

Petrogenesis and magmatic process of the Ikoma gabbroic complex in Kinki district, southwest Japan

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The Ikoma gabbroic complex is one of the largest Cretaceous mafic pluton in SW Japan are exposed at Ikoma mountains, consisting of mafic rocks (the Ikoma gabbroic rocks) and intermediate to felsic rocks, the Fukihata tonalites and the Kyuanji quartz diorites. These rocks show two modes in whole-rock compositional relation, (1) as mafic rocks with SiO₂ <48wt.%, major oxide contents change widely for constant SiO₂ contents, and (2) as intermediate rocks with SiO₂ >48wt.%, major oxide contents show linear trends with respect to SiO₂ contents. On the compositional variation diagrams, plagioclase compositions included in mafic rocks is located to the end-member on the trend of mafic rocks. Moreover, some samples show cumulus structures and their plagioclase mode are shown by a positive trend with respect to the variation of CaO contents. It suggests that the Ikoma gabbroic rocks were associated with the accumulation and/or fractionation of plagioclase. On the other hand, whole-rock compositions of intermediate rocks vary linearly with increasing SiO₂ contents, and their ⁸⁷Sr/⁸⁷Sr initial ratios at 82 Ma show a positive trend with variation of SiO₂ contents. These characteristics suggest a mixing of mafic and felsic magmas. The mafic end-member is plagioclase-poor mafic rocks. Granitoids occurred at the same time of the activity of the Ikoma gabbroic complex are plotted on the extrapolation of the compositional trend of intermediate rocks, suggesting that the granitoids may be the felsic end-member in a magma mixing.

Keywords: Ryoke belt, mafic rock, magmatic process, geochemistry

Fe₂O₃/FeO ratios and K-Ar ages of the Tadamigawa granitic rocks, northeastern Japan

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The early Paleogene Tadamigawa granitic rocks are located around Hinoemata village in the southwestern part of Fukushima prefecture, northeastern Japan. The granites are divided into two rock types, the Tadamigawa granite and the Hinoematagawa granite. The Hinoematagawa granite is medium-grained biotite-hornblend granite. The Tadamigawa granite is coarse-grained biotite granite and it is characterized by the phenocryst of K-feldspar. On the field occurrence, the Tadamigawa granite intrudes into the Hinoematagawa granite. Because these granites are located at high-mountain area, precise field research has not been attempted. In this study, 7 samples of the Hinoematagawa granite and 34 samples of the Tadamigawa granite were analyzed for major, minor and REE compositions by XRF and ICP-MS, respectively. Moreover, we obtained K-Ar ages of biotite isolated from both granites, and Fe₂O₃/FeO ratios by titrimetry with potassium permanganate.

SiO₂ contents of the Hinoematagawa granite and the Tadamigawa granite range from 59.6 to 69.4 wt.% and from 62.8 to 74.6 wt.%, respectively. K-Ar ages of the Hinoematagawa granite and the Tadamigawa granite are 102.3 Ma and 102.7 Ma, respectively. These ages are much older than 67 Ma of the previous K-Ar age data obtained by Kawata and Ueda (1966). Both of granites may be formed at same time by Cretaceous igneous activity and generated from the same magma origin because they show similar trend on the Harker's diagram. Those granites are I type because almost all samples show low degree of alumina-saturation (A/CNK < 1.1). REE abundance patterns of all samples normalized by chondrite show high-LREE pattern. Many samples show negative Eu anomaly (Eu/Eu* = 0.24-1.01), 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 large Eu anomaly of the Tadamigawa granite shows much differentiation of the granitic magma. The anomaly is caused by the differentiation of anorthite in the Tadamigawa granite. The Hinoematagawa granite shows low Fe₂O₃/FeO ratio (0.28-0.39). It may be generated from the magma which has low oxygen fugacity.

