Chondritic Xenon in the Earth’ s mantle: new constraints on a mantle plume feeding magmatism in Europe

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Noble gases are powerful tracers of the origin of terrestrial volatile elements and of the processes that controlled their distribution between the Earth's interior and the terrestrial atmosphere over geological ages. The compositions of magmatic gases provide insights into the evolution of the Earth’ s mantle and atmosphere. Despite recent analytical progress in the study of planetary materials and mantle-derived gases, the possible dual origin of the planetary gases in the mantle and atmosphere remains unconstrained.

Xenon deserves particular attention because its isotope systematic can be linked to specific processes during terrestrial accretion (e.g., Marty, 1989; Mukhopadhyay, 2012). The origin of heavy noble gases in the Earth's mantle is still debated, and might not be solar (Holland et al., 2009).

Here, we report high precision xenon isotopic measurements in gases from a CO_2 well in the Eifel volcanic region (Germany), where volcanic activity occurred between 700 ka and 11 ka years ago.

Our Xe isotope data (normalized to ^{130}Xe) show deviations at all masses compared to the Xe isotope composition of the modern atmosphere. The improved analytical precision of the present study, and the nature of the sample, constrains the primordial Xe end-member as being “chondritic”, and not solar, in the Eifel mantle source. The evidence of this primordial component is consistent with an asteroidal origin for the volatile elements in Earth's mantle. It also implies that volatiles in the atmosphere and in the mantle originated from distinct cosmochemical sources. Despite a significant fraction of recycled atmospheric xenon in the mantle, primordial Xe signatures still survive in the mantle.

Our data also show that the reservoir below this volcanic system (Eifel) contains heavy-radiogenic/fissiogenic xenon isotopes, whose ratios are typical of plume-derived reservoirs. The Xe contribution, coming from the spontaneous fission of ^{244}Pu, is 2.26±0.28 %. The Xe contribution from spontaneous fission of ^{238}U is always negligible, the remainder being atmospheric plus primordial. Our data support the notion that the fraction of plutonium-derived Xe in plume sources (oceanic as well as continental) is higher than in the MORB source reservoir. Hence, the MORB—type reservoirs appear to be well distinguished from and more degassed than the plume sources (oceanic as well as continental) supporting the heterogeneity of Earth’ s mantle.

Finally, this study highlights that xenon isotopes in the Eifel gas have preserved a chemical signature that is characteristic of other mantle plume sources. This is very intriguing because the presence of a mantle plume in this sector of Central Europe was already inferred from geophysical and geochemical studies (Buikin et al., 2005; Goes et al., 1999). Notably, tomographic images show a low-velocity structure down to 2000 km depth, representing deep mantle upwelling under central Europe, that may feed smaller upper-mantle plumes (Eifel volcanic district-Germany).

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Keywords: Xenon, terrestrial accretion, Earth's mantle, plume

Fumarolic vs hydrothermal fluxes of magmatic volatiles from Kuril island arc, NW Pacific

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Kuril island arc is a part of the Kamchatka-Kuril subduction zone, ~ 1100 km long, with ~40 active terrestrial volcanoes. In 2016 there were 4 erupting volcanoes within the arc with different types of eruptions: lava flows (Snow volcano), ash explosions (Chirinkotan and Chikurachki), phreatic explosions (Ebeko). Many volcanoes are characterized by a permanent fumarolic activity with temperatures of the vents from >900℃ (Kudryavy, Iturup Island), to the boiling-point temperature of the secondary steam vents from boiling volcano-hydrothermal systems. Many volcanoes host hydrothermal systems discharging ultra-acid Cl-SO_4 waters where Cl and S are of magmatic origin. At least five volcanoes of the arc: Ebeko (Paramushir), Sinarka and Kuntomintar (Shiashkotan), Pallas (Ketoy) and Kudryavy (Iturup) have fumarolic fields with strong and hot (>400℃) gas vents. In 2015-2016 we measured fluxes of SO_2 using scanning mini-DOAS instrument at the four most powerful volcanic gas emitters of the Kuril Chain that count for more than 90% of the whole permanent fumarolic activity of the islands (Ebeko, Kuntomintar, Pallas, Kudryavy). At each fumarolic field the direct sampling and MultiGas measurements have been performed allowing estimating fluxes of main components (S, CO_2, HCl). The hydrothermal flux of Cl and S from 10 most powerful volcano-hydrothermal systems of Kurils including the southernmost Kunashir and the northern Paramushir islands has also been estimated using measurements of flow rates and the chemistry of draining streams. The total volcanic (fumarolic) flux of SO_2, CO_2 and HCl from the Kuril arc can be estimated as 1200 t/d, 1000 t/d and 250 t/d, respectively (with about 20% of uncertainty) . The hydrothermal flux of magmatic S (as SO_2) and Cl is calculated as 250 and 130 t/d, respectively. Assuming that a significant part of S in hydrothermal systems is lost as minerals, the hydrothermal flux of magmatic volatiles can be estimated as a half of the fumarolic flux. The CO_2/S ratio for Kuril volcanoes is variable among volcanoes but nearly constant within a fumarolic field and is found in the range of 0.2 to 4.5 (mole ratio). The highest hydrothermal flux was measured for Ebeko volcano (80 t/d of HCl and 150 t/d of S as SO_2), with the hydrothermal S flux higher than the fumarolic flux. Hydrothermal output at Kuril islands is also manifested by numerous coastal hot neutral springs with a high chloride content, but this Cl has a mixed seawater-magmatic origin, and sometimes it is not easy to distinguish the magmatic fraction. This study was supported by Russian Science Foundation, project 15-17-20011

