

Geochemical connection between HIMU-FOZO-PREMA: two-stage dehydration of oceanic crust with layered structure

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Isotopic composition of the ocean island basalts (OIBs) can be explained by mixing of isolated reservoirs in the Earth (White, 1985; Zindler and Hart, 1986; Hofmann, 1997; Stracke, 2012). In early research on the mantle reservoirs, the isotopic composition of OIBs was explained by the mixing of depleted MORB mantle (DMM) and three enriched reservoirs, those are HIMU (high-u: $u = 238\text{U}/204\text{Pb}$) EM1 (Enriched Mantle 1) and EM2 (Enriched mantle 2). In addition to these reservoirs, importance of reservoirs whose isotopic compositions are common and intermediate has been pointed out, such as, FOZO (Focal Zone, Hart et al., 1992) and PREMA (Prevalent Mantle, Zindler and Hart, 1986). Although these intermediate reservoirs have been used to describe the isotopic distribution of OIBs, existences of the intermediate reservoirs, themselves, are still in debate. Therefore, elucidating the origin of the intermediate reservoirs should be also important from the perspective of production of mantle heterogeneity (e.g., Hofmann, 1997; Stracke et al. 2005; Stracke, 2012).

To elucidate the origin of mantle reservoirs, geochemical modeling has been conducted, in which origin of HIMU, FOZO and PREMA is discussed. The results suggest that MORBs with high frequency (common MORBs) without significant chemical modification during subduction have chemical composition that is suitable for producing PREMA. It suggests the importance of recycling of dry MORBs for the production of OIBs source. Dehydration of common MORBs in subduction zones can produce FOZO isotopic signatures if amount of dehydrated water is close to the maximum amount (4 %) of dehydrated aqueous fluid in subduction zones. Thus, FOZO-PREMA isotopic array can be explained by recycling of common MORBs that release various amount of aqueous fluid during subduction. For the production of HIMU, additional dehydration (~2%) at high pressure is required. As high pressure dehydration release supercritical fluid with relatively high U/Pb and low Th/Pb ratios, chemical fractionation during dehydration is different from the sub-arc process. This difference can explain isotopic difference between HIMU and FOZO.

Keywords: HIMU, FOZO, PREMA, MORBs, OIBs

Ocean Basalt Simulator version 1 : Trace element mass balance in adiabatic melting of a pyroxenite-bearing peridotite

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We present a new numerical trace element mass balance model for adiabatic melting of a pyroxenite-bearing peridotite for estimating mantle potential temperature, depth of melting column, and pyroxenite fraction in the source mantle for a primary ocean basalt/picrite. The Ocean Basalt Simulator version 1 (OBS1) uses a thermodynamic model of adiabatic melting of a pyroxenite-bearing peridotite with experimentally/thermodynamically parameterized liquidus/solidus intervals and source mineralogy. OBS1 can be used to calculate a sequence of adiabatic melting with two melting models, including (1) melting of peridotite and pyroxenite sources with simple mixing of their fractional melts (melt-melt mixing model), and (2) pyroxenite melting, melt metasomatism in the host peridotite, and melting of the metasomatized peridotite (source-metasomatism model). OBS1 can be used to explore (1) the fractions of peridotite and pyroxenite, (2) mantle potential temperature, (3) pressure of termination of melting, (4) degree of melting, and (5) residual mode of the sources. In order to constrain these parameters, the model calculates a mass balance for 26 incompatible trace elements in the sources and in the generated basalt/picrite. OBS1 is coded in an Excel spreadsheet and runs with VBA macros. Using OBS1, we examine the source compositions and conditions of the mid-oceanic ridge basalts, Loihi/Koolau basalts in the Hawaiian hotspot, and Jurassic Shatsky Rise and Mikabu oceanic plateau basalts and picrites. The OBS1 model shows the physical conditions, chemical mass balance, and amount of pyroxenite in the source peridotite, which are keys to global mantle recycling.

Keywords: Peridotite, Pyroxenite, Adiabatic melting, Trace element, Mass balance

Geochemical Composition of Dykes along the Cameroon Volcanic Line (CVL): Constraints on CVL magmatism and tectonism

