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