

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 diagrams 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, north-east

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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-hornblende 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