Keywords: Fe₂O₃/FeO ratio, K-Ar age, REE, Granite, Tadamigawa, Hinoemata

Generation of TH and CA suite magmas at Chokai volcano in the NE Japan rear-arc

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The Quaternary Chokai volcano is located in the rear-arc side of the NE Japan arc. Chokai volcano is a typical stratovolcano and the eruption activities are classified into Stages 1, 2, and 3 (Hayashi, 1984; Ban *et al.*, 2001). Stage 1 lavas are olivine two-pyroxene basalt to two-pyroxene andesite, and the lavas contain phenocrystic minerals in equilibrium with the host magmas with occasional dusty plagioclase, which exhibits disequilibrium. An-contents (An%) of the plagioclase phenocryst cores show unimodal distribution, and An% decreases with increasing SiO₂ in the host lavas (An₉₀₋₈₀ for basalts, An₇₀₋₅₀ for andesites). Stage 2 lavas are mostly amphibole-bearing olivine two-pyroxene andesite with a small amount of olivine two-pyroxene basalt. Stage 3 lavas are olivine two-pyroxene andesite. Most of the plagioclase phenocrysts in the Stage 2 and 3 lavas possess dusty zones or sieve textures. An% in these plagioclase cores exhibits wide range (An₅₀₋₈₀). Bulk-rock compositions of the Chokai lavas plot near the boundary between high-K and medium-K. On the FeO*/MgO vs. SiO₂ diagram, the Stage 1 lavas fall on tholeiitic (TH), whereas the Stage 2 & 3 lavas fall on calc-alkaline (CA) fields. The Stage 2 & 3 lavas collectively show straight trend on MgO vs. SiO₂ plots and MgO content is higher than those in the Stage 1 lavas. Sr isotope compositions of the Stage 1 lavas gently increase with increasing SiO₂ (⁸⁷Sr/⁸⁶Sr = 0.70303 - 0.70341) contrasting to the steep increase shown by the Stage 2 & 3 lavas (0.70288 - 0.70342). The Stage 1 geochemical trends can simply be explained by fractional crystallization of a basalt magma with minor crustal assimilation. The Stage 2 & 3 trends can be generated by mixing between basaltic and felsic magmas. The Stage 1 parental basalt magma differs from the Stage 2 & 3 basalt mixing end-member, chemically and isotopically. The petrological and geochemical characteristics of the Chokai TH (Stage 1) and CA (Stage 2 & 3) suite magmas are similar to those in the Zao and Azuma TH and CA suite magmas found at the volcanic front of the NE Japan arc. Tatsumi *et al.* (2008) and Takahashi *et al.* (2012) have argued that the TH basalt with radiogenic Sr was formed by melting of the lower crustal amphibolite, whereas CA basalt with unradiogenic Sr was formed by magma mixing between a mantle derived-basalt and a felsic magma generated from the TH basalt by fractional crystallization. The same mechanism would explain the TH and CA suite magmas at Chokai. The Sr isotopic composition of the Stage 1 TH lavas overlaps with that of amphibolite xenoliths from lower crustal depth beneath Ichinomegata volcano (0.7032 to 0.7051; Yamamoto and Takeda, 2008). The geochemical features of the xenoliths and the TH basalt suggest that the Stage 1 TH basalt can be formed by melting of the amphibolite.

Keywords: rear-arc, tholeiitic series, calc-alkaline series, Sr isotope ratio

Estimation of fluxes at mid-ocean ridges and geochemical cycles on the Earth's surface of sulfur and halogens

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[Introduction]

