

Improvement of data processing for Time-Resolved-Analyses (TRA) using LA-ICPMS

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Laser-Ablation Inductively Coupled Plasma Mass Spectrometer (LA-ICPMS) is commonly used for in-situ analyses of isotope ratios and elemental abundance. Laser-ablation sample introduction is destructive method, and the spatial resolution of an analysis is inversely related to total signal-intensity. It means that observed signal-intensity is never satisfied and unstable, because space-resolution of the analyses is always optimized as high as possible. Furthermore, a natural rock sample often contains mineral inclusions, and signal-intensities can be disturbed by them. Therefore, Time-Resolved-Analysis (TRA) mode is commonly used for most LA-ICPMS analyses.

Using TRA mode, we can estimate the preciseness of each run. However, the way of data processing has not been made enough discussions yet. For the data processing, most researchers regard flatness of the signal intensity as important. Integration time of each runs were decided based on flatten signal and/or signal ratio. Signals of the beginning and the end of ablation were not used for the calculation. However, this processing method has several problems. One of the problems was, signal intensity was not always flatten shape, because analyzed samples were usually limited. Furthermore, flatness of the signal was not commonly determined and different researchers use different criteria. In this study, we applied several calculation method for the same TRA dataset, and estimate the preciseness for each calculation method.

Keywords: LA-ICPMS, time resolved analyses, TRA, femtosecond laser, data processing

Fe isotopic study of Fe-Ni metal in ordinary chondrite using LAL-MC-ICPMS

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The ordinary chondrite is the most abundant and primitive meteorite in the solar system. It is widely believed that the formation sequence of the ordinary chondrites tell us details of the early solar system history. Among the various minerals or components found in the ordinary chondrites, the Fe-Ni metal is one of the characteristic materials of ordinary chondrite. Despite the major components, the formation processes of Fe-Ni metals have still been veiled. The Fe isotopic signature is one of the key information to unveil the formation processes of Fe-Ni metals in the ordinary chondrites, because (a) Fe is ubiquitously distributed in various minerals or phases in the meteorites, and (b) Fe isotope composition can vary through the formation processes. Standing on this view point, some previous studies measured the Fe isotopic ratios of Fe-Ni metals in the ordinary chondrites [1, 2]. In those studies, the ordinary chondrites were crushed in the mortar and Fe-Ni metals were sampled through handpicking or micro-mill technique to collect Fe-Ni metals. It should be noted that these techniques have the risk of the contamination from the equipments or apparatus used for the sample handling although these techniques have been widely accepted as the sampling methods of the solid materials for the isotopic analysis.

In this study, we applied a new sampling technique, LAL (laser ablation in liquid) [3, 4], to collect Fe-Ni metals from the ordinary chondrites for the Fe isotopic measurement using MC-ICPMS. For the LAL sampling, the sample surface was polished and the metal phase was ablated in the deionized water using the femtosecond laser (wavelength 780 nm). Unlike with the conventional sampling techniques applied in the previous studies, the LAL technique can provide minimum risk of contamination of Fe from equipments. After the LAL sampling procedure, the resulting sample suspension was collected using micropipette and was then subsided to acid digestion using conc. HCl and conc. H₂O₂. The sample solution was heated until dryness and the resulting sample cake was re-dissolved in 0.1% HCl, and then used for the isotopic analysis of Fe using MC-ICPMS connected to the desolvating nebulizer system.

Total 15 ordinary chondrite metals were analyzed in this study. The delta ⁵⁶Fe data for L chondrites did not vary with the delta ⁵⁶Fe data for LL chondrites. In contrast, Fe in the H chondrites was isotopically slightly lighter than those for L or LL chondrites. These Fe isotopic variations among H, L and LL chondrites are consistent with the data obtained by Theis et al. (2008) [1]. These Fe isotopic ratios within the metallic phase in the H, L and LL chondrites is possibly related to the formation processes of them, however, cannot be explained by the simple redox reaction suggested by Theis et al. (2008). Possible cause of the present variation of Fe isotopic ratios will be discussed in this presentation.

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Keywords: laser ablation, laser ablation in liquid, ordinary chondrite, iron isotope

Two noble gas components in the Udachnaya kimberlite magma, Siberia

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Kimberlites are unique igneous rocks which occasionally brought diamonds from deep in the Earth. Although their origins are considered to be deeper than 150 km in the mantle based on the P-T stability of diamonds (e.g., Haggerty, 1994), they have not been well constrained yet (e.g., Smith, 1983).

We are continuing noble gas analyses for minerals from kimberlites to constrain their origins. Sumino et al. (2006) showed that olivine phenocrysts in the Udachnaya kimberlite from Siberia contain plume-derived Ne. This data strongly suggest that the origin of kimberlite is a plume rising from deep mantle, possibly from the lower mantle or core-mantle boundary.

We analyzed seven fractions of olivines separated from four Udachnaya kimberlite rocks to further investigate the composition and evolution of noble gas characteristics of the Udachnaya kimberlite magma. To clarify crystal size dependence of noble gases trapped in olivines, one fraction was composed of only olivines 0.25 ~ 0.5 mm in size while the other fractions consisted of 0.2 ~ 2 mm olivines. Two mantle xenoliths included in the Udachnaya kimberlite were also analyzed. Since magmatic noble gases are generally concentrated in fluid inclusions, stepwise crushing method was applied to extract noble gases selectively from the inclusions.

³He/⁴He ratios decreased with progress of the stepwise crushing, due to increase in contribution of radiogenic ⁴He located in the olivine mineral lattice and/or in the solid phase of inclusions. Therefore, ³He/⁴He ratios of the magma at the point of entrapment of the fluid inclusions in olivines are deduced from the relatively constant ³He/⁴He ratios of the first several crushing steps. Most samples showed ³He/⁴He ratios ranging from 5.4 to 6.5R_A for magmatic He. In the meanwhile only the small-grained sample yielded lower ³He/⁴He ratio of 3.8R_A, which is close to those of the xenolith samples (2.5 ~ 3.2R_A).

Ne isotope ratios show two different trends in a plot of ²⁰Ne/²²Ne vs. ²¹Ne/²²Ne; one is the kimberlite magma trend reported by Sumino et al. (2006), and the other deviates from it toward rightward implying larger contribution of nucleogenic ²¹Ne. The latter trend is similar to that reported for subcontinental lithospheric mantle (SCLM) of European continent (Buikin et al., 2005), but differs from that for mid ocean ridge basalt (MORB) representing isotopic composition of convecting upper mantle. Small-grained olivine fraction belongs to the latter group, which exhibits strong SCLM affinity.

According to petrologic observation by Kamenetsky et al. (2008), true olivine phenocrysts entirely crystallized from the kimberlite magma should be smaller than 0.2 mm, while larger grains have core of olivine xenocryst which could have been derived from surrounding mantle. If this is the case the lower ³He/⁴He in the small olivine phenocrysts implies later crystallization after noble gases in kimberlite magma had significantly exchanged with those in surrounding SCLM. On the other hand, the large phenocrysts must have cores with low noble gas concentrations and their rim grew from the magma with noble gases less affected by SCLM.

This work clarified relation between two noble gas components in the Udachnaya kimberlite magma, one was intrinsic to the magma and the other derived from SCLM. The stepwise crushing experiment on different sized olivines revealed crystallization process under different degree of noble gas contribution from surrounding SCLM to the kimberlite magma.

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Keywords: noble gas, kimberlite, olivine, Udachnaya, Siberia, plume, subcontinental lithospheric mantle

Noble gas isotopic compositions of diamonds in the Udachnaya kimberlite pipe, Siberia

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Noble gas isotopes trapped in fluid/melt inclusions in diamonds can constrain the origin of such deep-mantle-derived materials because they show completely different values between the more primordial source, which contributes OIBs and which is possibly stored in the deep mantle, and the depleted MORB source in the convecting mantle. In contrast, in situ radiogenic/cosmogenic noble gas isotopes might be distributed homogeneously in the diamond lattices. In vacuo sequential dynamic crushing extraction-by which diamond stones are crushed mechanically in vacuum-is a powerful tool for selective noble gas extraction from the inclusions. This report presents a noble gas study, conducted using a combination of several non-destructive micro-spectroscopic methods, of inclusions in diamonds in Udachnaya kimberlite (Siberia).

Sumino et al. (2006) [1] analyzed noble gases in olivine phenocrysts in the Udachnaya kimberlite and obtained $^3\text{He}/^4\text{He}$ of kimberlite magma of ca. 5.7 R_A which resembles that of subcontinental lithospheric mantle (SCLM) and a less-nucleogenic feature in neon isotopes of the magma than in the MORB source. The He/Ne systematics revealed that helium and neon in the Udachnaya kimberlite magma are explainable by a mixing between a plume-like and the SCLM-like components. The results indicate that the source of the Udachnaya kimberlite has similar noble gas characteristics to those of OIBs, and constrain a depth of its origin to be deeper than the MORB source mantle. To clarify the origin of the Udachnaya diamonds and their genetic relation to the host kimberlite, diamond crystals of cubic habit with abundant micro-inclusions and of 1-3 mm were investigated in this study.

