diad, hot bands and a ”collision induced” band of carbon dioxide, we calculated intensity ratio of peaks originated from $^{13}CO_2$ and $^{12}CO_2$.

The most serious problem pointed out by Arakawa et al. was caused by positional relationship between a grating and a detector. We solved it by using a high-resolution spectrometer (0.27 cm^{-1}/pixel). On the other hand, we found a problem characteristic of natural samples that both accuracy and precision has deteriorated when we obtain intense Raman peaks other than carbon dioxide. In case of absence of such peaks, we can determine carbon isotopic composition (delta^{13}C) with an uncertainty of +/-2.5 per mil (1 sigma). Further development of the micro-Raman mass spectroscopy enables us to discuss the origin and cycle of carbon inside the earth.

Keywords: Raman spectroscopy, Carbon dioxide, Carbon isotope, Fluid inclusion, mantle xenolith

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Radiocarbon dating using new AMS system

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The Accelerator Mass Spectrometry(AMS) is effective in radiocarbon dating. By the conventional method, a large tandem accelerator(e.g.Accelerating voltage = 5MV) was used. The small accelerator(e.g.Accelerating voltage = 500kV) is used in the new AMS analysis.

The small AMS machine is handy.We installed small AMS machine in our laboratory. We will present the outline of new AMS system and the application research using that.

Keywords: AMS, Radiocarbon, Accelerator Mass Spectrometry, 14C

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Development of single-step column separation method for Hf and Nd isotopic analyses of geological rock samples

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Previous chemical separation technique of Nd and Hf requires at least two-column separation step. In this study, we tried to set up simple separation method of Hf and Nd using a single column. After sample decomposition, a sample solution was loaded on the column filled with 1 ml Ln-spec resin. After eluting major, La and Ce elements, Nd fraction was collected. Then, eluting Yb, Lu and the other unnecessary HFS elements, Hf fraction was collected. We used MC-ICP-MS (Neptune Plus) for measurement, with desolvating system (Aridus II). Application on silicate standard rocks from USGS and GSJ confirm the effectiveness of our new separation method. Nd and Hf recovery yields were normally $>$80 %; results of their isotopic composition were well within the recommended values.

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Determination of extremely small amount of U and Th by ID-TIMS for the study of U-Th cosmochronology

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Primitive chondrites are known to have internal isotope anomalies for various elements due to the existence of presolar grains. These grains provide information on stellar nucleosysthesis where the grains have formed before the onset of Solar System. In particular, abundance ratios of radioactive r-process nuclides such as ^{232}Th, ^{235}U and ^{238}U in presolar grains would provide the age of r-process nucleosynthesis. Of presolar grains, silicon carbide (SiC) can be a promising target because it has relatively larger grain size and contains abundant trace elements compared to the other presolar grains. The amount of U and Th in presolar SiC grains separated from 1 gram of carbonaceous chondrite is expected to be less than 1 pg. Therefore, we need to develop a micro analytical technique that enables to determine extremely small amount of U and Th.

Historically, presolar grains have been analyzed using secondary ion mass spectrometry (SIMS), but spot analysis of trace elements with $<$ppm abundance is very difficult. In contrast, thermal ionization mass spectrometry (TIMS) is suitable to measure very small amount of trace elements because it provides stable beam intensity relative to the other mass spectrometry, especially when chemical separation has been carried out before analysis. In this study, we have developed the determination of sub-pg amount of U and Th by using TIMS coupled with isotope dilution method.

The performance of TIMS measurement was evaluated by repeatedly analyzing variable amounts of U and Th standard materials with the addition of^{236}U and ^{229}Th enriched spikes. The analytical precisions for determining 1 pg of U and Th were 0.36% and 0.92%, respectively.

In addition to TIMS analysis, we have also developed a separation method for extremely small amount of U and Th utilizing two-step ion exchange column chemistry. In the first column, the sample solution was dissolved in 0.1 mL of 5M HNO_3 and passed through 0.01 mL of U/TEVA spec. Thorium was eluted with 0.1 mL of 5M HCl together with Zr, followed by U elution with 0.1 mL of 0.3M HF-0.1M HNO_3. The Th fraction was dried and dissolved in 0.1 mL of 8M HNO_3 to pass through the second column that consists of 0.05 mL of AG1x8. Using these systems, we were able to separate major elements from U and Th, and achieved U and Th recovery yields of 93% and 82%, respectively.