Volatile elements on the Earth's surface have been accumulated by degassing from the solid Earth. Noble gases have been used as tracers to constrain the degassing history. Such studies suggested that the most part of the atmospheric argon had been accumulated in the early Earth [1], and estimated carbon and nitrogen cycles by comparisons with well determined helium-3 (³He) fluxes from the inside to the surface of the Earth [2, 3]. They constrain the evolutionary history of the Earth's surface. On the other hand, though sulfur (S) and halogens (fluorine (F) and chlorine (Cl)) form various compounds on the Earth's surface and significantly affect the environment, their geochemical cycles are not well understood. Fluxes of S and halogens at MORs (Mid-Ocean Ridges), where material migrations are dominant because of intensive volcanic activities, have been estimated based on compositions of quenched glassy rims of MORBs (Mid-Ocean Ridge Basalts) which retain those of magmas derived from the upper mantle. However, they may be overestimated [4], and plausible estimations based on compositions of both silicate melts and fractions released as hydrothermal fluids are needed. We determined compositions of hydrothermal fluid and melt components retained respectively in vesicles and solids of MORB glasses (Fig. 1) and estimated MOR fluxes of S and halogens to constrain the evolutionary history of the Earth's surface.

[Analyses]

We analyzed glasses of MORBs collected at 2 sites on the East Pacific Rise, 2 sites on the Mid-Atlantic Ridge and 2 sites on the Central Indian Ridge. After volatiles in vesicles were extracted using the frozen crushing method [5], concentrations of ³He were measured using a noble gas mass spectrometer (VG-5400) and those of S and halogens were measured using an ion chromatography (ICS-2100). Concentrations of S and halogens in solids were measured using a secondary ion mass spectrometer (NanoSIMS 50). We calculated relative molar ratios of S and halogens to ³He (S/³He, F/³He and Cl/³He) and estimated MOR fluxes of S and halogens calibrating against the known ³He flux (527 mol/yr [6]) [2, 3]. Using molar ratios, it is not necessary to discuss variations of volatile concentrations due to differences in porosities of each sample.

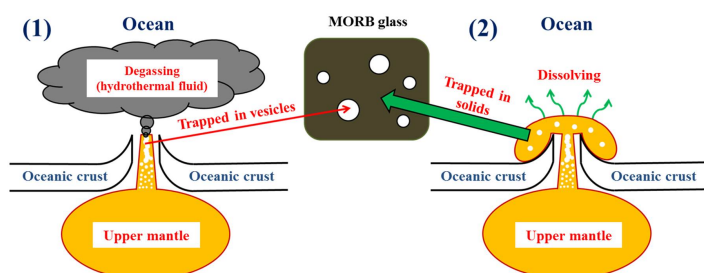
[Results and Discussion]

³He concentrations in vesicles were (1.8-6.3)×10⁻¹⁵ mol/g. Global averages of S/³He, F/³He and Cl/³He were calculated. For vesicle components, they are (4.2±1.6)×10⁷, (1.4±0.7)×10⁶ and (2.6±1.0)×10⁷, respectively. For bulk compositions, they are (0.3-1.2)×10¹⁰, (1.6-6.5)×10⁹ and (0.7-3.0)×10⁹, respectively. Using these ratios and the known ³He flux at MORs, MOR fluxes were estimated to be (2.2×10¹⁰-6.6×10¹²) mol/yr for S, (7.1×10⁸-3.4×10¹²) mol/yr for F and (1.4×10¹⁰-1.6×10¹²) mol/yr for Cl. Mass balances were discussed comparing MOR fluxes in this study with arc fluxes, influxes at subduction zones and rates of accretion to the continental crust. When we assume the continuous degassing with the low MOR fluxes estimated using vesicle (hydrothermal fluid) compositions, the amount of S accumulated on the Earth's surface are calculated to be 50 times lower than its surface inventory, and halogens are calculated not to be accumulated on the Earth's surface because of dominant influxes. This implies a possibility that significant amounts of chemically reactive volatile elements such as S and halogens were accumulated on the Earth's surface in the early Earth.

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Keywords: sulfur, halogen, helium, mid-ocean ridge basalt, flux, geochemical cycle



[Fig. 1. A schematic view of degassing processes at mid-ocean ridges]

(1) Bubbles connect each other and make paths in ascending magmas. Components fractionated into gaseous phases are released to the ocean.
⇒ MOR fluxes dominated by hydrothermal fluid (volcanic gas) components can be estimated based on compositions of vesicles in MORB glasses.