Keywords: magmatic volatiles, subduction zones, volcanic gases, hydrothermal systems

Helium isotopes, C/3He ratios, and radiogenic isotopes in the northern Lau and north Fiji basins

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The northern Lau Basin is host to a complicated pattern of volcanic activity, including the volcanoes of the Tofua Arc and several back-arc spreading centers such as the NE Lau Spreading Center (NELSC), the NW Lau Spreading Center (NWLSC), as well as various “rear-arc” volcanoes. We have employed helium isotopes, C/^{3}He ratios, and radiogenic isotope signatures to distinguish between various arc, back-arc, and hotspot affinities in the region. Along the NWLSC elevated ^{3}He/^{4}He ratios in the seafloor lavas (12 - 28 Ra) suggest that an OIB or mantle plume signature, possibly from Samoa, has influenced this extensional zone. However this hotspot helium is absent in the NE Lau Basin which has mid-ocean ridge (MOR) type helium (~8 Ra). In the NE Lau Basin, ^{3}He/^{4}He –C/^{3}He systematics indicate varying degrees of subduction influence among the volcanic centers. For example, the recently erupting West Mata submarine volcano in the NE Lau has a C-He signature indicating strong arc affinities. We have analyzed helium isotope ratios in 40 additional submarine rock samples which extend the geographic coverage farther west into the Fiji Basin. Surprisingly, several samples have elevated 3He/4He in the range of 12 –20.9 Ra, including a 14.4 Ra value on the NE Fiji Triple Junction ~1000 km to the west of the NWLSC. One might assume that these elevated 3He/4He ratios are related to the same OIB influence detected along the nearby NW Lau backarc spreading system. When radiogenic isotopes (Sr, Nd, Hf) are added to the picture, samples from the Futuna Volcanic Zone and from the NE Fiji Triple Junction fall on a mixing trend between depleted MORB mantle and FOZO, as do samples from the Rochambeau Rifts and NWLSC. However, this trend is distinct from that of Samoa proper, suggesting that only a restricted (FOZO) portion of the Samoan plume is responsible for the elevated 3He/4He in the northern Lau and Fiji basins.

Keywords: Helium isotopes, northern Lau basin, north Fiji basin, radiogenic isotopes, C/3He ratios