The individual micro-inclusions are usually smaller than several micrometers, with some exceptions reaching 10-15 micrometers [2]. According to the distribution of carbonates (i.e., inclusions) obtained by FT-IR investigation, doubly polished plates of the samples were cut into several pieces. Noble gases in the sample pieces (less 0.5-1 mg each) were extracted using in-vacuo stepwise heating or crushing. Although the samples released helium that was dominated by radiogenic ^4He at their graphitization (2000 degree C) during stepwise heating, the crush-released helium exhibited $^3\text{He}/^4\text{He}$ of 3.5-7.4 R_A , indicating that the inclusion-hosted helium has similar $^3\text{He}/^4\text{He}$ to that of the host kimberlite magma. This similarity implies diamond formation in a SCLM environment. A correlation between CO_3^{2-} content and ^3He suggests that mantle-derived noble gases are trapped in the carbonate-rich inclusions. In contrast, diamond-lattice-hosted helium is dominated by radiogenic ^4He , possibly produced in situ from trace amounts of U and Th after diamond formation.

Because the scarcity of neon released by stepwise heating and crushing of the sample pieces made it impossible to determine neon isotope ratios precisely, we extracted noble gases by crushing several diamond stones together which exhibits similar volatile compositions each other based on FT-IR investigation. The result showed that crush-released inclusion-hosted neon isotope ratios form a trend in a neon three-isotope plot which is almost identical to that of the host kimberlite magma reported by [1], suggesting a common source of the diamonds and host kimberlite magma. The diamond-forming fluids and incipient carbonatitic fluids/melts of the kimberlite magma may originate from partial melting of SCLM peridotite previously metasomatised by a plume.

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Keywords: noble gas, diamond, kimberlite, mantle plume, subcontinental lithospheric mantle, Udachnaya, Siberia

Systematic differences of I/Br ratios in kimberlites related to their origin

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Kimberlite is an igneous rock originated from deep mantle. Compared to common ultramafic rocks, kimberlites are rich in volatile components such as water and carbon dioxide. Because kimberlites are known to contain diamonds, it has been generally thought that their magma sources are located at a depth of more than 150km (e.g., Dawson, 1980). In addition, studies on the noble gas isotopes in kimberlites showed that kimberlite magmas have similar noble gas characteristics to those of ocean island basalts (OIBs; e.g., Sumino et al., 2006). Based on noble gas isotopic compositions of mid-ocean ridge basalts (MORBs) and OIBs, primordial noble gases still remain in the Earth's interior (e.g., Craig and Lupton, 1976; Kaneoka et al., 1978). Therefore, primordial components of other volatile elements including halogens might also be retained in the Earth's interior and be found out by analyzing kimberlites. In this study, we analyzed concentrations of Cl, Br, and I in kimberlites from six regions to investigate the characteristics and their origins.

Samples analyzed are 34 kimberlites collected from South Africa, China, Greenland, Brazil, Russia and Canada. For the Cl, Br and I determination, we used the pyrohydrolysis method combined with ICP-MS (Muramatsu and Wedepohl, 1998) and ion chromatography.

The I/Br ratios of kimberlite samples were classified into two groups. The first group (Group S) showed high I/Br ratios (about 1×10^{-1}), which are distinctively observed in the kimberlites from South Africa, Greenland, Canada and Brazil. The I/Br ratios of Group S are fairly similar to that of CI chondrite (I/Br ratio: about 1×10^{-1} , Anders and Ebihara, 1982), suggesting these kimberlites preserve the characteristics of halogens in the mantle from which the kimberlite magmas formed. In contrast to this, a group (Group C) composed of Chinese and Russian kimberlite samples showed markedly low I/Br ratios (about 6×10^{-3}). Similar low I/Br ratios have been observed in fluid inclusions in eclogite derived from seawater-altered oceanic crust (Svensen et al., 2001) and in seawater associated with halite precipitation (Zherebtsova and Volkova, 1996), suggesting an involvement of seawater-derived halogens having low I/Br ratios in the source regions of the Group C kimberlites.

Keywords: kimberlite, halogen, I/Br ratio, South Africa, China, Russia

Estimation of S, F, Cl and Br fluxes at Mid Ocean Ridges

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Introduction

Superficial volatile elements of the Earth have been accumulated mainly by degassing from the solid Earth. Noble gases have been used as tracers for constraining the degassing history. Argon isotopic systematics suggested that the significant degassing occurred in the early Earth, ~4 billion years ago [1, 2]. Carbon and nitrogen fluxes from the Earth mantle have so far been well documented by calibrating against the helium-3 (³He) flux, which constrains the models of atmospheric evolution [3, 4].

However, evolutions of other volatiles, such as sulfur (S) and halogens (fluorine, chlorine and bromine) forming various chemical species on the Earth's surface due to their high reactivity, have been poorly constrained. Additionally, halogen fluxes at Mid Ocean Ridges have been estimated by comparison with concentration and flux of CO₂ [5], while CO₂ flux itself was estimated by calibrating against the ³He flux. Thus, direct comparison of the volatile elements with ³He is more straightforward. In this study, we analyzed concentrations of S and halogens with ³He trapped in vesicles in Mid Ocean Ridge basalts (MORBs) and back-arc basin basalts (BABBs) to estimate their fluxes from the mantle by comparison with ³He directly.

Analysis

Approximately 1 g of fresh glassy aliquots were picked up from basalts and were put in a stainless-steel crusher with 1-2 cm³ of diluted aqueous sodium hydroxide (1-4 mol/L) and a stainless-steel ball. The alkaline solution was frozen at the temperature of liquid nitrogen (77K). When the crusher was shaken up and down, the glassy aliquots were crushed together with the frozen solution by the stainless-steel ball. Highly reactive elements including S, F, Cl and Br were extracted from vesicles of glasses by mechanical fracturing and immediately dissolved into a small portion of melted alkaline solution. While helium (He), not dissolved into the solution, was introduced into a vacuum line and purified. Helium-4 (⁴He) intensity and ³He/⁴He ratio were measured by a VG5400 mass spectrometer. S, F, Br and Cl concentrations in the alkaline solution were measured by ion chromatography (Dionex-320).

Results and Discussion

Concentrations trapped in vesicles were (4-31) × 10⁻¹⁵ mol/g for ³He, (20-430) × 10⁻⁹ mol/g for S, (60-5000) × 10⁻⁹ mol/g for F, (160-450) × 10⁻⁹ mol/g for Cl and (5-1300) × 10⁻⁹ mol/g for Br. Under an assumption that the samples analyzed in this study represent typical MORBs, global fluxes of S, F, Cl and Br were estimated using mole ratios X/³He of the samples and the ³He flux of (527±102) mol/yr from the mantle [6]. They are (1-26) × 10¹⁰ mol/yr for S, (2-120) × 10¹¹ mol/yr for F, (2-120) × 10¹⁰ mol/yr for Cl and (4-230) × 10¹⁰ mol/yr for Br when bulk MORBs and BABBs emit their volatiles entirely. We compared S, F and Cl fluxes at Mid Ocean Ridges with those at volcanic arcs, recycling rates at subduction zones, and accretion rates to continental crust. Thus, the respective lower limits of calculated accumulation times that is required to form the present atmosphere, are 92 Myr for S, 11 kyr for F and 1.0 Gyr for Cl. These values are significantly shorter than the age of the Earth, 4.55 Gyr. This may reflect the highly reactive natures of S, F and Cl contrasting to argon or nitrogen, which causes different accumulation histories.

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Keywords: atmospheric formation, sulfur, halogen, helium, global flux, mid ocean ridge basalt

Stable isotope geochemistry of strontium

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Strontium has four naturally occurring isotopes (⁸⁴Sr, ⁸⁶Sr, ⁸⁷Sr and ⁸⁸Sr). Among them, ⁸⁷Sr is a daughter nuclide of radiogenic ⁸⁷Rb, and its abundance changes due to the contribution of the radiogenic growth of ⁸⁷Sr produced by the beta-decay of ⁸⁷Rb; the radiogenic growth of ⁸⁷Sr has provided important constraints of the age and sources in cosmochemical and geochemical materials. Moreover, the isotopic composition of other Sr isotopes, such as ⁸⁴Sr, ⁸⁶Sr and ⁸⁸Sr may also vary due to mass-dependent isotopic fractionation through various physicochemical reactions in nature. This mass-dependent isotopic fractionation can provide key information about the sequence and/or mechanism of sample formation. The field of science that deals with them is widely known as stable isotope geochemistry. However, the application of stable isotopes of Sr has been retarded, mainly due to difficulty in obtaining an accurate and precise ⁸⁸Sr/⁸⁶Sr isotopic ratio. In the conventional isotopic analysis of ⁸⁷Sr/⁸⁶Sr, the ⁸⁸Sr/⁸⁶Sr isotopic ratio has been normalized to 1/0.1194 to correct the ⁸⁷Sr/⁸⁶Sr ratio for the mass-discrimination effect; the natural variation in the ⁸⁸Sr/⁸⁶Sr ratio has been neglected.