(2) Erupted silicate melts are altered and bulk components are released to the ocean.
⇒ MOR fluxes provided by intensive alteration processes of MORBs can be estimated based on bulk compositions of MORB glasses.

Experiments for development of new method for measurement of diffusion gas

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1) Introduction

Ascent of magma causes gasification of volatile components in magma, which provides the driving force for explosive eruption. Release of volatiles from magma highly changes its physical properties such as viscosity and density, and thus influences the violence of explosions. Examination of the behavior of volatiles can provide a better understanding of degassing processes and volcanic eruptions.

Carbon dioxide is major constituent of volatile in magma after water and less reactive with ground water and subsurface material after degassing. The emission rate of diffuse CO₂ can increase drastically prior to volcanic eruption (Hernandez et al., 2001). Hence, studies of diffuse CO₂ have become a powerful geochemical tool for monitoring volcanic activity (e.g. Hernandez et al., 2001; Perez et al., 2011). It is very important to map surface CO₂ efflux anomalies and to estimate the total output of this gas regularly in order to have a better understanding of on-going volcanic processes (Salazar et al., 2001). Measurement of diffuse soil CO₂ has been usually performed in-situ by means of a portable infrared absorption CO₂ analyzer (LICOR-800 system) interfacing to a palm-top computer that processes data. Actually, handling of LICOR-800 system is simple and easy, however, surveillance for spatial distribution by means of this system is time-consuming. In this study, some fundamental laboratory experiments were performed to develop a new chemical method for monitoring flux of diffuse soil CO₂.

2) Experiments

A vinyl chloride tube 20cm in diameter and 30cm in height is used for gas diffusion chamber. CO₂ gas diffuses through dry sand in the gas chamber. Small fan is equipped for convection of diffuse CO₂ in the chamber. A plastic box containing 5M KOH solution is within the chamber to absorb CO₂ in the chamber. Some experiments were performed parameterizing CO₂ gas flow rate, absorption time, surface area of the alkaline solution and so on.

3) Result and Discussion

Experimental results indicate that absorption for more than 2 hours can get the recovery efficiency of diffuse CO₂ gas reach around 1 although the flow rate of CO₂ is ten times higher than the diffusion rate at Kusatsu-Shirane and Usu volcanoes. Fan convection in the chamber has very positive impact for absorption of CO₂ in the alkaline solution. Further, flow rate of diffuse H₂S is estimatable through analysis of dissolved sulfur in the alkaline solution. This method newly enables to estimate diffuse CO₂ and H₂S flux in a short time, and monitor spatial distribution with high temporal resolution.

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Keywords: diffusion gas, chemical method

Effective pair potential for Ca-O bonds in CaGeO₃ perovskite, garnet, wollastonite

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The CaGeO₃ perovskite and garnet were synthesized in a cubic anvil type apparatus under high pressure. The measurements of Ca and Ge K-edge XAFS spectra were carried out in the transmission mode at temperature up to 700 K. The effective pair potentials $V(u)=au^2/2+bu^3/3!$, for Ca-O bond in various phases of CaGeO₃ have been investigated by the temperature dependence of EXAFS Debye-Waller factors. The potential coefficient a for the Ca-O bond in perovskite-type CaGeO₃ is small, 4.4 eV/Å², compared with those in garnet (6.0 eV/Å²) and wollastonite (6.4 eV/Å²). The potential for Ca-O bond in perovskite is broader than those in other CaGeO₃ polymorphs, which is one reason for the Clausius-Clapeyron's curve for perovskite-garnet phase boundary having a negative slope. The potential coefficients for the Ca-O in perovskite are significantly smaller than those for the longer Ge-Ge distances as the framework vibration though the potential coefficient decreases usually as a result of the larger bond distance.