Sulfur-rich primitive arc magmas and possible sulfur recycling beneath volcano

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Tephra of high-Mg basalts (8.9 wt% MgO) from the 1941 lateral eruption of Plosky Tolbachik volcano (Kamchatka) contains olivine and chrome-spinel phenocrysts with numerous naturally quenched melt inclusions (MI) 20–100 μm, sometimes up to 350 μm in size. Volatile contents in such inclusions measured by the electron and ion microprobes vary from near zero to exceptionally high values, containing up to 5.1 wt% H_2O, 1200 ppm CO_2, 0.30–0.35 wt% S and 0.28 wt% Cl. This includes the most primitive MI in Cr-spinel (15.6 wt% MgO in the melt) with ~0.3 wt% S. The original CO_2 content was possibly 3–4 times higher because the majority of the original CO_2 can be lost to a shrinkage bubble (e.g., Wallace, 2015). The d^{34}S of the inclusion glasses vary strongly, ranging from +6 to +11‰ and show positive correlation with S contents. Meanwhile, there is a population of MI with anomalously high sulfur (0.5 –1.08 wt% S), which is close to the maximum sulfur abundance measured in island arc magmas (Wallace and Edmonds, 2011). The origin of anomalous sulfur was attributed to wall rock assimilation, which is supported by positive correlation between δ^{34}S and total S. Considering the volcanic environment, assimilation of hydrothermally altered rocks rich in pyrite, gypsum, alunite and native sulfur seems plausible. High total sulfur suggests that a major fraction of sulfur in the magma was dissolved as sulfate, whereas S^{2-} contents were just below or slightly above the level of sulfide saturation. The latter was surpassed in some volumes of magma, resulting in segregation of Ni-rich sulfide melt, droplets of which were also trapped in olivine phenocrysts. At the same time, some melt inclusions contain crystals and aggregates of anhydrite $CaSO_4$. The origin of anhydrite is controversial. Some large aggregates of anhydrite could have been trapped from the melt. On the other hand, subaerial oxidation of melt inclusions containing large sulfide droplets could produce enough sulfate to form anhydrite in situ. In summary, primitive arc magma from Tolbachik demonstrates high volatile contents close to or exceeding the highest ever measured in an arc setting. Additional sulfur was possibly recycled from hydrothermally altered wall rocks and gave rise to sulfide saturation of magma. The presence of anhydrite in primitive melt inclusions requires further investigations.

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Keywords: Sulfur-rich magma, Sulfur recycling, Sulfide, Kamchatka

Sulfate in fluid inclusions of the Pinatubo harzburgite xenoliths as slab-derived oxidiser in the mantle wedge

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We found sulfate ion and sulfate minerals in the H_2O-CO_2-Cl fluid inclusions in the harzburgite xenoliths collected in the Pinatubo 1991 pyroclastic flow located at the volcanic front of the Luzon arc, the Philippines (Kawamoto et al. Proc Natl Acad Sci USA 2013). Thanks to a newly installed Raman mapping system, $SO_4{}^{2-}$ ion, gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$) were found in the fluid inclusions. Kumagai et al. (2014, Contrib Mineral Petrol) reported a possible presence of Mg-sulfate hydrite in CO_2-H_2O-Cl fluid inclusions in the Ichinomegata lherzolite xenoliths sampled in a rear arc side of northeaster Japan arc. In the previous paper at 2013, we had mentioned no sulfur phase found in the Pinatubo harzburgite, which was turned out to be wrong. Halogen systematics of the Pinatubo harzburgite xenoliths indicate that the fluid inclusions can be derived from dehydration of subducting serpentinites whose water was originally brought by sedimentary pore fluids through fractures (Kobayashi et al. 2017 Earth Planet Sci Lett). Sulfate and sulfide are present in serpentinites (Alt et al. 2012 Earth Planet Sci Lett). Our preliminary estimate of sulfur contents in the fluid inclusions (0.3 wt % as S) following methods by Binder and Keppler (2011 Earth Planet Sci lett) seems to be consistent with S contents in serpentinites, their dehydrated products and the dehydrated fluids (Alt et al. 2012). Our discovery of sulfate in the Pinatubo harzburgite may suggest slab-derived fluids contain sulfate beneath the cold forearc (<830 ˚C, Pinatubo) and the warm rear-arc (about 920 ˚C, Ichinomegata). Yoshikawa et al. (2016, Lithos) report trace element compositions in amphibole of the Pinatubo harzburgite and found enrichment of Pb, which can be transferred preferentially by the sulfate bearing fluids. Subduction zone magmatism has been characterized by its high water contents and oxidized conditions (Kelley and Cottrell 2009 Science). Presence of sulfate in the slab-derived fluids can explain the positive relation between the water contents and Fe^{3+}/Fe^{2+} ratios, and also proved insights on the presence of calc-alkaline rock series characterized by higher oxygen fugacity than tholeiitic rock series (Miyashiro 1974 Am J Sci). The present observation finds a missing link between high S concentration in arc magmas (Le Voyer 2010 J Petrol) and salfate in subducting slab including serpentinites (Alt et al. 2012) or high-pressure metamorphic rocks (Frezzotti and Ferrando 2007 PERIODICO di MINERALOGIA).