In this study, we present a method to determine ⁸⁸Sr/⁸⁶Sr and ⁸⁷Sr/⁸⁶Sr simultaneously. The former variation reflects the mass-dependent isotopic fractionation through the physico-chemical processes, and the latter originates from decay of the parent nuclide ⁸⁷Rb as well as the mass-dependent isotopic fractionation. In order to determine the mass-dependent isotopic fractionation, the mass-discrimination effect on ⁸⁸Sr/⁸⁶Sr was externally corrected by an exponential law using Zr. For the radiogenic growth of ⁸⁷Sr/⁸⁶Sr, the mass-dependent isotopic fractionation effect on ⁸⁷Sr/⁸⁶Sr was corrected by a conventional correction technique using the ⁸⁸Sr/⁸⁶Sr ratio. The reproducibility of the ⁸⁸Sr/⁸⁶Sr and ⁸⁷Sr/⁸⁶Sr measurements for a high-purity Sr chemical reagent was 0.006% (2SD, n = 20) and 0.007% (2SD, n = 20), respectively. Strontium isotopic ratios (⁸⁸Sr/⁸⁶Sr and ⁸⁷Sr/⁸⁶Sr) were measured on geochemical reference materials (igneous rock: JB-1a, JA-2 and JG-2; carbonate mineral: JLS-1, JDO-1, JCP-1 and JCT-1) and one seawater sample. The resulting ⁸⁷Sr/⁸⁶Sr ratios obtained here were consistent with previously published data within the analytical uncertainties. The resulting ⁸⁸Sr/⁸⁶Sr ratios for igneous rocks and carbonate minerals showed enrichments of the lighter Sr isotopes over the seawater sample. The ⁸⁸Sr/⁸⁶Sr ratio of geochemical samples could reflect the physico-chemical processes for the sample formation. Also, a combined discussion of ⁸⁸Sr/⁸⁶Sr and ⁸⁷Sr/⁸⁶Sr of samples will render multi-dimensional information on geochemical processes.

Keywords: Stable isotope geochemistry, Strontium, Isotopic fractionation

Contribution of anciently depleted mantle and slab derived components to boninite magma genesis

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Boninite is a volcanic rock derived from highly depleted hydrous mantle that melted at a shallower depth with water derived from the subducted slab. Boninite occurred at the inception stage of the Izu-Bonin-Mariana arc (~48-45 Ma), and thus, may record less modified upper mantle composition with the subducted slab components. In order to improve the understanding of Os recycling in the subduction setting, Cr-spinels from boninites, Cr-spinel/magnetite mixtures from tholeiites which erupted subsequently after boninites (<45 Ma), and the whole rock of those lavas were analyzed for Os isotopes. The initial Os isotope ratios of the Cr-spinel from the boninites show highly unradiogenic to unradiogenic values ($^{187}\text{Os}/^{188}\text{Os}(i) = 0.1179\sim 0.1256$), whereas those in the Cr-spinel/magnetite mixtures from the tholeiites ($^{187}\text{Os}/^{188}\text{Os}(i) = 0.1270$ and 0.1369) are slightly radiogenic. The initial Os isotope ratios of the whole rock samples are more radiogenic and have larger variety than those of Cr-spinel and Cr-spinel/magnetite mixtures, possibly because of contamination with the crustal materials during magma ascent or alteration after emplacement. Based on highly unradiogenic initial Os isotope ratios of the Cr-spinels from boninites, the source of the boninites should be highly depleted mantle with a small amount of the slab flux composed of altered oceanic crust (AOC) and unradiogenic components such as oceanic island basalt (OIB) volcanoclastics or very young mid-oceanic ridge basalt (MORB). In contrast, the Os isotopic compositions of Cr-spinel/magnetite mixtures of tholeiites are clearly higher than those of Cr-spinels of boninites and slightly higher or similar to chondrites and primitive upper mantle (PUM) values. They were possibly affected by radiogenic slab components such as pelagic sediments and AOC with depleted mantle.

Keywords: Os isotope ratio, boninite

Melting of a stagnant slab in the mantle transition zone: Constraints from Cenozoic alkaline basalts in eastern China

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The feasibility of the melting of oceanic igneous crust in stagnant slabs has been proposed by studies on experimental petrology, however, relevant geochemical evidence of melting has not yet been found from igneous rocks. We present evidence that proves that melts from the igneous layer in the stagnant Pacific slab have contributed to the source composition of basalts from eruption in eastern China. Fe-rich (>13 wt%), Si-poor (<43 wt%) basalts only occur above the leading edge of the stagnant Pacific slab in eastern China. Their source has Nd-Hf isotope compositions akin to the igneous layer in the Pacific slab, while they have Sr-Nd-Pb isotope compositions similar to those of mid-oceanic-ridge basalt. The extremely low Rb and Pb (Ce/Pb > 30) contents of these basalts suggest that this source material was modified by a subduction process. Together, these geochemical characteristics help us to conclude that these basalts have received a significant contribution from the melts derived from dehydrated carbonate-bearing oceanic crust, without a long time-integrated ingrowth of Sr-Nd-Hf-Pb isotope systems at the leading edge of the stagnant Pacific slab.

Keywords: Intraplate alkaline basalt, eastern China, Shandong Peninsula, HIMU basalt, stagnant Pacific slab, oceanic crust recycling

Thermal structure beneath Northeast China recorded in mantle xenoliths

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Back-arc areas have not attracted many researchers studying magmatism or heat flux. In Northeast China, however, there exists Cenozoic volcanism. If a long-term or a large-scale magmatism exists in such back-arc areas, both global heat flux and material circulation system in the Earth should be reconsidered with their effects. Such a significant magmatic activity can cause thermal disturbance in the lithosphere. We therefore studied lithospheric thermal structure in the area.

We estimated thermal structure using equilibrium temperatures and pressures recorded in mantle-derived peridotite (or spinel-lherzolite) xenoliths sampled in the Liaoning Kuandian volcanic field, Northeast China. Determination of residual density of CO₂ fluid inclusions in the xenoliths allowed us to estimate equilibrium pressures of spinel lherzolites, to which no petrological geobarometer have been applied before. Equilibrium temperatures and original depths obtained from five xenoliths are about 1000 degree Celsius and 30-40 km, respectively. This temperature and pressure conditions correspond to 110 - 140 mW/m² in heat flow. In contrast, Huang and Xu (2010, Journal of Earth Science) reported the heat flow of the area to be about 70 mW/m², based on P-T estimates using garnet pyroxenites whose original depths are 50 - 60 km. We suggest the higher heat flow in the shallow lithospheric mantle. This requires the existence of a high temperature area near the Moho discontinuity, suggesting a long-term magma activity in the uppermost mantle beneath the area. If such a long-existing magmatic activity is common in the back-arc areas, the areas have significant influences on global heat balance and thermal history.

Keywords: back-arc, geotherm, heat flow, Northeast China, mantle xenolith, fluid inclusion

Element partitioning between garnet, olivine and hydrous melt at 10GPa

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It is thought that the bottom depth of Earth's magma-ocean would be more than 1000km. In order to understand chemical differentiation of magma-ocean, it is important to estimate pressure dependence of element partition coefficients quantitatively. PC-IR diagram is modeled by strain energy of lattice site in crystal by Blundy and Wood (1994). We aim to expand the model to various conditions pertinent to the Earth's magma ocean (pressure, temperature, amount of water etc.). We determined PC-IR diagram of olivine / dry melt between 1 atm. and 10GPa, and found that the parabolic curve for trivalent cations becomes wider with pressure (Imai et al., Goldschmidt Conference 2009). The widening of parabola means that Young's modulus of crystal site decreases with pressure, but it is unreasonable because lattice site is compressed by pressure (Imai et al., JpGU 2010). The widening parabola can be explained with adopting Young's modulus of 'melt' which was not considered in Blundy and Wood's model. In other words, we propose that melt becomes 'harder' with pressure. In this study, we focus on element partitioning and PC-IR diagram for hydrous magma ocean.

According to two component model, early earth might contain about 2 wt. % H₂O. Ikoma and Genda (2006) suggested that hydrogen atmosphere covered early earth and might coexist with magma-ocean. Thus, we may not ignore the effect of water for chemical differentiation of magma-ocean.

In present study, we investigated partition coefficients between garnet, olivine and melt which contain various amounts of water at 10 GPa using a Kawai-type multi-anvil apparatus and compared with previous studies at dry and hydrous conditions (dry: Suzuki et al., in prep.; Imai et al., in prep, hydrous: Inoue et al., 2000; Mibe et al., 2006). We prepared two mafic starting materials (45 and 39 wt. % SiO₂), doped with 26 trace elements and added 5 to 13 wt. % H₂O. Platinum was used as sample container. Major, minor and trace elements analysis of garnet, olivine and coexisting hydrous melt were performed with EPMA and LA-ICP-MS. After experiment, some amount of iron in samples reacted with capsule, and alkali ions escaped with aqueous fluid when it was quenched.

Partition coefficients (D) between garnet, olivine and hydrous melt were calculated using obtained elements concentrations in each phase, and were compared with previous experimental results at dry conditions. For major elements in garnet, D values for divalent ions (Mg²⁺, Fe²⁺, Ca²⁺) at hydrous conditions are smaller and those of Al³⁺ and Si⁴⁺ are higher than those at dry conditions. For trace elements in garnet, D values of other ions (REE₃⁺, Sc³⁺, Y³⁺) are the same between dry and hydrous conditions. D values for divalent cations in olivine at hydrous conditions are slightly smaller, and that for Si⁴⁺ is larger than at dry condition. All D values for trivalent cations in present study are obviously smaller than those at dry condition (Imai et al., in prep.). When PC-IR diagrams at 5 GPa are compared between hydrous and dry condition (Mibe et al., 2006; Imai et al., in prep., respectively), similar features are present.