Development of an ultra high precision stable isotopic analysis of Sr by DS-TIMS technique

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Stable isotope fractionation is a frequently used geochemical tool to trace geological and geochemical processes, to estimate the temperature of the process, to discriminate the geological source of the material and to constrain marine elemental budgets (e.g. Hoefs, 2004). Application of the stable isotope fractionation of heavy elements, such as Fe, Zn, Cu and Sr to geology or environmental science is limited compared with the "traditional" light gaseous elements, such as H, C, O and N. One of the reasons for this is that the analytical precision is not small enough compared with the typical isotopic variability among geological and environmental samples. For example, the typical analytical uncertainty of $\delta^{88}\text{Sr}$ measured by MC-ICP-MS is around 0.05 to 0.1 permil, while the typical isotopic variability is about 1 per mil and about 3 permil for geological and meteorite samples, respectively (Ohno et al., 2008; Moynier et al., 2010; Charlier et al., 2012). To discuss the sub-permil order stable isotopic difference in nature, improvement of the analytical precision is required.

We are developing a technique for ultra high precision stable isotopic analysis of Sr by double spike thermal ionization mass spectrometry (DS-TIMS) using Thermo Finnigan Triton at Kochi Core Center. DS-TIMS has advantages over MC-ICP-MS technique in sensitivity and higher analytical precision for measuring isotope ratios of elements with low first ionization potential, including Sr. We will discuss the current state of the analytical precision and accuracy as well as the sources of analytical error that may affect the analytical results.

Keywords: stable isotope, Sr isotope

Ni isotopic analyses of meteorites using TIMS and MC-ICP-MS

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The isotope analysis of the meteorites can provide important information about the origin and evolution of our solar system. As for Ni, the isotopic anomalies on ⁶⁰Ni (decay product of ⁶⁰Fe), as well as ⁶²Ni and ⁶⁴Ni have been reported from both undifferentiated and differentiated meteorites (e.g. Shukolyukov et al. 1993, Steele et al. 2011). However, there have also been reports of disagreement between data obtained using different analytical approaches (e.g. Cook et al. 2008, Chen et al. 2009, Moynier et al. 2011), which need to be clarified in order to fully understand the cosmochemical implications of the isotope data. Here we report the results of Ni isotope analysis for carbonaceous chondrite Allende and iron meteorites Carbo, Toluca, and Bueba Ventura.

The Allende and iron meteorites were dissolved in HF-HNO₃ and HCl-HNO₃, respectively, and Ni was extracted using a method modified from Yamakawa et al. (2009). The chemical yield and the level of impurities in the Ni cut were monitored using ICP-MS. The high-precision Ni isotopic analyses were performed using TIMS (MAT262, TRITON) and MC-ICP-MS (NEPTUNE). The activator for the analysis using TIMS was prepared by modifying the Si-Al-B type activator of Yamakawa et al. (2009) to gain higher beam intensity for a longer period of time.

The data for the iron meteorites obtained using both TIMS and MC-ICP-MS clustered around epsilon ⁶⁰Ni = 0. They were broadly similar to the data reported by Chen et al. (2009), however, no obvious correlation between the ⁵⁶Fe/⁵⁸Ni and epsilon ⁶⁰Ni ratios was observed. Anomalies on ⁶²Ni and ⁶⁴Ni were also not detected in this study, but improvement in the analytical precision is necessary to further explore this issue. Bulk Allende also showed no anomaly on epsilon ⁶⁰Ni, implying the low abundance of ⁶⁰Fe in the early solar system and/or homogenization of Ni isotopes after the accretion of its parent body.

The data obtained so far in our laboratory is restricted to samples with relatively small variation in the ⁵⁶Fe/⁵⁸Ni ratio. Thus, additional analyses of samples from different meteorite classes, as well as phases with high Fe/Ni ratio (such as troilite) is required to shed light on the nature of the Ni isotope in meteorites.