Keywords: fluid inclusion, aqueous fluid, subduction zone, calc-alkali magma, oxygen fugacity, saline fluids

Existence of CO_2-rich melt in the asthenosphere evidenced by petit-spot

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Carbon dioxide (CO_2)-induced partial melting of mantle peridotite is recently expected as the cause of the seismic low-velocity and high electrical conductivity in the asthenosphere (e.g., Hirschmann 2010; Sifré et al., 2014), but not directly evidenced. To investigate the nature of the asthenosphere, petit-spot should provide important insights because of following discussions and observations. Models for the eruption of petit-spot volcanoes suggest that magma exudes from the upper-most mantle asthenosphere in response to plate flexure (Hirano et al., 2006; Valentine and Hirano, 2010; Yamamoto et al., 2014; Machida et al., 2015). The primary petit-spot magma includes 10% of CO_2 and 1% of H_2O (Okumura and Hirano, 2013). The petit-spot volcanic fields ubiquitously distribute in the region of plate deformation, such as plate subduction or glacial melting (Hirano et al., 2008; Uenzelmann-Neben et al., 2012; Hirano et al., 2013; Taneja et al., 2014). However, because these previous studies discussing about petit-spot volcanism have not constrained the processes and conditions of the generation of petit-spot magmas, we must clarify whether or not the petit-spot melt is generated in the asthenosphere. In this study, we thus conduct melting experiments to define the genesis of the CO_2-rich petit-spot primary magmas from the two youngest knolls of petit-spot in the northwestern Pacific plate.

Melting experiments were conducted using 1/2-in.-diameter piston cylinder type high-temperature and high-pressure apparatus at Kyoto university. Starting materials were prepared at Kyoto University by mixing pre-dried reagents of oxides, hydroxides, phosphate, and carbonates to represent the major elements, CO_2 and H_2O composition of the primary magma for each petit-spot volcano. As the result of our experiments, the liquidus mineralogy constrained that the petit-spot magma last equilibrated with harzburgite at 1.8–2.1 GPa (approximately 60 km deep, corresponding to the lower lithosphere) and 1280–1290 degree C (slightly lower temperature than the adiabat of the mantle potential temperature (MPT) of 1250 degree C). To explain the equilibration temperature of petit-spot primary magma, we consider that CO_2-rich silicate melt are produced in the asthenosphere because of the existence of CO_2-rich fluid or carbonate. Based on solidus for the peridotite–CO_2–H_2O system at approximately 3 GPa, the CO_2-rich silicate melt is likely stable in the asthenosphere at the MPT of 1320 degree C. Such temperature corresponds to temperature of the upper asthenosphere (1400 degree C) calculated assuming normal thermal gradient of 135 Ma lithosphere beneath the petit-spot volcanoes. Then, the following model can reasonably explain the last equilibration pressure and temperature of the primary petit-spot melt; that is (1) CO_2-rich silicate melt in the upper-most asthenosphere ascends the overlying lithosphere owing to plate flexure, (2) temperature of melt decreases during ascending and (3) melt equilibrates with ambient peridotite in the lower lithosphere before eruption. A rebuttal case is the in situ CO_2-induced melting of mantle peridotite in the lower lithosphere. However, temperature of melt (1000–1100 degree C) is significantly lower than the estimated temperature of petit-spot primary magma. Furthermore, we have no observation indicating the upwelling of hot deep mantle as the heat source to explain the temperature of petit-spot primary magma.

Based on results of our experiments, we can posit petit-spot as the definitive evidence for partial melting in the asthenosphere caused by CO_2. For future studies, geochemistry of petit-spot lavas could contribute to quantitative determination of amount of CO_2 in the asthenosphere. Furthermore, the linkage between the lithology of the seismic low-velocity layer and global carbon recycling should be investigated by petit-spot lavas.

