

Helium and halogen compositions in MORB vesicles

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Degassing behavior of halogens through submarine volcanism is not well understood. We determined helium and halogen compositions of MORB vesicles to constrain halogen flux at ridges. Samples collected at 8 sites (13oN-17oS on EPR; 15oN-37oN on MAR; 24-25oS on CIR) were crushed in dilute NaOH or NH₃ solution at liquid nitrogen temperature and volatiles were extracted from vesicles. Helium isotope compositions were determined with a VG-5400 MS and F and Cl contents were measured with ICS-2100 ion chromatography. For glass matrix, concentration of F and Cl were determined with a NanoSIMS.

For vesicles, the average ³He concentration was $(4.5 \pm 2.1) \times 10^{-15}$ mol/g of sample and the average F/³He and Cl/³He ratios were $(1.4 \pm 0.5) \times 10^6$ and $(2.9 \pm 0.6) \times 10^7$. This provides F and Cl flux of $(7.1 \pm 2.8) \times 10^8$ mol/y and $(1.5 \pm 0.4) \times 10^{10}$ mol/y at ridges calibrating against the known ³He flux of 530 mol/y. They may be defined as lower limits of MOR flux because F and Cl contents in glass matrix are >7000 and >100 times higher than those in vesicles and dissolution of only a small part of volatiles staying in oceanic crust into the ocean will increase volatile flux significantly. The large difference between F/Cl ratios in vesicles and glass matrix reflects difference in vesicle/glass partition coefficients of these elements, which suggests that they have significantly different degassing behavior at ridges. From the data of the noble gas method on MORB in literature, Br/Cl and I/Cl ratios in vesicles were calculated to be $(1.8 \pm 0.1) \times 10^{-3}$ and $(5.4 \pm 0.1) \times 10^{-5}$ which are almost equivalent with those in glass matrix [1], suggesting their vesicle/glass partition coefficients are similar in submarine basaltic magma. Br and I flux at ridges were calculated to be $(2.7 \pm 0.8) \times 10^7$ mol/y and $(8.3 \pm 2.4) \times 10^5$ mol/y based on the Cl flux estimated in this study. They are the first estimate of Br and I flux obtained by indirect calibration against ³He flux and may be lower limits of MOR flux by the same reason as Cl. Combination of the method in this study and the noble gas method on the same sample will give us new insight into degassing behavior and geochemical cycles of halogens.

Reference: [1] Kendrick et al. (2012) GCA 81, 82-93.

Keywords: Mid-ocean ridge basalt, Helium, Halogen, Flux, Geochemical cycle

Magmatic process of Cretaceous plutonic complex in Ikoma mountains, SW 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 three modes in whole-rock compositional relation, 1) as Plagioclase (Pl) cumulate, 2) as Hornblende-plagioclase (Hbl-Pl) cumulate and 3) as Hornblende (Hbl) gabbronorite.

The SiO₂ contents of the Ikoma gabbroic complex show 44 to 63 wt.%. Plagioclase cumulate and Hbl-Pl cumulate with SiO₂<50wt.%, their major oxide contents change widely for SiO₂ contents. Hbl gabbronorite are mafic to intermediate with SiO₂>50wt.%, major oxide contents show linear trends with respect to SiO₂ contents on compositional variation diagrams.

Plagioclase cumulate shows cumulus structure and consists of mainly Ca-rich plagioclase (An₈₅₋₉₀). On the compositional variation diagrams, plagioclase compositions included in Plagioclase cumulate is located to the end-member on the trend of Plagioclase cumulate. Moreover, their plagioclase mode are shown by a positive trend with respect to the variation of CaO contents. It suggests that Plagioclase cumulates were associated with the accumulation of plagioclase. On the other hand, plagioclase compositions in Hbl-Pl cumulate and Hbl gabbronorite are Ca-poor (An₇₀₋₇₅). It suggests Hbl-Pl cumulate and Hbl gabbronorite occur after forming Plagioclase cumulate. Whole-rock compositions of the Ikoma gabbroic complex vary linearly with increasing SiO₂ contents, and their ⁸⁷Sr/⁸⁶Sr initial ratios at 82 Ma show a positive trend with variation of SiO₂ contents. These characteristics suggest a mixing of mafic magma and felsic materials. The mafic end-member is mafic magma of Ikoma gabbroic complex. Granitoids occurred at the same time of the activity of the Ikoma gabbroic complex are plotted on the extrapolation of the compositional trend of Hbl gabbronorite, but their ⁸⁷Sr/⁸⁶Sr initial ratios at 82 Ma is too low as the felsic end-member in a mixing. It is suggesting that the felsic end-member may not be the granitoids, but other crustal materials.

Keywords: Ryoke belt, Magmatic process, cumulate, accumulation

Volatile compositions 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 early Earth 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 inclusions in ~4.4 Ga zircon from Jack Hills in Australia. Because apatite has volatile components, it is expected to determine the amount of water in the interior of the early Earth from OH composition of the Jack Hills apatite. However, partitioning of OH between apatite and melt is unclear.