Keywords: Ni isotope, Meteorite, TIMS, MC-ICP-MS

Metal-silicate partitioning of lithophile elements and implications for potassium and light elements in the core

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The partitioning of lithophile elements (K, O, Si, Mg, Al, and Ca) between liquid metal and silicate melt were investigated up to 138 GPa and 5450 K in S-free/S-bearing Fe + K-doped pyrolite system, in order to constrain the amounts of radioactive ⁴⁰K and other light elements in the core. The obtained iron-potassium exchange coefficients show strong temperature (T) dependence but negligible effects of pressure (P) and sulfur content, not supporting the transition-metal-like behavior of potassium at high pressure. As a consequence, present experiments suggest only ~10 ppm potassium in the core, which yields present-day heat production of ~0.1 TW, even when we assume the entire core-mantle chemical equilibrium at 136 GPa and 5300 K (liquidus of pyrolitic mantle). On the other hand, the core dissolves substantial amounts of silicon and oxygen as a consequence of reaction with a basal magma ocean at 4500-5000 K, which account for the 10% core density deficit. In addition, quenched liquid iron obtained in relatively high-temperature experiments included certain amounts of Mg, Al, and Ca, suggesting that these elements may have been once incorporated into the core at the time of giant impact. A more realistic model for the Earth's core must consider the combined effects of material that equilibrated at modest P-T with the material that was added at very high P-T, and the effect of latter components are focused in this study.

Keywords: metal-silicate partitioning, high pressure, core formation, magma ocean, potassium, light elements

Rarotonga magma as a mixing product of EM-1 and HIMU in the Cook-Austral volcanic chain, the South Pacific.

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We present radiogenic isotope (Os, Pb, Nd, Sr) and major and trace element data on lavas from Rarotonga Island, the Cook-Austral volcanic chain in the South Pacific, and examine the origin of the source of these lavas. Relationship between Ni, MgO and Os concentrations of the lavas indicates that Os contents in magma are controlled by fractionation of sulfide. Osmium concentration of the samples with high-Os and Ni (over 80 ppt and 100 ppm, respectively) are least affected by magma differentiation. Since Os is a highly compatible element and is readily removed from magma during sulfide crystallization, shallow-level assimilation of crustal material and sediment with extremely high $^{187}\text{Os}/^{188}\text{Os}$ during magma ascent significantly alters the original Os isotopic compositions of magma. The lavas with low-Os, therefore, do not preserve the initial Os isotopic composition of magma and possess the elevated Os isotope ratios. The $^{187}\text{Os}/^{188}\text{Os}$ ratios of the Rarotonga lavas with Os concentrations more than 80 ppt (or Ni > 100 ppm) fall in a relatively limited range from 0.1282 to 0.1343 with an average of 0.132, which is possibly the initial Os isotopic composition of the Rarotonga mantle source. Evaluation of published data on the Pitcairn lavas known as originated from EM-1 in the similar manner to that used for that of Rarotonga data suggests that the lavas with high-Os and Ni (over 80 ppt and 300 ppm, respectively) keep the original Os signature of EM-1 with least assimilation. The Os isotopic compositions of such samples lie in a small range between 0.1350 and 0.1381 with an average of 0.1369. This value is much lower than the value of approximately 0.15 widely accepted as the $^{187}\text{Os}/^{188}\text{Os}$ of EM-1. If in the case, the Os-Pb-Nd-Sr isotopic data of the Rarotonga lavas suggest that they are mixing products of EM-1 and HIMU.