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Mafic dykes along the Cameroon Volcanic Line (CVL) align in a general N 30° - N 70° direction. These alignments are consistent with the tectonic lineaments and the orientation of the CVL, indicative of a time and space relationship between the dykes and CVL lavas with the tectonic activities of the African plate. However, sub-alkaline volcanic rocks studied in some areas along the CVL are thought to be older than and not related to the CVL magmatism. Mafic dykes outcrop in the Oku Volcanic Group (OVG) but have not been studied. The aim of this study is to 1) characterize volcanic dykes in the OVG and Mt. Bambouto, 2) constrain the geochemical relationship between the dykes and CVL alkaline lavas, and 3) establish a tectonic history of emplacement of these dykes. Three dykes in the OVG and two along the Dschang-Santcho escarpment (flank of Mt. Bambouto) were systematically studied. An alkaline dyke is observed intruding a sub-alkaline dyke for the first time along the CVL, indicating a time and space relation between the two series. The dykes are weathered and show chemical evidence of crustal contamination. Contamination of less than 20 % for the alkaline dykes (BD2 and BDS alkaline) and 30 - 40% (BDS sub alkaline, BD3 and DS), can explain the varying degrees of crustal signatures in the samples. Geochemical characteristics suggest that the Batibo alkaline intrusions and the sub-alkaline intrusions were derived from a similar mantle source with OVG lavas. These characteristics are similar to those of the CVL alkaline lavas and OIBs. However, the differences in elemental concentrations and isotope composition of the sub alkaline dykes and the alkaline dykes in the OVG can be ascribed to varying degrees of weathering, assimilation of crustal components and different degrees of partial melting. The Low MgO, Ni, Cr, and V in the Batibo alkaline intrusion are due to the rapid rate of chemical weathering of olivine. The dykes in this study are related to the CVL magmatism in space and time. Fractures cutting through the basement rocks, but not the dykes suggest that the dykes are younger than the tectonic activities. The Sub-alkaline intrusion that is also intruded by the alkaline dyke in the BDS is older (43 - 422 Ma). This indicates that its emplacement was earlier than the surface expression of the alkaline CVL magmatism in the Tertiary (<31 Ma).

Keywords: Oku volcanic group, Dykes, Crustal contamination, Cameroon Volcanic Line, Magmatism, Tectonism

The Hf isotope evolution of the bulk silicate Earth: Evidence from meteorite zircon

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The ^{176}Lu - ^{176}Hf radioactive decay system has been widely used to constrain the timescales and mechanisms of Earth's crust-mantle differentiation, but the interpretation of Lu-Hf isotope data requires an accurate estimation of Hf isotope evolution of the bulk silicate Earth (BSE). Because both Lu and Hf are refractory and lithophile, the isotope evolution can be potentially reconstructed from the present-day $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ in undifferentiated chondrite meteorites. Unfortunately, however, these ratios in chondrites are highly variable due to the metamorphic re-distribution of Lu and Hf, making it difficult to ascertain the correct reference values for the BSE. In addition, it has been proposed that chondrites contain excess ^{176}Hf due to the accelerated decay of ^{176}Lu resulting from photoexcitation to a short-lived isomer in the early Solar System. If so, the paradigm of a chondritic BSE would no longer be valid for the Lu-Hf system. Herein we report the first high-precision Lu-Hf isotope analysis of meteorite zircon, a mineral that is resistant to metamorphism and has low Lu/Hf. The analyzed zircon grains were extracted from the non-cumulate eucrite Agoult. Based on the zircon Lu-Hf isotope data as well as the Agoult whole-rock Lu isotope data, we determine the initial $^{176}\text{Hf}/^{177}\text{Hf}$ of the Solar System to be 0.279791 ± 0.000018 . Reconciling the Solar System initial $^{176}\text{Hf}/^{177}\text{Hf}$ value with Lu-Hf isotope systematics of chondrites indicates a constant decay rate of ^{176}Lu throughout the history of the Solar System, thereby removing the requirement for a non-chondritic BSE. We further use the initial value to identify chondrites that preserve the primary Lu-Hf signatures and, therefore, are the best representative of the BSE. Our newly established Lu-Hf parameters for the BSE ($^{176}\text{Hf}/^{177}\text{Hf} = 0.282793 \pm 0.000011$; $^{176}\text{Lu}/^{177}\text{Hf} = 0.0338 \pm 0.0001$) strengthen the evidence that the most primitive Hf in terrestrial zircon reflects the development of a chemically enriched silicate reservoir on Earth as early as 4.5 billion years ago on Earth.

Keywords: bulk silicate Earth, zircon, hafnium isotopes, crust-mantle differentiation, eucrite, early solar system

Partitioning behavior of elements between metal and sulfide melt

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The partitioning behavior of elements between solid and liquid metal is key information to resolving the evolution of metallic core of the terrestrial planets. In the case of silicate mineral-melt system, it is well known that partition coefficients closely relate to size of cation and crystal structure. Thus similar size dependences in partition coefficients were also considered in metallic systems. For example, Van Orman et al. (2008) measured partition coefficient of Re, Os and Pt in Fe-S system under high pressure, and proposed that partition coefficients of these elements are fitted by Lattice Strain Model (Blundy & Wood, 1994) when they are plotted against atomic radius. Stewart et al. (2009) proposed that partitioning behaviors in metallic system can be explained by Lattice Strain Model when Neutral Atom Radius (Clementi et al. 1967) is adopted. However, it seems very strange that maximum of partition coefficient is found in Os, whose size is considerably larger than that of iron, which constructs the fundamental framework of crystal structure. In these metallic systems, it is well known that partition coefficient strongly depend on light element contents (sulfur, phosphorus or carbon) of metallic liquid. Therefore, we have to carefully consider the chemical affinity of elements to find the systematics in partitioning behaviors. In this study, we performed melting experiments of FeNi-S system under high pressure in various sulfur contents, and examined the systematic change in partitioning behaviors.

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 LA-ICP-MS installed at Kyoto University.