Keywords: asthenosphere, CO2-rich silicate melt, petit-spot, multiple saturation experiment

Role of volatiles in melting process of mantle plume: Case study in Hawaii

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In order to understand the role of water in magma genesis of a plume consisting of peridotite and eclogite (recycled ancient oceanic crust), melting experiments were carried out at 1300-1550˚C and 3, 5 and 8 GPa pressure conditions with 0 to 5wt% of water. In order to test the effect of mafic bulk rock composition on the chemistry of reacted melts, 2 basalt compositions were chosen (NMORB and CRB). Compared with NMORB, CRB is enriched in Fe, K, Ti and LREE. H_2O promotes melting of only basalt layer under low water concentration, while it enhances melting and chemical interaction between both layers. Reacted dry melts formed from MORB/peridotite layered experiments were tholeiitic (basalt/basaltic andesite/andesite) while those from CRB/peridotite layered experiments were alkalic (alkali basalt/basanite/trachy-basalt/ trachy-andesite/ phono-tephrite).

Based on experimental results combined with field occurrence of tholeiite and alkalic magmas in Hawaiian plume, a new model for the role of volatiles in melting of mantle plume is proposed. Alkali acidic magma such as mugearite, hawaiite, trachyte, and phono-teprite appears in many hot spots. These alkali acidic magmas have been considered as products of fractional crystallization from alkali basalt magma in shallow level magma chambers. However, based on our experiments, we propose a new model, that at least some alkali acidic magma may have derived directly from partial melting of elogite at 3 to 5 GPa under slightly hydrous conditions. Under activie shiled volcanoes (e.g., Kilauea and Mauna Kea) tholeiitic magma is being produced by extensive reaction melting of entrained eclogite with surrounding peridotite at the top of the plume 2.7-2.8 GPa. This model gives explanation for the origin of alkali achidic rocks found from south flank of Kilauea by Sisson et al (2002). This model can also explain why alkali acidic magma (mugearite, hawaiite) prevails in volume in the post-shield stage of Hawaiian volcanoes.

Keywords: Hawaii plume, magma genesis, role of volatiles

Seawater cycled throughout Earth's mantle in partially serpentinised lithosphere

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Recent work has indicated that about 90% of non-radiogenic xenon in the Earth’s mantle has a subducted atmospheric origin, suggesting that other seawater-derived components may also have subducted origins in the mantle. In order to test this proposition, we investigated the concentrations of water and halogens (F, Cl, Br, I) in samples of magmatic glasses collected from globally distributed mid ocean ridges and oceanic islands including melts derived from all the mantle end-member reservoirs: Depleted MORB mantle (DMM), Enriched mantle (EM1 and EM2) and high-μ (HIMU). After eliminating samples that show evidence for late-stage assimilation of seawater components, our data show unexpected broad correlations between mantle H_2O/Ce, Cl/K, F/Pr, Nb/U and Ce/Pb. The data confirm that EM reservoirs with low Nb/U and Ce/Pb ratios have low H_2O/Ce, Cl/K and F/Pr that demonstrates a relative depletion in water and halogens, consistent with the presence of dehydrated sediments or continental crustal material in EM sources. In contrast, HIMU reservoirs, which are depleted in most fluid mobile trace elements and characterised by high Nb/U and Ce/Pb ratios, are substantially enriched in H_2O and halogens. The H_2O and halogen enrichment of these sources is at odds with HIMU reservoirs being derived solely from dehydrated ocean crust, but can be easily explained if subducted ocean crust is associated with variable quantities of serpentinised lithospheric mantle. Our data also show that the abundance ratios of the most incompatible halogens (Br/Cl and I/Cl) have overlapping and narrow ranges in MORB and all OIB. Furthermore, the median I/Cl of the mantle is estimated as 0.000063 ±0.000005 which is substantially lower than the calculated primitive mantle value of 0.00027 ±0.00012. Given that I and Cl have similar incompatibilities in the mantle, this cannot be explained by melting related extraction but can be explained by preferential subduction of Cl relative to I, which is suggested by the relative abundances of these halogens in amphibolites and antigorite-serpentinites. We calculate that subduction of 1-2 % serpentine in the uppermost 10 km of the lithospheric mantle is enough to generate the maximum H_2O/Ce (280-400), Cl/K (0.12-0.16), F/Pr (140-160) and Nb/U (65-70) ratios observed in a HIMU reservoir. Furthermore, a figure of this magnitude, equivalent to a subduction flux of $1\text{-}3\times10^{11}$ kg yr^{-1} H_2O and $2\text{-}4\times10^{9}$ kg yr^{-1} Cl, is required to balance global input of H_2O into the mantle with global output of H_2O into the surface reservoirs, and maintain constant sea level through the Phanerozoic. This level of subduction suggests that the entire mantle inventory of H_2O and halogens could have been subducted in about 4 billion years and an equivalent amount transferred to the surface reservoirs. Therefore the Earth’s mantle is now dominated by subducted H_2O, Cl, Br and I and the exchange of volatiles between Earth’s surface reservoirs and mantle is much greater than previously anticipated.