We fitted our results using lattice strain model (Blundy and Wood, 1994) on PC-IR diagram and obtained three parameters, optimum ionic radius in lattice site (r_0), the partition coefficients of host cation (D_0) whose ionic radius is r_0 , and apparent Young's modulus of lattice site for crystal and melt (E). The change in partition coefficients between dry and hydrous can be explained by the effect of only D_0 and temperature. The r_0 and E remains constant for both dry and hydrous conditions. The change of D_0 is explained by the variation in composition of melt. Although absolute value of partition coefficients decrease dramatically from dry to hydrous conditions, our analysis can predict the changing value with limited information (i.e., temperature and concentration of some key elements in melt, Takahashi and Irvine, 1981).

Keywords: element partitioning, hydrous, olivine, garnet, high pressure, trace element

Trace element partitioning between Fe-Ni Alloy and sulfide melt under high pressure

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Knowledge of the partitioning behavior of elements between solid-liquid metal is fundamental for resolving the evolution in metallic core of the terrestrial planets. Hence we performed high pressure melting experiments of Fe-Ni-S system at 10 and 15 GPa, and measured the partitioning coefficient of elements.

We synthesized Fe-Ni(95:5) alloy doped with 14 trace elements (Co, Cu, Ge, Mo, Ru, Ph, Pd, W, Re, Os, Ir, Pt, Au, Pb) in approximately 150 ppm, by arc-melting method. A small chip of this alloy and a small amount of FeS powder were packed in the MgO capsule, and high pressure melting experiments were performed using Kawai-type multi-anvil press installed at Tokyo Institute of Technology. Quenched samples were polished and major element compositions were measured by EPMA. Trace element abundances were determined by fs-laser ablation system with sector-type ICP-MS installed at Kyoto University.

Among measured elements, Ru, Re, Os, Ir, and Pt were distributed into the solid metal, while Mo, Pd and Au were enriched in the sulfide melt. These observations may suggest the influence of sulfur in the partitioning behaviors. In the case of silicate mineral-melt system, it is well known that the partition coefficients are controlled by the crystal structure and ionic radius (e.g., Onuma et al., 1968). Similar relationship has been also pointed out for metallic system that the partition coefficients are correlated with atomic radius (e.g., Orman et al., 2008). However, we cannot find any relationships between atomic radius and the observed partition coefficients. Further investigations are required to find out the systematics in the partition behaviors of metallic solid-liquid systems.

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Keywords: High pressure, Element partitioning, Metal, Sulfide

Nb-Zr systematics of U-Pb dated achondrites

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The short-lived radionuclide ^{92}Nb decays to ^{92}Zr with a half-life of 36 Ma [1]. Nb and Zr are both refractory lithophile elements and can fractionate from each other during partial melting of the mantle. Thus, Nb-Zr isotope systematics can potentially place chronological constraints on early planetary silicate differentiation. This application requires the initial abundance of ^{92}Nb (or $^{92}\text{Nb}/^{93}\text{Nb}$) and its homogeneity in the solar system to be unambiguously defined. Yet previously reported initial $^{92}\text{Nb}/^{93}\text{Nb}$ values range from $\sim 10^{-5}$ to $>10^{-3}$ [2-6], and remain to be further constrained. All but one of the previous studies estimated the initial $^{92}\text{Nb}/^{93}\text{Nb}$ using Zr isotope data for single phases with fractionated Nb/Zr in meteorites such as zircons and CAIs, under the assumption that their source materials and bulk chondrites had had identical initial $^{92}\text{Nb}/^{93}\text{Nb}$ and Zr isotopic compositions [2-5]. To evaluate the homogeneity of the initial ^{92}Nb abundance, however, it is desirable to define internal mineral isochrons for meteorites with known absolute ages. Although Schonbachler et al. [6] defined Nb-Zr internal isochrons for two meteorites (Estacado and Vaca Muerta), their absolute crystallization (or possibly recrystallization) ages are not precisely constrained, leading to uncertainties in the resultant estimate for the initial $^{92}\text{Nb}/^{93}\text{Nb}$ of the solar system.

To establish the solar system initial $^{92}\text{Nb}/^{93}\text{Nb}$ and its homogeneity, we are studying the Nb-Zr systematics of minerals from achondrites whose absolute crystallization ages were precisely determined with the U-Pb chronometer. Abundances of trace elements including Nb and Zr were determined by LA-ICPMS for pyroxene, plagioclase, pyrite, spinel and/or opaque minerals from 3 eucrites (Agoult, Ibitira and A-881394), 5 angrites (SAH99555, D'Orbigny, NWA2999, NWA4590 and NWA4801) and Acapulco. The results reveal that Agoult, Ibitira and NWA4590 contain phases with reasonably high Zr contents and a good spread in Nb/Zr (<0.01 for pyroxene and ~ 3 for opaque minerals and spinel) to define precise internal isochrons. These minerals and whole rock samples were further processed for Zr separation and analyzed for Zr isotopes by MC-ICPMS. We found that the spinel and opaque mineral fractions have restricted positive ^{92}Zr anomalies up to 30 ppm relative to the terrestrial standard samples. We are still in the process of determining their Nb/Zr isotopic ratios, but preliminary results of Zr isotope analyses, combined with the approximate Nb/Zr of minerals estimated by LA-ICPMS, suggest that the initial $^{92}\text{Nb}/^{93}\text{Nb}$ is in the order of $\sim 10^{-5}$, consistent with the results of previous work using the internal isochron approach [6].

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Keywords: early Earth differentiation, short-lived radionuclide, solar system chronology

Magma variety and its origin for Shatsky Rise

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Shatsky Rise, a large oceanic plateau in the northwest Pacific, consists of thick (>22 km) basaltic crust with various geochemical compositions. Geochemistry of fresh glass and whole rock samples from one site (Site 1213) of Ocean Drilling Program (ODP) and five sites (Sites U1346 to U1350) of Integrated Ocean Drilling Program (IODP) indicates that mainly four magma types exist on the plateau; namely normal, low-Ti, high-Nb, and U1349 types. The normal type is the most abundant in volume and appears all three large edifices of the plateau; Tamu (Sites 1213 and U1347), Ori (Site U1350), and Shirshov (Site U1346) massifs that are aligned from southwest to northeast. Composition of the normal type is a relatively uniform and similar to normal mid-ocean ridge basalt (N-MORB) composition, but slight relative enrichment in the more incompatible elements. The low-Ti type, which is present in one stratigraphic unit at Site U1347 and the upper stratigraphic units at Site 1350, is distinguished from the normal type basalt by slightly lower Ti, Fe, and Mn contents at a given MgO. The high-Nb type is found in the upper stratigraphic units at Site 1350 and one fresh glass from Site U1348 (on Tamu Massif), and the composition is characterized by distinctively high contents in incompatible trace elements such as K, Nb, and La. All basalts at Site U1349 (on Ori Massif) are composed of more primitive and distinctly depleted compositions compared with the others, and they are defined as an independent U1349 type. Examination of stratigraphic and geographical distributions of the magma types clarifies that about 1/3 of lava units are composed of non-normal type basalts (the high-Nb, low-Ti, and U1349 type basalts). The normal type basalts constitute most lava units of Tamu Massif but the non-normal type basalts are voluminous in Ori Massif, implying that geochemical compositions may have become heterogeneous with time. We will mainly focus on origin and evolution of the normal type magmas on Shatsky Rise.

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Keywords: Integrated Ocean Drilling Program, Expedition 324, Large Igneous Province, Oceanic Plateau, Plume

Highly siderophile element behavior during oceanic LIP emplacement

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Causal mechanisms and ultimate trigger for the global environmental catastrophes, such as mass extinction and oceanic anoxia events are long-standing matter of debates. Since the discovery of global Ir anomaly in Cretaceous-Tertiary boundary layer and the Chichxulub crater, the highly siderophile elements (HSEs) in sedimentary sequences have been recognized as useful geochemical tracers for identifying extraterrestrial impacts. However, an important question remains as to whether enormous supply of HSEs to the surface environment is also caused by massive volcanism leading to the formation of large igneous provinces (LIPs). This classic idea has been recently revived by the Cenozoic-Mesozoic marine Os isotope record that displays frequent negative excursions over the time intervals of LIP eruption. In this contribution, we present HSE concentration data of oceanic LIP basalts recovered from Hole U1349A on summit site of Ori massif of the Shatsky Rise. The drillcore provides an ideal opportunity to evaluate the possibility of HSE loss due to volcanic degassing and/or contrasting alteration styles because it is separated into subaerial and submarine portions from a single magma type of narrow compositional range. The results demonstrate that Os, Ir, Ru and Pt values are nearly uniform throughout the core, whereas Pd and Re values in subaerial portions are systematically lower than those in deeper submarine portion. Current dataset may therefore lend no support to the notion that degassing and alteration processes are responsible for significant release of HSEs except for Pd and Re.

This research was supported by IODP After Cruise Research Program, JAMSTEC.