The observed partition coefficients in the present experiments were generally in agreement with the previous works, and indicating strong dependences to sulfur content in liquid phase. When we accept that partition coefficients are mainly controlled by chemical affinity of elements, then size dependence of partition coefficients must be found in sulfur free system, which includes no chemical affinity effects on partition coefficients. Although we have no data for such pure metallic system, partitioning behavior in the pure metal system can be predicted from the observed sulfur dependence in partitioning behaviors. It was found that the differences in partition coefficients between elements become smaller with sulfur content of liquid phase decreases. This means that partition coefficients in pure metal system may show similar values, even if in large sized elements, such as Au or W.

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Keywords: element partitioning, metal, sulfide, high pressure

Single shot laser ablation-multiple collection-ICP-mass spectrometry for U-Pb age

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Combination of laser ablation sample introduction technique and ICP-mass spectrometry (LA-ICPMS) has been widely used for element and isotopic analyses for solid samples¹⁾. One of the great advantages of LA-ICPMS is high quantitative capability achieved by the "post ionization" configuration. With the post ionization, ionization and atomization of the analytes in the plasma source will be independently carried out, and therefore, the optimization of the operational conditions for both the sampling and ionization can be made. This suggests that the hard ionization can be carried out even under the "soft" laser sampling. One of the major source of the analytical error is an elemental fractionation during the laser ablation (down-hole fractionation)²⁾. In fact, the measured Pb/U ratio can change with time when the larger ablation was made with ablation spots of higher aspect ratios³⁾. To overcome this, we have tried to measure U-Pb ages from the ablation spots of smaller aspect ratio (i.e., shallower pit).

The shallower ablation pit could be obtained when a smaller number of laser shots were adopted. To achieve this, a multiple collector-ICPMS was adopted to the U-Pb age determinations. With the multiple collector system, precision in the isotope ratio measurements can be improved even from the transient signals produced by the smaller number of laser shots. Hence, six isotopes were monitored by the six independent multipliers ; ²⁰²Hg (IC), ²⁰⁴Pb (IC), ²⁰⁶Pb (IC), ²⁰⁷Pb (IC), ²⁰⁸Pb (IC), ²³²Th (F) and ²³⁵U or ²³⁸U (IC).

Three natural zircons (OD-3⁴⁾, Plesovice⁵⁾ and GJ-1⁶⁾) were employed to evaluate the reliability of the resulting U-Pb ages. Nancy 91500⁷⁾ zircon was used as a calibration standard for the Pb/U ratio measurements. The glass standard (NIST SRM 610) was used for the calibration in the ²⁰⁷Pb/²⁰⁶Pb isotope ratio measurements. Laser ablation system used in this study was a New Wave Research femto laser ablation system (Fremont, CA 94538, USA), and the ICPMS instrument used in this study was a Nu Instruments (Wrexham, UK) Nu Plasma II multi-collector ICPMS. For comparison, U-Pb ages were also measured by the single collector-ICPMS instrument (Nu Instruments AttoM). In our presentation, we will demonstrate the high analytical capability of the MC-ICPMS technique from the single shot laser sampling.

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Keywords: LA-MC-ICPMS, U-Pb age, zircon, single shot, elemental fractionation, aspect ratio

Isotope analysis of ng-sized Nd samples: toward the isotopic analysis of foraminifera extracted from deep-sea sediments

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Modern seawater has heterogeneous Nd isotopic compositions. The source rocks of Nd in the ocean, continental rocks and igneous rocks derived from the mantle, show wide range of variation in their radiogenic ¹⁴³Nd/¹⁴⁴Nd ratios (~5 permil). The short residence time of Nd in the ocean (300-500 yr: Tachikawa et al., 2003; Amakawa et al., 20004; Arouze et al., 2009) compared with the ocean mixing timescale of 1500 yr (Broecker and Peng, 1982) prevents the homogenization of seawater Nd isotopic compositions. The Nd isotopic variation of the seawater has been used to distinguish different water masses, to trace the ocean circulation and to estimate the flow rate and contribution of Nd from various sources (ca. Piepgras and Wassurburg, 1980; Amakawa et al., 2013).

Calcareous shells of foraminifera are now drawing attention as a proxy of seawater Nd in the past, which can be used to trace the changes of the oceanic Nd isotopic composition related with paleoclimate changes (Tachikawa et al., 2014). One of the difficulties in analyzing Nd isotopic composition of foraminifera comes from the low Nd concentration of the foraminiferal shells. The low Nd concentration (up to several ppm) of foraminiferal shells requires quite large sample sizes (several mg) to meet the minimum sample size required for Nd isotope analysis (Nd amount of 2-5 ng). Lowering the sample size limits for Nd isotope analysis may expand the applicability of the technique to foraminifera-poor sediments derived from oceanic drilling sites.

We have developed a new technique to measure isotope ratios of ng to sub-ng sized Nd samples using total evaporation normalization method (Wakaki et al., 2007) together with the low-blank Nd separation chemistry. Isotope ratios of Nd are measured using thermal ionization mass spectrometer (Thermo TRITON) at Kochi Core Center.