We analyzed volatile compositions of apatite grains from pyroclastic flow deposits of Aso volcano in order to reveal the relationship between OH composition of apatite and H₂O composition of melt. The H₂O concentrations in the host magma have been estimated from those of melt inclusions in plagioclase phenocrysts. It shows that mafic melt contains more H₂O than silicic melt does. F concentrations in apatite in each sample show large variations while Cl concentrations are constant, suggesting that F and OH substitute for each other. OH concentration in apatite of mafic sample was larger than that of silicic one, that is, OH concentration in apatite and amount of H₂O in melt show negative correlation.

The negative correlation would have been caused by difference in Ca content between mafic and silicic samples. It is possible that Ca in melt combines F and affect partitioning F between apatite and melt (Mathez and Webster, 2005). Mafic melt contains more Ca than silicic melt and Ca may disturb partitioning F for apatite and OH concentration can be increase in apatite. Another possibility is that the water compositions of melt inclusions do not represent those in the host melt. The melt inclusions have many bubbles, and the more bubbles they have, the less H₂O they contain. It means that H₂O in melt inclusions was lost to the bubbles, resulting in underestimation of water contents in the host melt. Actually another study calculated the amounts of H₂O in the mafic and silicic melts of the Aso pyroclastic flow and results were 4.1-7.7wt% and 4.1-5.7wt% respectively (Kaneko et al., 2007). If these results are correct, then OH concentration in apatite and the amount of H₂O in melt are positively correlated.

Range of the amount of F and OH in each sample could mean that melt composition gradually changed by degassing or/and crystallization differentiation. For precise determination of OH partitioning between apatite and melt, it is necessary to reveal the effect of Ca or other components to partitioning behavior of volatile components between apatite and melt.

Keywords: apatite, water, volatile component, the early Earth, magma

Measuring osmium isotopic composition of natural polycrystalline diamond (carbonado) and implications for its origin

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The origin of natural polycrystalline diamond, carbonado, has long been enigmatic. Carbonado is characterized as high porosity, no genetic relations to kimberlites, light carbon isotope ratio, and lack of mantle-derived mineral inclusions. Based on these observations, several hypotheses about the origin of carbonado have been proposed: transformation of subducted organic carbon into diamond in a cold slab (Robinson, 1978); shock metamorphism of organic carbon by meteorite impact (Smith and Dawson, 1985); radiation-induced diamond formation by spontaneous fission of uranium in crustal environment (Ozima *et al.*, 1991); formation in an interstellar environment (Garai *et al.*, 2006); crystallization from C-O-H fluid in cratonic upper mantle (Ishibashi *et al.*, 2012). However, no conclusive evidence has been provided to settle a controversy about the origin of carbonado. In this study, we first tried to measure Os isotopic composition of carbonados collected from placer deposits in the Central African Republic in order to identify its origin.

Natural samples have a wide variety of Os isotopic ratios, $^{187}\text{Os}/^{188}\text{Os}$, depending on their origin because ^{187}Re , the parent nuclide of radiogenic ^{187}Os , is a mildly incompatible element during mantle melting whereas Os is a strongly compatible element. $^{187}\text{Os}/^{188}\text{Os}$ ratio of upper continental crust ranges from 1.0 to 1.4 (Peucker-Ehrenbrink and Jahn, 2001), whereas that of primitive upper mantle is about 0.13 (Meisel *et al.*, 1996). Os isotopic ratio of the micro diamond crystal itself can reflect the environment where diamond grains crystallized. Carbonado is a porous aggregate of micrometer-size diamond crystals and original chemical characteristics of the grain boundaries could be heavily altered after the diamond growth.

This study was designed to determine Os isotopic ratios within diamond crystals of carbonados and in the grain boundaries separately. Two-step sample chemical leaching was carried out by Carius tube method (Shirey and Walker, 1995). First, carbonado samples were crushed to submillimeter grains and were sealed in a Carius tube with spike solutions and inverse aqua regia ($\text{HCl} + 3 \text{HNO}_3$). The solution was heated at 220 °C for 24 hours. This procedure was for extract Os in the grain boundaries. Second, the residue of solid samples was heated in a vacuum chamber to convert diamond to graphite. A graphitized sample was decomposed in acid solution in the same way as the first leaching process. The second process was to extract Os within diamond grains. Osmiums in the both solutions were purified with the solvent extraction (Cohen and Waters, 1996) and microdistillation (Roy-Barman, 1993). Osmium isotopic compositions of the samples were determined using thermal ionization mass spectrometry (TIMS). Blank levels of Carius tubes and inverse aqua regia solutions prepared from several chemical reagents were checked. As a result, a quartz glass tube was found to have the lowest blank level compared with other glass tubes made from borosilicate glass.