Keywords: highly siderophile elements, large igneous provinces, oceanic plateau, Integrated Ocean Drilling Program, Expedition 324

A comparative geochemical and petrological study of the Siberian and Ethiopian large igneous provinces (LIPs)

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This study is mainly targeted to find the possible eastern marginal extension of Siberian LIP and to compare them with the central Siberian LIP and is also aimed to compare and contrast the geochemical and petrological characteristics of Siberian LIP (~ 250 Ma) with the Ethiopian LIP (~ 30 Ma) to consider the mantle and crustal processes in view of magmatic diversity among those LIPs. A review of previous geochemical data from the Siberian and Ethiopian LIP confirms notable differences in their major and trace element compositions. Siberian LIP comprises a variety of rocks (such as basalts, andesitic basalts, picrites and meimechites) with a wide range of SiO₂ (40-62 wt.%). In contrast, Ethiopian LIP is characterized by bimodal volcanism with the absence of intermediate rock. The Ethiopian high-Ti basalts and picrites have higher TiO₂ (3-6 wt.%), lower CaO/Al₂O₃ (0.5-1.5) and MgO (5-26 wt.%) than the Siberian high-Ti picrites and meimechites (2-4, 1.8-2.3 and 13-36 wt.% respectively). Siberian LIP shows more significant depletion in HFSE (mainly Nb) and higher La/Sm ratios than Ethiopian LIP. This may suggest contamination of Siberian LIP magma by continental crustal rocks. Triassic volcanic and intrusive rock samples are collected from the Chukotka province (Northeast Russia), which is geographically far to the east from the central Siberian flood basalt province. The petrography of the studied samples includes basaltic rocks (i.e. hornblende basalt, lamprophyre, pyroxene phyric basalt, and ankaramite) and gabbroic rocks (i.e. hornblende gabbro, pyroxene-hornblende gabbro, pyroxene gabbro, and quartz diorite). Basaltic rocks exhibit porphyritic texture with phenocrysts of plagioclase+ clinopyroxene+ hornblende, whereas gabbroic rocks show granular, ophitic and poikilitic textures with a crystals of hornblende+ clinopyroxene+ plagioclase and rare phlogopites. Opaque minerals are usually magnetite with a size reaching about 7 mm in hornblende gabbro and also iron sulphides in pyroxene-phyric basalt. The chemical composition of clinopyroxene phenocrysts from basalts are in the range of Wo₂₉₋₅₁En₃₈₋₄₉Fs₄₋₃₃ with a general ferrosilite (Fs) increase from core to rim, but a few phenocrysts in the pyroxene-phyric basalt show a reverse zoning. The clinopyroxene phenocrysts from the pyroxene phyric basalt have a range of Mg# (0.72- 0.91), whereas those from hornblende basalt, ankaramite and lamprophyre units have 0.54-0.76, 0.83-0.92, and 0.83-0.93 respectively. Clinopyroxene phenocrysts from hornblende basalt are highly differentiated and richer in FeO (average ~ 16.4 wt.%) than clinopyroxenes from the high-Ti and alkaline meimechite (Siberian LIP) and Ethiopian High-Ti basalt. Clinopyroxenes both from basalts and gabbros show only low-Ti (<1 wt.%) characteristics. Hornblendes both from basalts and gabbros have tschermakitic composition with alkali content ranges from 3.41 to 4.39 wt.%. Phlogopites occurring as a minor phase in the pyroxene-hornblende gabbro with Mg# ranges from 0.64 to 0.66. The groundmass plagioclases from the lamprophyre includes the three feldspar end members, i.e. An₈₋₇₃Ab₂₋₈₅Or₁₋₈₉. This suggests relatively high alkali content of the magma. The Triassic basalts and gabbros of Chukotka province may represent the easternmost portion of the Siberian LIP characterized by a low-Ti, HFSE depleted and hydrous basic magma.

Keywords: Siberia, Chukotka, Ethiopia, LIPs, hornblende basalt, meimechites

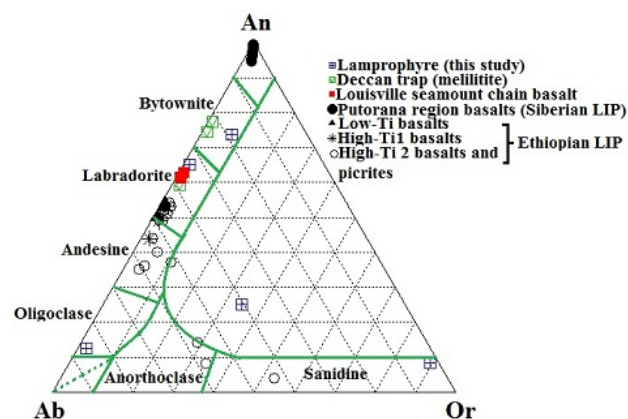


Fig. 1 Ab-An-Or ternary diagram for feldspars from lamprophyre. Ab, albite; An, anorthite; Or, orthoclase.

East-west geochemical mantle hemispheres and their implications on mantle dynamics

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Oceanic basalts, including mid-ocean ridge basalts (MORB) and ocean island basalts (OIB), have been extensively studied as geochemical messages from the mantle to decipher differentiation and convection within the Earth [Hofmann, 2003]. However, the spatial coverage of MORB and OIB is insufficient for resolving even a global feature of the compositional variability. We analyze the oceanic basalts together with the arc basalts in subduction zones that extend over a long distance comparable to mid-ocean ridges and cover the areas with a few mid-ocean ridges or hotspots. Combining the arc data with those from oceanic basalts, and by using Independent Component Analysis [Iwamori and Albarede, 2008; Iwamori et al., 2010] to remove influences from the subducted materials, global geochemical domains appear primarily as east-west hemispheres, rather than north-south hemispheres as has been long argued for [Hart, 1984]. The eastern hemisphere, ranging roughly from the Mid-Atlantic Ridge to Eastern Eurasia and Australia, is underlain by a subducted component-rich mantle being created possibly by extensive subduction beneath the supercontinent Pangea. The primary feature of this spatial pattern and relationships is that the geochemical domains have been anchored to asthenosphere for at least 300 m.y. in the past, and the continents dispersed without significantly disturbing the asthenospheric structure, possibly due to mechanical decoupling between lithosphere and asthenosphere. The second (thus less obvious but important) feature is as follows: distribution of a subducted component-poor domain beneath the western hemisphere, including the American Plates that had been a part of the supercontinent, suggests eastward flow of asthenosphere once located under the Panthalassic Ocean, i.e., migration over several thousands km during the last ~300 million years. The flow pattern and velocity seem consistent with the westward lithospheric rotation against the asthenosphere [Ricard et al., 1991] that exhibits internal deformation.

Keywords: mantle, isotope, hemisphere, supercontinent, lithosphere, subduction

Origin of Suppressed Matrix Effect by 200Fs-SF-ICPMS Elemental Analysis

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We have tested an ultraviolet 200nm femtosecond laser ablation (200FsLA) sector-field inductively coupled plasma mass spectrometry (SF-ICPMS) system for major and trace element analyses in silicate glasses and minerals. By optimizing the 200FsLA optics and the analytical protocol and employing a modified ion sampling interface in the SF-ICPMS, the sensitivity of the system has been improved with reduced backgrounds, achieving accurate spot analyses of 44 elements from ppb to wt.% levels at a crater diameter of 30 microns. Corrections for differences in the laser sampling efficiency between samples and the standards were performed by 100% normalization of the sum of the oxides of all the elements analyzed. Use of 200FsLA minimized the matrix effect by 50% compared to that by a 193-nm nanosecond excimer LA. The origin of this improvement was identified as the suppression of melting point-induced element fractionation at the laser ablation site due to a decreased thermal effect by 200FsLA. Sensitivity enhancement in some elements with high first ionization energy still remained in the basalt aerosols relative to silica-rich aerosols. This is inferred to be due to the higher thermal conductivity of the basalt aerosols in the inductively coupled plasma enhancing ionization. Accurate determination of trace elements (within 5% of the accepted values) was achieved for glasses ranging from MPI-DING komatiite to rhyolite, using single basalt glass BHVO-2G as the calibration standard. This method is also applicable to various anhydrous silicate minerals such as plagioclase, pyroxenes, and garnet. However, SRM610 glass, which has a very different matrix than BHVO-2G, is preferred for zircon. Apart from this exception, the proposed method does not require any external analytical techniques when the amounts of unmeasured elements such as halogens or water in the materials are negligibly low, which is the case for many geological materials.

Keywords: Femtosecond laser ablation, ICP-MS, Elemental analysis, Matrix effect

Global recycling of materials in the Earth's interior and noble gas isotopes

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Based on isotope ratios including radiogenic isotopes, it has been inferred that global recycling of surface materials in the Earth's interior through such processes as generation of plates at ridges, igneous process including volcanic eruption and subduction of slabs around island arc areas. Furthermore, seismic tomography indicates an image of subduction of slabs into the mantle.

However, there remain many issues to be solved such as details of the depth and the state of recycling of materials. For example, it has been argued that dehydration from the surface of a slab would contribute to produce an arc magma. But among researchers, there are large differences in their images about the degree of related materials and the effect of remained materials to the deeper mantle.

Since noble gas is chemically inert, its behavior can be regarded to be controlled only by physical processes. Furthermore, it is well known that the elemental and isotope compositions of noble gases are significantly different between those of the atmosphere and the Earth's interior. Since noble gases are volatile, it has been known that most materials formed near the surface exchange noble gas compositions from those of original one in a magma to the atmospheric ones. Hence we can identify surface materials from the signature of the atmospheric compositions except for radiogenic components. By combining noble gas isotope signatures such as $3\text{He}/4\text{He}$ and $40\text{Ar}/36\text{Ar}$, we can also identify different magma sources.