The ¹⁴³Nd/¹⁴⁴Nd values of the isotopic reference reagent JNdi-1, measured at sample sizes of 0.5, 1 and 2 ng of Nd, all agreed with the values obtained by large sample measurement (100 ng of Nd) within statistical errors. The reproducibility of ¹⁴³Nd/¹⁴⁴Nd values are 100 ppm (n = 8), 60 ppm (n = 9) and 40 (n = 8) ppm for 0.5, 1 and 2 ng measurements, respectively. The precision and accuracy of the sample analysis, including chemical procedure, is checked by analyses of two GSJ reference rocks, JB-2 (basalt) and JCp-1 (coral). The basalt sample was decomposed by mixed HF-HNO₃-HClO₄, and the coral sample was decomposed by HNO₃. Sample aliquots, containing 0.5 and 1.2 ng of Nd, respectively, were processed by using the low-blank Nd separation chemistry. The measured ¹⁴³Nd/¹⁴⁴Nd ratios of JB-2 (n = 9) and JCp-1 (n = 8) samples all agreed with the values obtained by measurements with large sample sizes within statistical errors. These results demonstrate that our technique gives reliable results even for samples as small as 0.5 ng of Nd. Preliminary results of subsurface-dwelling planktonic foraminifera samples, *Globorotalia tumida*, collected from a Quaternary sediment core from the West Caroline Basin (western equatorial Pacific Ocean) will be presented.

Keywords: paleoclimate, Nd isotopes, foraminifera

Origin of Bowers Ridge and its Oligocene arc magmatism: Results from the IODP Expedition 323, Hole U1342

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The Bowers Ridge is an 800 km-long arcuate aseismic ridge extending northward from the Central Aleutian Ridge. IODP Expedition 323 drilled a total of 41.54 m of igneous basement at site U1342 in the northwestern Bowers Ridge, where an 800 m-deep wave-eroded platform exist. The recovered basement, composed of andesitic lavas and basaltic to andesitic volcanoclastic rocks (Kawabata et al., 2011), provide an opportunity to explore temporal change in magma composition at Bowers Ridge just before the cessation of arc magmatism in the Oligocene.

The recovered volcanic samples yield 26-34 Ma ⁴⁰Ar-³⁹Ar ages (Sato et al., 2015) and have arc signature characterized by depletion of HFSE and enrichment of LILE on the multi-element diagrams normalized to NMORB. The trace element features, with the presence of anorthitic plagioclase phenocrysts (An₉₃), confirm the arc-origin of the ridge that was deduced from dredge samples around Site U1342 (Cooper et al. 1987; Wanke et al., 2012). In arc magmatism, flux from subducted oceanic crust played an important role as suggested by high Ce/Pb and unradiogenic ²⁰⁶Pb/²⁰⁴Pb.

Temporal change of magma chemistry was examined from both the core and reported dredge samples. Lower units of core samples exhibit low to middle-K series, whereas both the upper units of core and dredge samples show middle to high-K series. In addition, the dredge samples are more enriched in LREE, Rb, and Ba, and show higher (LREE, MREE)/HREE ratios than the core samples. The dredge basalts and andesites fall within the adakite field on the discrimination diagrams of Sr/Y vs Y and La/Yb vs Yb (Wanke et al., 2012), whereas all the core samples are non-adakitic basalts and andesites. These geochemical results suggest that the difference in magma compositions between the core and dredge samples could mainly reflect the difference in the amount of slab-derived flux and/or the flux compositions. In this context, the inferred slab melting event (Wanke et al., 2012) may not be a unique scenario for producing the adakitic dredge basalts and andesites. Larger amount of slab-derived flux and higher melting pressure can also explain the change in magma compositions from the non-adakitic core samples to the adakitic dredge samples. Thus, more careful examination is required to determine whether or not the already inferred extraordinary high geothermal gradient is essential for the Oligocene magmatism at the Bowers Ridge.

Keywords: adakite, Bowers Ridge, remnant arc

Fluorine content reveals new insight into arc magmatism of Southern Volcanic Zone, Chile.

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The halogen elements have high partition coefficients in aqueous fluid (Bureau et al., 2000), but the difference in their partition coefficients for aqueous fluid/silicate melt/silicate minerals/organic matter results in distinct elemental ratios in seawater, pore fluid, sediment, oceanic crust and mantle (e.g., Johnson et al., 2000; Burgess et al., 2002; Palme and O'Neil, 2004). For instance, fluorine is incorporated into apatite, amphibole and phengite (Svensen et al., 2001) while iodine has a high abundance in organic-rich marine sediments because it is an essential element for life. These characteristics make halogens useful to trace water cycling in subduction zones (e.g., Fehn et al., 2003; Muramatsu et al., 2007; Sumino et al., 2010). Recently, subduction of marine pore fluid into the mantle has been suggested based on noble gas isotopes in the mantle (Holland and Ballentine, 2006) and halogen compositions of exhumed mantle wedge peridotites (Sumino et al., 2010). However, only a little is known about the behavior of halogen elements during subduction processes and their fate in the earth's mantle. Therefore, we newly analyzed halogen concentrations in regional representative lavas obtained from 13 volcanoes on the Quaternary volcanic front of the Southern Volcanic Zone (SVZ) of Andean arc in Chile. In this presentation, we focus on fluorine content that has least influence of degassing on volcanism.