Keywords: Polynesia, hot spot, Rarotonga island, EM1, HIMU

Re-Os mineral isochron age of peridotite xenoliths from Hannouba, China: Implications for Os behavior in mantle

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Geochemical and isotopic data on mantle peridotite xenoliths provide key constraints on the evolution of lithospheric mantle beneath the thick continental crust. Especially, Os isotopes could give us information on the age of continental roots (Pearson, 1999) and genetic relation of the lithospheric mantle to the overlying continental crust. The continental crust was possibly formed by extraction from primitive upper mantle to form both the lithospheric mantle and the continental crust. However, Re introduction from the host magma or through metasomatism leads to rarely observed reliable Re-Os isochron for peridotite xenolith suites. Gao et al. (2003) successfully obtained the Re-Os whole-rock age of 1910 ± 220 Ma with an initial $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.1156 ± 0.0009 for peridotite xenoliths from Hannouba, China. However, five out of thirteen analyses were plotted out of the isochron trend and were eliminated from the regression, which indicates disturbance of the Re-Os system of the samples or analytical problem. In this study, we have analyzed whole-rock samples and minerals such as olivine, orthopyroxene, clinopyroxene and spinel of fresh peridotite xenoliths in continental basalt in Hannouba to make detailed age constraints on the evolution of sub-continental mantle in this area.

As shown in the figure, most of the Re and Os isotopic data of the whole-rock samples obtained in this study are plotted on the isochron line reported by Gao et al., (2003), implying the geological event at 1.9 Ga. Preliminary results of mineral analysis suggest a Re-Os mineral isochron with a younger age for a suite of Hannouba peridotite xenoliths, indicating that minerals possibly record a younger geological event such as metasomatism or shallow-level processes within the continental crust.

Keywords: Hannouba, peridotite xenolith, dating, Re-Os system, sub continental mantle

Does E-chondrite relate to the chemical state of the Earth?

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The chemical state of the Earth has been estimated based on chemical and isotope analyses of terrestrial materials which compose the crust and the mantle, taking the physical and geological information on physical properties account. However, to understand the chemical state of the early Earth and the whole Earth from the view of material science, it is required to use materials which could represent them even as approximated ones. As geochemical approaches to pursue this purpose, CI-chondrite has been generally used, because it maintains most abundant volatile elements among meteorite groups and show similar chemical compositions of the Sun which have been estimated by spectroscopy.

However, it does not always guarantee that CI-chondrite directly represents the chemical state of the Earth when it was formed. Hence, some different models have been proposed so far based on the other meteorite groups. Here, noting the importance of similarities with the Earth in oxygen isotopes, the significance of E-chondrite group is reexamined to estimate the chemical state of early and deep Earth.

Three oxygen isotopes of terrestrial and extraterrestrial materials have been extensively studied since 1970's, initiated by R.N. Clayton's group and followed by some other groups. Through such studies, it has been revealed that in the (Δ)17O/16O- (Δ)18O/16O diagram data of terrestrial materials lie on an isotope mass fractionation line (TFL) and the other extraterrestrial materials are mostly off the line and each group forms a different isotope mass fractionation line. Among extraterrestrial materials, only lunar samples and E-chondrite group lie on the TFL. Even Martian meteorites do not lie on the TFL. Such results indicate that the Moon and E-chondrite group might have been possibly formed in the similar chemical state to that of the Earth. This is compatible with the observation that stable isotopes such as C and N of the Earth are more similar to those of E-chondrite rather than C-chondrite groups.

In the (Fe+FeS)/Si-FeO/Si diagram, it has been clearly demonstrated that E-chondrites represent quite reduced conditions, while C-chondrites show much oxidized conditions. In the same diagram, mantle xenoliths are plotted in a rather reduced region. It has been suggested that the surface condition of the early Earth might have been in a relatively reduced condition. The Redox state of E-chondrites and the Moon might reflect it.

Furthermore, the estimated chemical state of the lower mantle would highly depend on the model of the reference material. If we assume C-chondrite as a starting material to form the Earth, the Redox state of the lower mantle would be estimated to be less reduced condition. However, if E-chondrite is assumed to have been related to the early Earth, the inferred state of the lower mantle would be in a rather reduced state. It might be compatible with the observation that kimberlite magma, which might have been originated in the lower mantle, show a rather reduced condition which is different from those of the other volcanic rocks.