By applying noble gas signatures, many trials have been performed to investigate the state of the Earth's interior and it is inferred that the magma source of OIBs should be located deeper than that of MORBs based on $3\text{He}/4\text{He}$ and $40\text{Ar}/36\text{Ar}$ isotope systematics. Furthermore, it is commonly accepted that He is not recycled into the Earth's interior. Noble gases become a useful tool to get information on recycling of materials in the Earth's interior by applying their properties. For example, heavier noble gases such as Ar, Kr and Ar are regarded to be recycled with H₂O and it has been reported that recycled atmospheric noble gases play an important role in the magma source of OIBs associated with seawater. If it is, recycled materials contribute much to the magma sources of OIBs and island arc basalts, but not so much in case of the magma source of MORBs. Furthermore, atmospheric components spread over the region of the source of OIBs and their effects are reflected in the isotope compositions of noble gases of OIBs. However, no clear relation is observed between the degree of atmospheric contribution and the isotope signatures of solid elements. On the other hand, in case of He, which is regarded to have much larger mobility than those of heavier noble gases, OIBs with the $3\text{He}/4\text{He}$ lower than those of MORBs are regarded to be affected by recycled materials and they also show signatures of solid element isotopes by effect of recycled materials. Such characteristic $3\text{He}/4\text{He}$ signature suggests that the effect of recycled materials is limited in case of He isotopes. Since even mobile He shows its effect to be limited in case of recycled materials, it is likely that the observed atmospheric components of heavier noble gases in OIBs might contain the components not only of recycled materials but also the other kinds of sources. Thus, in order to investigate the effect of recycled materials based on noble gas isotopes, it is important to clarify the source of signatures observed in samples and should be reconsidered carefully.

Keywords: Global recycling, Earth's interior, Noble gas, Isotope

FOZO-HIMU connection: link to chemical heterogeneity of MORB

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One of fundamental concepts of the mantle geochemistry is a hypothesis called 'mantle reservoir model' (White, 1985; Zindler and Hart, 1986), in which isotopic composition of the ocean island basalts (OIBs) are explained by mixing of distinct and isolated reservoirs in the Earth's interior. In early research on the mantle reservoirs, the isotopic compositions of OIBs were mainly explained by the mixing of depleted MORB mantle (DMM) and three enriched reservoirs (HIMU, EM1, and EM2) whose isotopic compositions are enriched extremes. In addition to these 'extreme reservoirs', the importance of reservoirs whose isotopic compositions are common and intermediate has been pointed out, such as FOZO (Focal Zone, Hart et al., 1992), C (common component; Hanan and Graham, 1996), PREMA (Prevalent Mantle, Zindler and Hart, 1986) and PHEM (Primitive Helium Mantle, Farley et al., 1992). Although the existence of these 'intermediate reservoirs' is still in debate, the isotopic compositions of these reservoirs, in particular FOZO, have been commonly used to describe the isotopic distribution of OIBs.

The origin of mantle reservoirs is considered to be recycling of oceanic crust with/without sediments. Thus recycling of pure oceanic crust is important because the oceanic crust is the major constituent of recycled material. As the recycling of pure oceanic crust is inferred to produce HIMU and FOZO components, elucidating the origin of these reservoirs should be important from the perspective of production of mantle heterogeneity (e.g., Stracke et al. 2005). A major question about the origin of these reservoirs would be the process that made the difference between HIMU and FOZO. Additional question about their origin is the process that can explain the rare occurrence of HIMU and ubiquitous presence of FOZO.

In the present study, we have conducted geochemical modeling for understanding the origin of HIMU and FOZO. For the model, MORB compositions from East Pacific rise and Mid-Atlantic ridge are compiled from published data. The results suggest that oceanic crust with various stages of magmatic evolution can produce U and Th enrichment that is suitable for the origin of HIMU and FOZO, i.e., less evolved common MORB can be the source for FOZO and strongly evolved rare MORB can be the source for HIMU. Although the magmatic evolution processes also produce high Pb concentration that is inappropriate for the origin of HIMU, sulfur enrichment during the evolution can erase the effect of Pb enrichment due to desulfurization and Pb loss beneath subduction zones. Depleted Sr isotopic composition of HIMU seems to contradict high Rb concentration of evolved MORB magmas. However, high degree of dehydration and Rb loss beneath subduction zones can produce depleted Sr isotopic composition of recycled crust. In this context, magma evolution at mid-ocean ridges and variable degree of dehydration beneath subduction zones play an essential role in producing the isotopic variations between HIMU and FOZO.

Keywords: FOZO, HIMU, Mantle reservoirs, MORB, recycling, OIBs

Behavior of platinum-group elements during peridotite partial melting

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Platinum-group elements (PGE) are key tracers for the chemical differentiation of the early Earth and the subsequent chemical evolution of the Earth's interior. PGE abundances in the mantle are much higher than expected from core-mantle equilibration, which is often attributed to late meteorite bombardment (so called "late veneer") on the Earth after core formation, although alternative hypotheses have also been proposed. A critical point to testify the models for the excess PGE in the mantle is accurate estimation of the PGE abundances in the primordial mantle. Many peridotite samples with relatively primitive composition have broadly chondritic relative abundances of PGE, which is in favor of the late veneer hypothesis. However, absolute concentrations of PGE are strongly variable among rock types and sample locations, because PGE concentrations in peridotite samples are likely to be modified by partial melting processes the samples experienced. Thus it is highly required to understand the PGE behavior during partial melting processes in order to accurately estimate the PGE abundances in the mantle. Since PGE in peridotite samples are dominantly concentrated in base metal sulfides (BMS) and platinum-group minerals (PGM), it is necessary to know the phase relations of BMS and PGM in partially molten peridotite minerals. I will review the experimental studies on the stability of PGM and BMS during partial melting of peridotite, and discuss the role of these minerals for the generation of the diversity of PGE concentrations in peridotite samples.

Keywords: platinum-group element, platinum-group mineral, mantle, partial melting

Sr-Nd isotopic and trace element geochemistry of the Finero peridotite massif, southwestern Alps, Italy

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The Finero mafic-ultramafic complex is one of the orogenic peridotite massifs emplaced into granulite facies metabasites of the Ivrea-Verbano Zone of Northern Italy. The Finero mafic-ultramafic complex is an antiformal body that comprises four main units from core to rim: a Phlogopite Peridotite, an layered Internal Gabbro, an Amphibole Peridotite, and an External Gabbro (e.g. Cawthorn, 1975, JG; Coltorti & Siena, F, 1984, N. Jb.Mineral. Ab). The Phlogopite Peridotite and other units have been interpreted as residual mantle left after extraction of 18 % mid-ocean ridge basalt (MORB) and a crustal cumulate body, respectively (Coltorti & Siena, 1984, N. Jb.Mineral. Ab.; Siena & Coltorti, 1989, N. Jb.Mineral. Ab. Hartmann & Wedepohl 1993, GCA). The Phlogopite Peridotite unit consists of dunite and harzburgite with minor pyroxenites and chromitite. Amphibole and phlogopite are remarkable in the phlogopite peridotites of the Finero Phlogopite Peridotite massif than other Ivrea-Verbano peridotite massifs (Balmuccia and Baldissero, Hartman & Wedepohl, 1993, GCA). Amphibole ubiquitously occurs, and amphibole and/or phlogopite-bearing segregations and veins are locally abundant of the Finero Phlogopite Peridotite unit (e.g., Selverstone & Sharp, 2011, EPSL). These hydrous minerals were believed to be formed by interaction with residual peridotite and slab derived fluid/melt (e.g. Zanetti et al., 1999, CMP). Apatite and carbonate also founded in the phlogopite peridotite as sporadic region and thin layer (e.g. Zanetti et al., 1999, CMP; Morishita et al., 2003, Lithos). The sporadic region seems to be influenced by mantle derived melt (Raffone et al., 2006, MCA) or slab-derived CO₂ bearing hydrous agent (Morishita et al., 2008, CG), whereas the thin layers was expected to result from passage of evolved slab-derived CO₂ bearing hydrous agent (Morishita et al., 2003, Lithos; Matsumoto et al., 2005, EPSL; Morishita et al., 2008, CG). In recent, Selverstone and Sharp (2011, EPSL) divided the Finero phlogopite peridotites into the four groups (from type 1 to type 4) based on the petrographic feature of hydrous minerals and suggested at least two chemically distinct metasomatic fluids from the Cl, H, and O stable isotope geochemistry with petrologic and major and trace element data.