Fluorine contents of most analyzed samples are 100-300 ppm. To understand behavior of fluorine on fractional crystallization, the correlations of SiO₂ and FeO*/MgO with fluorine data from a volcano are plotted. This result indicates that the fluorine dependency with these parameters changes at SiO₂ = 55 wt% and FeO*/MgO = 4.2, resulting from apatite crystallization and removal from the magma. Thus, the evolved rock samples from which apatite crystallized were excluded from further discussion.

We compared fluorine with major and trace element data obtained by previous study (Shinjo et al., 2013) and newly revealed that the fluorine concentrations of selected samples were not correlated with boron concentrations. This means that fluorine shows different behavior in the subduction zone magmatism though both fluorine and boron are fluid-mobile elements. The basaltic samples from Hudson, the southernmost volcano of SVZ, show very high fluorine concentration (~1000 ppm). Similar anomalies were confirmed also with Nb and Ta. The chemical characteristics suggest that the magma source of this region has been derived from the metasomatized mantle wedge by influence of slab-derived melt (Kilian and Behrmann 2003; Shinjo et al., 2013). The fluorine concentration possibly becomes new sensitive detector of slab-derived melt in arc volcanism.

Keywords: fluorine, subduction zone, slab melt, slab fluid

Volatile components of apatite grains from pyroclastic flow deposits of Aso volcano

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Water in the Earth is important for life and mantle dynamics. The amount of water in the interior of the early Earth and chondrites is one of the most essential constraints for revealing the origin of the Earth's water. An important clue to the water budget in the early Earth is apatite grains in chondrites and in -4.4 Ga zircon from Jack Hills in Australia. Since apatite has volatile components, it is expected to determine the amount of water in chondrites and the interior of the early Earth from OH composition of the apatite. However, partitioning and exchanging of volatile components, especially water, between apatite and melt has been unclear. Mathez and Webster (2002) and Webster et al. (2009) tried to reveal partitioning of F and Cl between apatite, melt, and fluid with high-temperature and high-pressure experiments, but they did not discuss the exchange relationship in volatile components' site (X site) in apatite. Pan and Fleet (2002) suggests that volatile components in apatite should be affected by other cation components. Accordingly, the goal of this study is to reveal the relationship of volatile components between apatite and melt, including revealing the exchange relationship in volatile components' site in apatite and other components which affect on it.

We analyzed volatile compositions of apatite grains and melt inclusions in plagioclase phenocrysts from pyroclastic flow deposits of Aso volcano with EPMA and nano-SIMS. We analyzed 4 samples, rhyolitic and andesitic of Aso-3 and Aso-4. EPMA and nano-SIMS analysis revealed that F concentrations in apatite in each sample show large variations while Cl concentrations are constant, suggesting that F and OH substitute for each other in the X site. OH concentration in apatite of mafic sample was larger than that of silicic one.

We find that F and Cl in apatite and these in melt inclusion have no correlation, while OH in apatite and water in host magma, which is estimated from temperature, pressure, the composition of plagioclase, and so on (Kaneko et al., 2007), have a positive correlation. We also find that the amount of OH and that of CaO, P₂O₅ and MgO in apatite have positive correlations, therefore Ca, P, and Mg could affect on the behavior of F and/or OH. Additionally, Number of cations in M site (assuming oxygen number = 13) was 4.66-4.88, which is smaller than expected from stoichiometry, suggesting that other components, such as rare earth elements, would be present in M site.

Keywords: apatite, volatile component, water

Garnet-amphibole fractionation generating basalt to dacite magmas of Pre-Komitake volcano, Japan

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The Pre-Komitake volcano, which was discovered by scientific drilling into Mt. Fuji, is an older volcanic body than Fuji and Komitake volcanoes buried beneath the NE flank of Fuji volcano (Nakada et al., 2004; Yoshimoto et al., 2010). The Fuji, Komitake, and Pre-Komitake volcanoes are situated in a complex tectonic setting near the junction of three plates: the North American Plate in the east, the Eurasian Plate in the west, and the Philippine Sea Plate in the south, under two of which the Pacific Plate subducts from east to west. The magmas of Pre-Komitake are different from those of Fuji and Komitake (Yoshimoto et al., 2010). According to Yoshimoto et al. (2010), the Pre-Komitake lavas are characterized by hornblende-bearing andesites and dacites, in contrast to the hornblende-free basaltic rocks of Fuji and Komitake. These authors also suggested that the concentrations of incompatible elements increase with increasing SiO₂ in the magmas of Pre-Komitake, whereas those of Fuji increase despite SiO₂ remaining fairly constant (Fujii, 2007). They suggested that the variations in magma chemistry in this area between 250 ka and recent times might have occurred as a result of a change in regional tectonics that occurred ~150 ka, although this remains unproven. To our knowledge, no detailed research has yet been carried out into Pre-Komitake magma genesis on the basis of comprehensive major and trace elements, and isotopic compositional data sets. Therefore, we analyzed the trace element and Sr-Nd isotopic compositions of the Pre-Komitake magmas in order to better understand their genesis.