It should be noted, however, that the chemical composition of the E-chondrite does not always represent that of the whole Earth, just as in the same manner that the Moon does not have the same composition of the Earth.

Keywords: Earth, chemical state, E-chondrite, relationship

Role of crystal fractionation and effect of degree of dehydration in producing FOZO and HIMU reservoirs

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It has been widely accepted that recycling of oceanic crust with/without sediments produced at least three enriched reservoirs in the mantle (HIMU, EM1 and EM2). This fundamental concept of the geochemistry is 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. The origins of enriched components are usually explained by recycling of oceanic crust (HIMU) with variable amounts of sediments (EM1 and EM2).

In early research on the mantle reservoirs, the isotopic composition of OIBs was 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 reservoirs, the importance of reservoirs whose isotopic compositions are intermediate has been pointed out, these are, 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 reservoirs is still controversial, the isotopic compositions of these reservoirs, in particular FOZO, have been used to designate the isotopic distribution of OIBs.

In the present study, geochemical modeling has been conducted to evaluate the origin of HIMU and FOZO reservoirs. For the modeling, MORB compositions from East Pacific rise and Mid-Atlantic ridge are compiled from published data (PetDB: <http://www.earthchem.org/petdb>). The results suggest that crystal fractionation at a mid-ocean ridge can increase U and Th concentrations relative to Pb content, producing high U/Pb and Th/Pb ratios in evolved MORBs. In addition, dehydration beneath a subduction zone can increase U/Pb and Th/Pb ratios of recycled oceanic crust, i.e., strongly dehydrated oceanic crust can be a suitable source material of HIMU magmas and less dehydrated MORBs can produce material with FOZO isotopic signature. Although depleted Sr isotopic composition of HIMU magma seems to contradict with high Rb concentration of evolved MORBs, high degree of dehydration beneath subduction zones can produce large Rb loss, producing depleted Sr isotopic composition of recycled crust that is suitable for the HIMU source. 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. Combination of crystal fractionation at mid-ocean ridges and degree of dehydration beneath a subduction zone can produce observed isotopic array of OIBs.

Keywords: Mantle reservoir, Recycling, HIMU, FOZO, Mid-ocean ridge, Subduction zone

Geochemical variations in Quaternary magmas along the volcanic front of Kyushu, Japan

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The Quaternary magma genesis of central Kyushu, Japan, was investigated by geochemical lateral variations. This area is underlain by the Philippine Sea Plate including the older Kikai Basin segment (60-40 My old) and the younger Shikoku Basin segment (26-15My old) divided by the Palau-Kyushu Ridge. Sr/Y ratios of the Quaternary lavas decrease from north to south along the volcanic front of the Kyushu arc. All analyzed Sr-Nd-Pb isotope compositions plot close to or along mixing curves between MORB-type mantle wedge and Philippine Sea Plate sediments, or between Shikoku Basin basalts and the Shikoku Basin sediments on the plate. ⁸⁷Sr/⁸⁶Sr ratios negatively co-vary with the Sr/Y ratios and increase from north to south. These geochemical characteristics suggest that Quaternary magmatism in central Kyushu was controlled by various contributions of the materials from the Philippine Sea Plate slab. The negative correlations between Sr/Y and Sr isotope ratios suggest that extent of addition of the partial melts derived from the subducting slab is the prime control of the spatial variations. These observations also suggest that the high Sr/Y slab component in the north would have been derived from the partial melts from the hot and young Shikoku Basin slab, whereas the low Sr/Y flux in the south may have derived from slab fluids from the older Kikai Basin slab.

Keywords: adakite, Philippine Sea plate, volcanic front, trace elements, Sr-Nd-Pb isotopic compositions