Our purpose of this study is to confirm the relationship between the petrographic features and other geochemical signatures such as trace element and Sr-Nd isotopic compositions. Sr-Nd isotopic compositions of acid washed amphibole separates from the spinel harzburgite with minor amphibole and/or phlogopite (type 1), harzburgite with segregation phlogopite and/or amphibole (type 2) and amphibole-rich segregations (type 3) are significantly enriched character ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7075 - 0.7091$, $^{143}\text{Nd}/^{144}\text{Nd} = 0.51232 - 0.51237$) similar to those of the continental crust as suggested by previous studies (Voshage et al., 1987, CMP; Lu et al., 1997, CG; Zanetti et al., 1999, CMP; Matsumoto et al., 2005, EPSL). Such enriched isotopic feature is common for the peridotite xenoliths from cratonic subcontinental lithospheric mantle (e.g. Pearson et al., 1995, GCA). Amphibole of type 1 spinel harzburgite has most enriched Sr-Nd isotopic compositions. Amphibole of the type 2 and type 3 spinel harzburgites have similar Sr-Nd isotopic compositions with each other. Selverstone and Sharp (2011, EPSL) inferred that these segregations had originated hydrous melt induced by H₂O-CO₂ fluid derived subducting slab. Our results combined with previous studies, therefore, suggest that hydrous silicate melt formed amphibole-rich segregation has relatively depleted Sr-Nd isotopic compositions.

Keywords: phlogopite peridotite, Finero mafic-ultramafic massif, Sr-Nd isotopic compositions, trace element compositions

Redox condition in subduction system elucidated from Os in Cr-spinel from Bonin Island beachesands

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The Os isotopic system is a potential tracer of a recycled crustal component in mantle or volcanic rocks because of the significant contrast between Os isotope ratios of crust and mantle. It is because, fractionation between Re and Os during mantle partial melting leads to a significant contrast in $^{187}\text{Os}/^{188}\text{Os}$ between high values ($^{187}\text{Os}/^{188}\text{Os} > 0.5$) in crustal rocks and low values ($^{187}\text{Os}/^{188}\text{Os} < 0.13$) in mantle rocks. For instance, a recycled ancient crustal component with high $^{187}\text{Os}/^{188}\text{Os}$ is involved in the production of hotspot volcanic rocks in Polynesia (Hofmann, 1997). However, the potential for crustal contamination overprinting this possible signal has hampered the utility of Os isotopic ratios.

We explored the use of Os isotopes in chromian spinel (Cr-spinel) as a discriminator of primitive magma Os compositions in the Izu-Bonin arc, using beach sands as composite samples of the boninite and tholeiite magmas in three different islands. Cr-spinel is an early-stage crystal that preserves its isotopic composition even during later crustal contamination of the bulk rock. We found highly unradiogenic Os isotopic compositions in Cr-spinels from boninites, suggesting that they represent primitive magmas with slight or no Os contribution from the subducting slab during the generation of boninites in the infant arc stage (48-46 Ma). Conversely, the radiogenic Os isotopic ratios in Cr-spinels from tholeiites most likely reflect the contribution from a slab-derived component, because more oxidative conditions in the subarc mantle probably allowed Os to mobilize from the subducting slab during the transitional arc stage (45-41 Ma). Although shallow-level assimilation of crustal components with radiogenic Os may overprint the original Os signature of tholeiite magma during its ascent, Cr-spinel allows us to compensate such possibilities.

Possible mechanism for the difference in Os transfer from the subducted slab between the early stage and transitional stage of the Izu-Bonin arc system is redox condition in the wedge mantle. We suggest that during boninite formation in the infant arc stage, the mantle beneath the Izu-Bonin arc was not strongly oxidized, resulting in less mobile Os in the subduction system. This leads to minimal input of radiogenic Os derived from the subducting slab to the primitive boninite magma. During formation of the Mukoojima tholeiites, the mantle was well oxidized by continuous input of slab-derived fluid and/or melt, providing mobile Os to the source mantle. This may account for the oxidative chemical compositions of Cr-spinel and the elevated Os isotopic compositions in the mantle source of the Mukoojima tholeiites.

Keywords: osmium isotope, Cr-spinel, Bonin Islands, redox condition

Mineralogy and petrology of the basalts from the Erdenetsogt Formation, Hangay-Hentey fold belt of central Mongolia

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This paper deals with the first mineralogical and petrological study of the basaltic rocks from the Erdenetsogt Formation (EF) in middle Paleozoic accretionary complex hosted by Tsetserleg terrane, which is westernmost part of the Hangay-Hentey fold belt (HHFB) of central Mongolia. EF is mainly made up of intensively deformed oceanic plate stratigraphy (OPS): pelagic radiolarian/ribbon chert, red and green quartzites (metachert), fine to medium-grained sandstone, siltstone with minor amount of limestone, and some basaltic rocks which have been discovered lately during geological mapping in the south Hangay region. The basaltic rocks exhibit mostly metabasalts, dolerites, microgabbros, and occasional meta-picrites composition with subophitic, intersertal, and partly intergranular textures. The phenocryst assemblage is composed of olivine (completely altered by chlorite, carbonate and serpentine and is only observed in meta-picrite) and clinopyroxene (well-preserved in all basaltic rocks) and smaller matrix plagioclase (replaced by albite). Accessory minerals include chromian-spinel, titanomagnetite and pyrite. Here, we present preliminary major element data for phenocryst and groundmass clinopyroxene (Ca-rich augite/diopside) and chromian-spinel measured by electron microprobe from the north and south of Uyanga Soum (village), where these basaltic rocks are exposed. There was no chemical variation in relict minerals observed from the basaltic rocks from these two parts. The preserved clinopyroxenes in basaltic rocks have a Mg# between 78-85, and follow a typical tholeiitic trend in the Ca-Mg-Fe diagram with rims slightly enriched in Fe relative to the cores. On the basis of Ca +Na vs. Ti and Ca vs. Ti+Cr discrimination diagrams, our results are consistent with tholeiitic magma of non-orogenic origin. The relict chromian-spinels (up to 0.25 mm in size) are found only in completely altered olivine phenocrysts of meta-picrite and its chemistry exhibits very limited in composition with Cr# of 55-68 numbers, which consistent with intraplate tholeiite. Spinel plot of Al₂O₃ wt.% vs. TiO₂ wt.% (range from 0.9 to 1.8 wt.%) ratio suggests OIB rather than MORB. In the Cr-Al-Fe+3 diagram, along with the Cr-Al line with low ferric iron content, resembling spinel among spinel peridotite xenoliths. In Mg# vs. Cr# diagram, it implies more fractionated magma than MORB. From this fact it is concluded that the chromian spinel of meta-picrite may have been derived from a mantle plume source. Our review of previous limited geochemical studies suggests enriched OIB for these basalts. In general, the mineral chemistry of the basalts from EF indicates tholeiitic OIB (hot spot/seamount) affinity in agreement with previous suggestions by some researchers. The OIB have been developed within Paleo-Pacific Ocean plate located between the Siberian and the North China Cratons, and then accreted to the active continental margin of Siberian Craton during middle to late Paleozoic.

Keywords: Hangay-Hentey fold belt, Erdenetsogt Formation, mineral chemistry, basaltic rock, clinopyroxene, chromian spinel

Whole-rock chemical compositions and REE analyses of the Muro pyroclastic flow deposit and related tuffs

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The Muro pyroclastic flow deposit is the rhyolitic tuffs that are distributed from the central part of Nara prefecture to the western part of Mie prefecture, southwestern Japan. It consists of a 15 km (north-south) x 28 km (east-west) body. The tuff is classified into two main lithologies. One is a glassy dense welded tuff called "black lava" and the other is a cryptocrystalline tuff "white lava" that have suffered devitrification¹). Both FT and K-Ar dating methods indicate that the age of the tuffs is about 15 Ma²). Several studies have been done for the Muro pyroclastic flow deposit (Shinjoe.H. et al, 2002; Iwano.H et al, 2007), however, the source is less well understood. In this study, we present newly obtained whole rock major, trace and rare earth element compositions of the Muro pyroclastic flow deposit and related tuffs. The related tuffs we analyzed are the Tamateyama tuff and the Sekibutsu tuff in Kii peninsula, and the Kn-1 tuff in Boso peninsula. A total of 15 samples were analyzed for chemical compositions. The whole-rock major-trace element compositions and REE compositions were analyzed by XRF and ICP-MS, respectively. Most of the samples except the Kn-1 tuff indicate that the SiO₂ contents vary from 73.0 to 75.5 wt% and the alumina-saturation index (A.S.I.) are more than 1.1 which shows those rocks are peraluminous. However, the Kn-1 tuff indicates especially low values of SiO₂ (SiO₂ = 59.9 wt%) and A.S.I. (c. 0.3). It shows that the Kn-1 tuff is metaluminous. Furthermore, the Kn-1 tuff has higher value of CaO, MnO, and P₂O₅ than the other samples. The Kn-1 tuff might have different type of source from the Muro pyroclastic flow deposits. When compared with the chemical compositions between the white and black lavas, SiO₂ content of the white lava is higher than the black lava, whereas the CaO, MnO, FeO*, MgO and Na₂O content of the black lava is higher than the white lava. However, both white and black lavas show similar chemical trends on the Harker's variation diagrams. Most of the samples show nearly same pattern on the REE composition diagram s normalized by CI-chondrite. They are LREE-rich, mid-to HREE flat and negative Eu anomaly pattern. The chemical compositions of the Muro pyroclastic flow deposits have relevance to the related tuffs (Tamateyama and Sekibutsu) except the Kn-1 tuff.