In the presentation, we will report preliminary results of Os isotopic ratios of the carbonado, which have the potential for a decisive evidence to close the debate on the origin of carbonado.

Keywords: carbonado, TIMS, Os isotope, diamond

High-pressure high-temperature phase transitions in ZnTiO_3

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It is widely accepted that perovskite-type MgSiO_3 is the most abundant mineral in Earth's lower mantle. Ilmenite-type MgSiO_3 transforms to perovskite at 23 GPa and 1600 °C. It was reported that ilmenite-type ZnTiO_3 , an analogue to ilmenite-type MgSiO_3 , decomposes into ZnO and TiO_2 at about 20-25 GPa (Ito and Matsui, 1979). However, phase relations in ZnTiO_3 have not been studied yet in detail. Therefore, we investigated the phase relations in ZnTiO_3 by high-pressure high-temperature experiments.

A starting material of ilmenite-type ZnTiO_3 was synthesized by heating a mixture of ZnO and TiO_2 with 1:1 mol ratio at 800 °C for 32 hours in air. High-pressure phase relation experiments were made by using a Kawai-type 6-8 multi-anvil apparatus in the pressure and temperature ranges of 13-35 GPa and 1000-1400 °C, respectively. After keeping the starting sample at desired conditions for 1-2 hours, the samples were quenched, and then decompressed to ambient pressure. Recovered samples were identified by using the powder X-ray diffraction method.

We found that the recovered samples which were compressed between 15 and 20 GPa at 1000-1400 °C had the LiNbO_3 -type (LNO) structure. The ilmenite-LNO phase boundary was determined as $P(\text{GPa})=19.9-0.0038T(^{\circ}\text{C})$. FeTiO_3 ilmenite which is an analogue to ilmenite-type MgSiO_3 transforms to perovskite above 15 GPa, and the perovskite transforms to the LNO-type structure during decompression (Ming et al., 2006). The ilmenite-perovskite phase boundary in FeTiO_3 has a negative slope which is caused by a positive entropy change for the transition due to increase of coordination number of divalent cation from 6 to 8. If the LNO-type ZnTiO_3 is a stable phase, the slope of the boundary should be positive because of no change in the coordination number of the divalent cation. Therefore, the negative slope of the boundary implies that the recovered LNO-type ZnTiO_3 was originally perovskite-type at 15-20 GPa.

The recovered samples synthesized above 20 GPa were identified to be an assembly of wurtzite-type ZnO and α - PbO_2 -type TiO_2 . The post-perovskite phase boundary in ZnTiO_3 is determined as $P(\text{GPa})=9.5-0.010T(^{\circ}\text{C})$. Wurtzite-type ZnO transforms to NaCl-type at about 6 GPa (Kusaba et al., 1999). Also, α - PbO_2 -type TiO_2 transforms to baddeleyite-type at about 17 GPa (Tang and Endo, 1993). Therefore, we suggest that the phase assembly of NaCl-type ZnO and baddeleyite-type TiO_2 is stable above 20 GPa.

Keywords: ZnTiO_3 , Perovskite, LiNbO_3 , High pressure

Quantitative multi-element imaging of geological materials by femto-second LA-ICP-MS

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Elemental mapping analysis of geological materials using X-ray related methods (EPMA, XRF) or SIMS suffers from insufficient sensitivity and poor quantification. LA-ICP-MS has advantages of high sensitivity and less matrix effect, therefore has been developed for elemental and isotopic imaging analyses over the last decade. However, quantification problem by this method remains unsolved because of the lack of a suitable sampling volume correction method and necessity of matrix-matched standard. This work presents multi-element imaging/mapping analysis of orthopyroxene and plagioclase minerals by femto-second LA-ICP-MS using a novel normalization process. Laser sampling volume is corrected for by analyzing ten major elements (SiO₂, TiO₂, Al₂O₃, FeO, MnO, MgO, CaO, Na₂O, K₂O, and P₂O₅) followed by normalization of the analyzed total sum to 100 wt% to obtain correction factor. This correction method is free from any external analysis (e.g., EPMA) for at least one internal standard element (e.g. Ca), and can be applied for both spot and line scanning LA mode. This allows LA-ICP-MS method standalone and liberates from errors inherited from any local heterogeneity of the samples picked up differently by the different analytical techniques used. Use of USGS basalt glass as a standard eliminates matrix effect in the levels less than 10% RD for these silicate minerals. Two-dimensional elemental distribution images of 43 elements were acquired from 4-6 μm depth of the sample surface with a $\sim 40 \mu\text{m}$ lateral resolution. An area of $500 \times 500 \mu\text{m}$ can be scanned simultaneously for 43 elements in less than 2.3 hours. Trace elements in silicate minerals can be imaged at sub-ppm concentration level, while major elements were mapped at sub-percent concentration.

Key words: femto-second LA-ICP-MS, elemental mapping, minerals