The Sr and Nd isotope ratios ranged from 0.703320±0.703476, and 0.512885±0.513087, respectively, which are very similar to those of the lavas from Fuji and Komitake volcanoes (Nagai et al., 2004) that erupted subsequently. Enrichment of large ion lithophile elements, Pb and Sr, can be seen in the primitive mantle-normalized multi-element diagram of the Pre-Komitake, Komitake, and Fuji lavas. These collectively show island arc lava signatures, however, the middle to heavy rare earth elements are more depleted in the Pre-Komitake lavas, compared to those from Fuji. Positive Eu anomalies are observed, although the extents of these anomalies decrease with increasing SiO₂ in the Pre-Komitake lavas, whereas this is not observed in Fuji lavas. The Sr/Y ratios of Pre-Komitake lavas increase from basalt to basaltic andesite, but decreases through andesite to dacite. This occurs in combination with a rapid increase in La/Yb ratios, followed by a more gradual increase. A gradual decrease in Dy/Yb ratios is also seen over the entire compositional range. These data suggest deep (>12 kbar) fractionation of garnet and amphibole followed by shallow (i.e., ~5 kbar) fractionation of amphibole and plagioclase. Such variations are not observed in the Komitake and Fuji lavas, for which deep fractionation of clinopyroxene and shallow fractionation of plagioclase have been suggested. All three lavas, including those from the Pre-Komitake volcano, show similar isotopic, major, and trace element compositions in the unfractionated basalts. The differing geochemical trends found in the Pre-Komitake lavas are likely to be due to different mineral fractionations occurring in the hydrous Pre-Komitake basalts compared to the dry Fuji and Komitake basalts.

Keywords: Pre-Komitake volcano, Fuji volcano, Trace elements, Sr-Nd isotope ratios, Garnet fractionation

Partition of the platinum group elements between Cr spinels and whole rocks in boninites from Ogasawara islands

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Abundance of the platinum group elements (PGEs) in volcanic rocks are expected to have some information about source mantle or magma genesis as other elements. Sulfides and Cr spinel are known to important host of PGEs, for example, enrichment of PGEs are reported in chromitites from layered intrusions, ophiolites and alpine-type peridotites (Ahmed and Arai, 2002, Buchl et al., 2004). Among volcanic rocks, however, Cr spinel can be observed in mafic-ultramafic magmas as komatiite and boninite. The correlation between whole rock Cr and PGEs in magmatic rocks are observed (Hamlyn et al., 1985), whether PGEs status in Cr spinels unresolved. Experimental studies on partitioning of PGEs between spinels and silicate melts are reported and showed significant amounts of IPGEs (Iridium-group PGE; Ru, Os, Ir) can be held in solid solution in spinel species as Cr spinels with high partition coefficient under oxidized conditions ($fO_2 > QFM + 2$). In empirical studies, the partitioning of Rh, Ru and Ir into Cr spinels increases with increasing oxygen fugacity are shown in komatiites by Jung-Woo et al. (2012). Here newly PGE data of Cr spinels and whole rocks from boninites Ogasawara and Guam islands are shown and have a discussion about PGE partitioning in boninite and tholeiite magma.

Keywords: platinum group element, boninite, partition

Determining the deep crustal composition of Japan island arc using xenoliths

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Understanding the composition of the continental crust is central for deciphering its evolutionary history. The composition of the deep continental crust has been inferred by combining seismic data and chemical data for metamorphic rocks and xenoliths. Seismic wave speed reflects the density of the underground which is governed by the major elements. Thus, seismic data provide insights into the structure and major element composition of the continental crust, but no constraints on the trace element composition. By contrast, analyses of metamorphic rocks and xenoliths are the best methods to measure the major and trace elements of the deep continental crust, but the occurrence of these rocks is restricted.

So far, the deep crustal composition has been extensively investigated for continental regions, but that for island arc remains poorly constrained. Because seismic data show differences in the thickness and the major element composition between continental shields and island arcs, it is important to independently determine the deep crustal compositions of island arcs. For this purpose, we have analyzed ca. 100 xenolith samples from Ichinomegata in Akita and Takashima in Saga for the major and trace element abundances.

The major element concentrations were measured by XRF, whereas the trace element concentrations were measured by LA-ICPMS.