Keywords: Muro Pyroclastic Flow Deposit, rare earth elements (REE), Tuff

Whole-rock chemical compositions and rare earth element compositions of the Paleogene Tadami-gawa granitic rocks, northea

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The Paleogene Tadami-gawa granitic rocks are located at the border between Fukushima and Niigata prefectures, northeastern Japan. The granite is divided into two rock types, the Tadami-gawa granite and the Hinoemata-gawa granite. The Tadami-gawa granite is coarse-grained biotite granite and it is characterized by the phenocryst of K-feldspar. The Hinoemata-gawa granite is medium-grained biotite-hornblend granite, and it is intruded by the Tadami-gawa granite. In this study, we have analyzed whole-rock chemical compositions including REE of the Tadami-gawa granitic rocks, and discuss the petrogenesis of the pluton. 7 samples of the Hinoemata-gawa granite and 18 samples of the Tadami-gawa granite were analyzed for major-minor chemical compositions and REE compositions by XRF and ICP-MS, respectively. SiO₂ contents of the Hinoemata-gawa granite and the Tadami-gawa granite range from 59.6 to 69.4 wt.% and from 62.8 to 74.6 wt.%, respectively. The Tadami-gawa granite and the Hinoemata-gawa granite may be generated from the same magma origin because they show similar trend on the Harker's diagram. The Tadami-gawa granitic rocks are plotted within the field of non-alkaline rock on the graph of SiO₂-(Na₂O+K₂O)(Miyashiro, 1978). It is also assumed that the pluton belongs to calc-alkaline rock series because SiO₂ contents increase with increasing FeO/MgO ratio. Additionally, almost all samples were classified into VAG (Volcanic Arc Granite) on the Rb-(Nb+Y) diagram(Pearce et al., 1984). Therefore, the Tadami-gawa granitic rocks magma might be originated from the partial melting of the basaltic crust. REE abundance patterns of all samples normalized by chondrite show high-LREE pattern. Many samples show negative Eu anomaly, and the value of Eu anomaly increase with decreasing anorthite content calculated by CIPW norm. The value of Eu anomaly might be concerned with the crystallization differentiation of the original magma. The degree of Eu anomaly of the Tadami-gawa granite is higher than that of the Hinoemata-gawa granite. Whole-rock chemical composition analyses suggest that the Tadami-gawa granite is more differentiated than the Hinoemata-gawa granite.

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Keywords: Tadami-gawa, Hinoemata, Granite, rare earth elements (REE)

REE compositions of the Kumano acidic rocks, outer zone of southwestern Japan

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The Kumano Acidic Rocks (KAR) which distributes in south-eastern part of the Kii peninsula, outer zone of southwestern Japan, are igneous rocks that were formed c.15 Ma (Iwano et al., 2007). Around the same time when KAR were formed, many tectonic events occurred in this area (Shinjoe et al., 2007). The formation of KAR may have an important relationship with these tectonic events.

KAR is composed of the Konogi rhyolite, rhyolitic tuff, the Kumano granite porphyry south unit and its north unit. An arc intrusion body that has a characteristic like the Kumano granite porphyry intrudes in the Koza area, southern part of the study area. KAR intrudes into Early Miocene sedimentary rocks of the Kumano Group (KG). In this study, we report the whole rock chemical composition of each rock types of KAR and KG. A total of 19 samples of KAR and KG were analyzed. The major-trace element compositions and REE compositions were measured by XRF and ICP-MS, respectively. The chemical compositions of KAR indicate that KAR is per-aluminous ($Al_2O_3 / (Na_2O+K_2O+CaO) = 1.10-1.69$). It suggests that the original magma melted the wall-rock of KG when it intruded, and/or the original magma was formed by the direct melting of other sediments. Because no whole-rock chemical relationship between KAR and KG was found on the Harker diagram, KAR may have formed by the direct melting of the sediments except KG. REE compositions normalized to CI-chondrite show the high-LREE and flat-HREE pattern. In addition, LREE patterns are divided into two patterns, such as higher and lower value, on the normalized diagram. KAR magma might be differentiated into two types in the magma chamber.

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Keywords: Kumano acidic rocks, rare earth elements, granite porphyry

Origin of TH and CA suits in Chokai volcanic rocks - examination of Sr isotope ratio in plagioclase phenocrysts

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Tholeiitic (TH) and Calc-alkaline (CA) series lavas is coexisting at Quaternary volcanos in NE Japan arc. Generally, CA lavas have evidence of magma mixing, e.g. disequilibrium phenocrystic assemblage such as olivine and quartz. Therefore, many previous works discussed that the former is evolved from mantle-derived basalt magma by fractional crystallization, and the latter is generated by magma mixing between basic and acidic magmas, both derived from the common TH basalt through fractionation. However, based on Sr isotope micro-analysis of plagioclase phenocrysts in lavas from Zao and Azuma volcanos at central area of NE Japan arc, Tatsumi *et al.* (2008) and Takahashi *et al.* (submitted) argued that isotopically radiogenic TH basalt was formed by melting of the lower-crustal amphibolite and CA was formed by magma mixing of the unradiogenic mantle-derived basalt, the radiogenic crust-derived basalt and the differentiated magma which relates to basalt magmas. Additionally, although estimated primary CA basaltic melt composition at Zao and Azuma volcanos is in frontal-arc, it is medium-K basalt and similar in composition to back-arc side basalt at Chokai volcano. This result is not in agreement with traditional across-arc variation model for mantle-derived basalt magma in island-arc magmatism (e.g. Kuno, 1966), and need reconsideration of the mechanism for geochemical across-arc variation in island-arc volcanic lavas.

The Quaternary Chokai volcano is located at the rear-arc side of NE Japan arc, and this is typical of stratovolcano in Chokai volcanic zone. Chokai volcano activity is divided into Stage1 to Stage3 (Hayashi, 1984; Ban *et al.*, 2001). Stage 1 lavas has not disequilibrium texture or rarely has plagioclase phenocryst which has dimly dusty zone. Stage 2 is composed largely of olivine two-pyroxene andesite with a small amount of olivine two-pyroxene basalt. Most of them contain hornblende as phenocryst. Stage 3 is olivine two-pyroxene andesite and two-pyroxene andesite. The almost plagioclase phenocryst in Stage 2 and 3 lavas has dusty zone and sieve texture. An% of plagioclase phenocrysts core in Stage 1 basalt shows monomodal distribution (An%: 80 to 90), whereas these in Stage 2 and 3 basalts have wide range (An%: 50 to 80). Chokai lavas are plotted on boundary of high-K and medium-K on the SiO₂ vs. K₂O diagram. On the FeO*/MgO vs. SiO₂ diagram, trend of Stage 1 and Stage 2 & 3 lavas show the TH and CA, respectively. The range of bulk Sr isotope ratio of TH (Stage 1) and CA (Stage 2 and 3) are very similar (TH: 0.70303 to 0.70341, CA: 0.70297 to 0.70342). But, Sr isotope ratio of TH is constant or look like slightly ascent with increasing SiO₂, whereas CA is distinctly ascent with increasing SiO₂. Petrographical and petrological feature of Chokai volcanic lavas indicate that TH is produced by fractional crystallization from basic magma and CA is formed by magma mixing between basic and felsic magma. And, it is thought that a parent magma of TH and the basic end-member magma of CA has different geochemical features.

In this study, we investigated the generation and evolution process of TH and CA suites in Chokai lavas using Sr isotope ratio of whole-rock and plagioclase phenocrysts, and compared them with the frontal-arc volcanic lavas (Zao and Azuma).

Keywords: tholeiitic series, calc-alkaline series, Sr isotope ratio, plagioclase

Pb isotope analysis of low-Pb geological glasses by femto-second laser ablation-multiple ion counter-ICP-MS

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In-situ analysis of Pb isotopes for the sample with limited size and low Pb content is still great challenging. Such samples include basaltic melt inclusions in olivine ranging from a few ten to one hundred micrometers in size and Pb contents of ~10 ppm. We tested the suitability of femto-second laser ablation sampling coupled to an ICP-MS equipped with multiple Faraday cups (MFC) and ion counters (MIC). Pb isotope ratios of $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ can be precisely determined with MFC for samples with high Pb (> 40 ppm) at large crater size (>100 micrometer in diameter), but this approach is not applicable to small melt inclusions. In contrast to ion current measurement by MFC, direct ion counting using MIC provides ~100 times better signal-to-noise ratio allowing measurement of Pb isotopes with lower intensities (i.e. small ablation crater on low-Pb materials). However, use of MIC detection system is a big challenge due to its poor performance in both linearity and stability. We found that mass bias factor obtained by MIC is signal intensity dependent. Standard bracketing method using similar ion intensities between standard and sample can correct for both the linearity and time dependent decay of MICs. However, control of signal intensity is not always easy for sample with unknown Pb content, especially for melt inclusion with limited sample volume. To overcome this problem, we attempted a dual intensity standard bracketing approach. Different laser repetition rate was utilized for measuring bracketing standard glass in order to cover expected intensity range of Pb signal of unknown sample. Response of each ion counter is calibrated by using linear regression which is then applied to determine the isotope abundance of unknown sample. This method was tested by analyzing Pb isotopes of well characterized reference material BHVO-2G (1.7 ppm Pb). The obtained analytical precision and accuracy of $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ are 0.3-0.4% (2sd) for a spatial resolution of ~30 micrometer. The precision and accuracy are comparable to published works, but spatial resolution is improved.

Keywords: UV-fs laser ablation, Multiple ion counter-ICP-MS, Pb isotope