Keywords: TIMS, small amount samples, uranium, thorium, contamination, chemical separation

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Determination of in-situ Os isotope compositions in metal phases from CB chondrites using a micro sampling technique

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Metal has played a major role in the early Solar System for fractionating siderophile elements from lithophile elements, generating different chemical reservoirs in the early Solar System. In particular, metal in chondrites has a historic record of thermal and chemical processes in the solar nebula. To examine metal phases, highly siderophile elements (HSEs: Re, Os, Ir, Ru, Pt and Pd) are powerful tracers because HSEs have a great affinity to Fe-Ni metal relative to silicate phases. The origin of metals in chondrites has been extensively studied based on HSE data obtained by LA-ICPMS [e.g. 1-2]. Of all chondrites, CB and CH are metal rich (60-70 vol. %) and thus are interesting target to investigate. The CB chondrites are subdivided into CB_a and CB_b depending on the metal abundances, chondrule sizes and chemical compositions. The origin of CB metals is still debated. One argued that CB_a metals may be the product of an impact plume at planetary collision or other non-nebular event [1], while those in CB_b are thought to be a condensation product in the solar nebula [2]. However, Rubin et al. [3] raised a possibility that CB_b metals formed by condensation in a gas of non-nebular origin, such as an impact plume.

Here we present Os isotopic compositions in metal phases from three CB chondrites with high spatial resolution. In-situ Os isotope analysis by LA-ICP-MS has been hindered because of ^{187}Re interference. In this study, we collected metal samples using a micro milling system equipped with a diamond drill bit (Geomill 326, Izumo-web) from three CB chondrites, Bencubbin (CB_a), Gujba (CB_a), and Isheyevo (CB_b). A sliced meteorite specimen was drilled with a single drop of Milli-Q water. The drilled metal powder was recovered in a glass vial together with water. To obtain sufficient amount of Os for isotopic analysis, one or two conic pit(s) with a radius of 500 um and depth of 550 um was dedicated for a single measurement. The meal powder was dissolved by the mixture of HCl and HNO_3 in a sealed Carius tube, and Os was purified by solvent extraction and micro distillation. Osmium isotopic composition was measured by N-TIMS. The major element compositions and HSE abundances in metals adjacent to the drill pit were measured by EPMA and fs-LA-ICP-MS, respectively.

All the ^{187}Os/^{188}Os ratios of CB metals obtained in this study have limited variation (0.1251-0.1273) which fall within the range of bulk carbonaceous chondrites. Interestingly, the majority of CB metals have ^{187}Os/^{188}Os ratios close to the bulk CI chondrite (0.1264-0.1265), while the rests have lower values. Furthermore, these data generally plot on the 4.56-Ga Re-Os reference isochron of IIIAB iron meteorites. Therefore, the ^{187}Os/^{188}Os variations in CB metals reflects the variation of Re/Os in individual grains at the time of their formation at 4.56 Ga. Osmium isotopic deviation from the CI value would suggest Re-Os fractionation from a putative bulk nebula composition, either in a hot nebula or impact plume. Early removal of a high-temperature condensate may have generated a reservoir with Re/Os less than CI, assuming that Re has been preferentially incorporated into high temperature condensates relative to Os. Our data also suggest limited variation of the other HSE relative abundances such as Os/Ir. However, Pd/Fe and Ni/Fe ratios in CB_a and CB_b metals are all variable with a positive correlation, which cannot be explained by nebular condensation but condensation in extremely high gas pressure (10^7 x solar nebula). This reconciles with the formation of CB metals in impact plume of planetary collision, while fractionation of HSEs with relatively high 50% condensation temperatures (e.g., Re, Os, Ir) was restricted during metal formation.

References: [1] Campbell, A. et al. (2002) GCA 66, 647 [2] Campbell, A., Humayun, M. (2004) GCA 68, 3409 [3] Rubin A. et al. (2003) GCA 67, 3283

Keywords: Chondrite, Metal phase, CB chondrite, Osmium isotopes, Highly siderophile elements, In-situ analysis