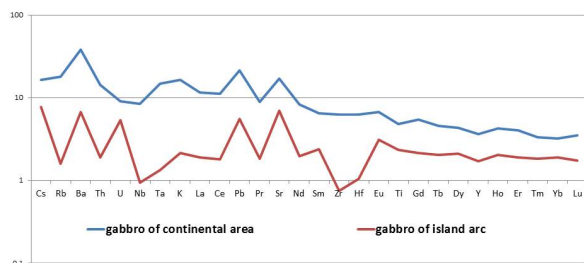
The major element measurements revealed that the analyzed xenoliths from Ichinomegata have compositions ranging from ultramafic to intermediate, whereas those from Takashima are ultramafic to felsic. The trace element data for the Ichinomegata and Takashima mafic xenoliths indicate that these rocks are depleted in high field strength elements (HFSE) such as Nb, Ta, Zr, Hf, and enriched in large ion lithophile elements including Pb. The observed geochemical features are well explained by the generation of the lower crust of Japan island arc by fluid-related partial melting of the mantle wedge. When the data for the Japanese mafic xenolith samples are compared with those for the average lower (mafic) continental crust that is mainly based on analyses of metamorphic rocks and xenoliths from continental regions (Fig. 1), it is evident that the Japanese xenolith samples are less enriched in most incompatible elements, despite their similar SiO₂ contents to the average lower continental crust. In addition, the relative depletion in the Japanese samples is more relevant for HFSE. These findings may indicate a higher degree of mantle partial melting due to more efficient fluid supply in Japanese subduction zones relative to settings where most lower continental crusts were generated. Notably, the Japanese mafic xenolith samples have similar U contents to that of the average lower continental crust. It is well known that U behaves as a fluid-mobile element under oxidative conditions, but as a fluid-immobile element under reducing conditions. Also, it has been indicated that about 2.2 Ga, the Earth's surface changed from reducing to oxidative environments. Taking these into account, the agreement in U contents together with different contents in other most incompatible elements can be interpreted as reflecting that the significant part of the lower continental crust was formed when the Earth's surface was under reduced conditions and, therefore, U behaved as a fluid-immobile element during dehydration processes. We found that among the analyzed xenolith samples in this study, major and trace element abundances are weakly correlated. Although we need to investigate more xenolith samples from various areas to verify this inference, such correlation would be useful to combine seismic data and chemical data for rock samples to develop a model of the deep crustal composition of Japan island arc.

Keywords: Xenolith, Ichinomegata, Takashima, Neutrino, island arc, crustal composition

SGC50-13

Room:102A

Time:May 25 17:30-17:45



Genesis of carbonatite melt by partial melting of COH-bearing peridotite

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On the Earth's surface, nutrients are one of the most important factors to hosting life.

The nutrients (C,O,N,P...) have to be supplied sustainably and enough. Carbon, oxygen and nitrogen can be supplied from the atmosphere, but phosphorus must be supplied from the interior of the Earth.

A potential source of phosphorus will be carbonatites, because carbonatites have the highest phosphorous concentrations among igneous rocks on the Earth. The genesis of carbonatites will be a key to understand possible mechanism for supplying phosphorus from the interior to the surface of the Earth.

The most popular theory for the origin of carbonatites is that carbonated silicate liquids generated by deep melting of carbonated mantle materials rises through the mantle and separates immiscibly into silicate melt and carbonatite melt. Veksler et al. (2011) experimentally investigated partitioning behavior of 42 elements between synthetic silicate melt and immiscible carbonate melt. They suggest that phosphorus concentrated to carbonate melt under hydrous conditions much more than under anhydrous conditions. Brooker (1998) experimentally determined the maximum extent of the silicate-carbonate immiscible field in a multicomponent system, and found that under CO₂-saturated condition the silicate-carbonate immiscible field is wider than under CO₂ undersaturated condition, leading more concentration of phosphorus to carbonate melt. However, it is still unclear whether immiscible separation of silicate and carbonate melt will occur within mantle-derived melt.

In this study, we performed high-pressure melting experiments on primitive mantle + CO₂ + H₂O in order to examine the possibility of liquid immiscibility in mantle-derived melt and the behavior of phosphorus between those melts.

We packed synthetic KLB-1 peridotite with ~10wt% oxalic acid dehydrate within a Au-Pd capsule, and performed melting experiment at 2.5GPa and 1100 °C for 26 hours using an end-loaded piston cylinder apparatus. The run product contains MgO-rich, SiO₂-poor partial melt.

The composition of the melt is not plotted within the silicate-carbonate immiscibility field in the (SiO₂+Al₂O₃+TiO₂)-(Na₂O+K₂O)-(CaO+MgO+FeO) pseudoternary system of Brooker (1998), so it is not likely that the melt itself will separate immiscibly into silicate and carbonate melts during ascending in the mantle. However, crystal fractionation of olivine in the melt will lead the composition more alkali rich, which may cause immiscible separation into silicate and carbonate melts.

It is possible to produce carbonatite melt from mantle-derived melt. A further study should be conducted on what conditions are needed to generate immiscible carbonatite melt on the early Earth.

Keywords: phosphorus, carbonatites, partial melting, liquid immiscibility, the early Earth

Determination of precise age corrected Sr-Nd-Pb-Hf isotope ratios of the clinopyroxene from Raivave OIB samples

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In Sr-Nd-Pb-Hf isotope analyses of whole rock samples, the leaching technique is used for removing the effect of secondary alteration and contamination from outside environments. Especially for the rock samples collected from sea area, the leaching is indispensable to eliminate the effect of seawater alteration. However, even if the strong leaching condition is applied, it is difficult to remove the altered components completely. In order to overcome this problem, clinopyroxene (CPX) was paid attention because of its early crystallization phase and its high resistibility against alteration. It is expected that the CPX preserve more primitive isotope signature than the leached whole rock samples. Using the CPX sample from ocean island basalt (OIB), Hanyu and Nakamura (2000) and Jackson et al. (2009) revealed the Sr and Nd isotope signature of OIB source mantle. Hanyu et al. (2011; 2014) also analyzed Sr and Nd isotopes as well as Pb and Hf isotopes of CPX to investigate the mantle end-members in the OIB samples from Polynesia and St. Helena.

Parent/daughter (P/D) ratios such as Rb/Sr, Sm/Nd, U/Pb, Th/Pb, and Lu/Hf were used for determining the age-corrected isotope ratios (initial ratios) of Sr, Nd, Pb, and Hf isotopes. The most suitable method for correction is using P/D ratios determined from the same CPX aliquot used for each of the isotope measurements. However, due to the limitation of the decomposition method used for the Pb isotope analysis in our laboratory, there was difficulty in determining the U/Pb and Th/Pb ratios from the CPX aliquot used for the Pb isotope. Therefore, Hanyu et al. (2011) determined the U/Pb and Th/Pb ratios from the whole rock U, Th, and Pb concentrations and partition coefficients, although the Rb/Sr, Sm/Nd, and Lu/Hf ratios were determined from the same CPX aliquot used for the Sr, Nd, and Hf isotope analyses. To overcome the uncertainty using partition coefficients, Hanyu et al. (2014) determined the U/Pb and Th/Pb ratios using the U, Th, and Pb concentrations of the CPX aliquot used for the Sr, Nd, and Hf isotope measurements, although the uncertainty of inhomogeneity in the CPX separates still remained.

In this study, we reexamined our analytical method, especially for the determination of U/Pb and Th/Pb of the CPX separates. We determined the Rb/Sr, Sm/Nd, and Lu/Hf ratios from the CPX aliquot used for the Sr, Nd, and Hf isotope measurements (Sr-Nd-Hf aliquot) and the U/Pb and Th/Pb ratios from the CPX aliquot used for the Pb isotope measurement (Pb aliquot) to determine the precise age-corrected Sr-Nd-Pb-Hf isotope ratios of the CPX sample from the Raivavae OIB samples. Comparisons between the Sr-Nd-Hf and Pb aliquots showed inhomogeneity in the U, Th, and Pb concentrations and revealed 0.34 and 0.88 of $\Delta U/Pb$ and $\Delta Th/Pb$, in maximum. These $\Delta U/Pb$ and $\Delta Th/Pb$ yielded 1052, 61, and 448 ppm in the $\Delta^{206}Pb/^{204}Pb$, $\Delta^{207}Pb/^{204}Pb$, and $\Delta^{208}Pb/^{204}Pb$ when the age correction used was 6 Ma. These $\Delta^{206}Pb/^{204}Pb$ and $\Delta^{208}Pb/^{204}Pb$ were beyond the analytical uncertainty of the standard samples. Therefore, using P/D ratios determined from the same CPX aliquot used for each of the isotope measurements is an important factor for the determination of precise age-corrected Sr-Nd-Pb-Hf isotope ratios of the Raivavae CPX sample.

Keywords: Sr-Nd-Pb-Hf isotopes, CPX, Raivavae, Age correction, P/D ratio

Laser-ablation Sr isotopic analyses of small glass samples using MC-ICPMS

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An analytical protocol was developed for correcting Kr baseline-induced bias and Rb isobaric overlap factors to analyze Sr isotope ratios for small glass samples using laser ablation (LA) with a desolvating nebulizer dual-intake system and MC-ICP-MS. The combined use of a low-oxide interface setup along with high-gain Faraday amplifiers with a $10^{12} \Omega$ resistor enabled precise determination of Sr isotope ratios from 50-100 μm diameter craters using 10 Hz laser repetition rate. Residual analytical biases of $^{84}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios induced from Kr baseline suppressions (Kimura et al., 2013), were found to be nonlinear, but the correction method was applicable to 50-200 $\mu\text{m}/10$ Hz craters. We also found that the $^{85}\text{Rb}/^{87}\text{Rb}$ overlap correction factor changed with time with a change in the surface condition of sampler-skimmer cones. The correction factor of $^{85}\text{Rb}/^{87}\text{Rb}$ was thus determined at least once per five unknown measurements using the nebulizing intake line. We determined $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios from MkAn anorthite (Sr = 305 ppm, Rb = 0.07 ppm), BHVO-2G, KL2-G, ML3B-G (Sr = 312-396 ppm, Rb = 5.8-9.2 ppm), and BCR-2G (Sr = 337 ppm, Rb = 48.5 ppm) basalt glasses using a 50-100 $\mu\text{m}/10$ Hz crater. The results agree well with their reference values determined by thermal ionization mass spectrometry, even with the high Rb/Sr ratio (0.14) in the BCR-2G glass. The internal/intermediate precisions were ± 0.0002 (two-standard deviation: 2SD) for 100 μm craters and ± 0.0005 for 50 μm craters. The new instrument settings and analytical protocol improved the precision by a factor of two compared to the previous report using LA-(sector field)-ICP-MS and enables the analysis of sample volumes that are ten times smaller than those used in previous LA-MC-ICP-MS analyses with equal precision.

Keywords: Sr isotope, geological glasses, LA-MC-ICP-MS, Kr baseline-induced bias, Rb overlap correction