Keywords: halogens, water, HIMU, Ocean Island Basalt, Mid Ocean Ridge Basalt

Fluorine as a proxy of water in mantle

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Water-cerium ratio of basalt has been utilized for evaluating the water abundance in its source mantle due to its inheritance from the source mantle. However, dissimilar chemical properties of cerium (Ce^{3+}; lithophile) to water (OH^-; volatile) in the mantle limit its quantification. Fluorine is an effective element for this purpose, because it is volatile element and has similar chemical properties to the mantle water. We precisely determined water and fluorine concentrations of deep submarine basaltic glasses from mid-oceanic ridges (MOR) of Pacific, Atlantic and Indian Ocean, a Hawaii hotspot, and a Fiji back arc basin using an FTIR and an ion chromatography. We found a strong linear correlation of F [ppm] = $(477 \pm 7) \times H_2O$ [wt.%] + (47 ± 2). This F–H_2O mantle array represents melting of mantles ranging from a near-dry depleted MOR mantle (DMM: H_2O = 100ppm; $H_2O/F=10$) to a hydrous primitive mantle (PM: H_2O = 750ppm; $H_2O/F=18.5$). Other data of ours, produced by nanoSIMS, and existing data of submarine basaltic glasses and olivine-hosted melt inclusions plot on the mantle array in most MORs, deviate positively (H_2O-enrichment) in arcs, negatively (H_2O-defficient) in hotspots. These are consequences of melting of a pristine depleted mantle (MORs), the selective water enriched mantle by the subducting slab (arcs), and water depleted mantle by the dehydrated recycled slab materials (hotspots), respectively. The F–H_2O systematics of basalt glass is a versatile tool for understanding the origin and behavior of mantle water.

Keywords: Fluorine, volcanic glass, volatile element, water

Possible redox state control on the cycle of volatiles in the Earth's interior

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Based on noble gas isotope signatures such as 3He/4He and Ne isotope systematics for MORBs and OIBs, the occurrence of degassed and less degassed mantle has been inferred. Since He(and possibly Ne) is quite easily movable and chemically inert, it is expected to be easily degassed from the magma reservoir during magmatic processes at a shallow depth. To explain the occurrence of primordial components such as 3He in the Earth's interior, among various proposals the existence of non-recycled mantle has been conjectured to be most likely by many noble gas researchers. Since noble gases are not related to any chemical reaction, they shall not be controlled by the redox state of the Earth's interior.

On the other hand, volatiles composed of active elements such as H,

C,N,S and so on are more or less change their properties according to the redox state of the environments. For example, CO2 is a typical form in the oxidized state and if it is saturated in a magma at a depth, it is easily degassed at a shallow depth as CO2 bubbles due to the decrease of solubility of CO2 in a magma with the decreasing pressure. While in the reduced state, CO2 is difficult to remain as stable and C exists as diamonds (or graphites) and/or hydrocarbons. C and hydrocarbons are not easy to work as volatiles at a depth and would remain there unless they might be carried to a shallow place associated with mantle plumes.

In the same manner, the behavior of S is much variable depending on its chemical form controlled by the redox state. In the oxidized state, SO2 is degassed easily at a shallow depth from a magma. In the reduced state, S reacts easily with metal elements such as F or Cu and forms sulfide minerals like FeS, FeS2 or CuS. When sulfide minerals are formed, they remain at a depth wothout forming volatiles. H2S also works as volatiles, but its chemical behavior in volcanic gas would be different from that of SO2.

N exists generally as N2 at the surface of the Earth and soluted in a magma to some extent. However, it has been inferred that the solubility of N in a magma might be increased in a much reduced state compared to that in an oxidizzed state. Furthermore, in a much reduce state, N would exist as NH3 and it might be not easy to be degassed from a deep mantle.

In the case of H, H2O is most common form at a shallow depth in the oxidized state. When recycled H2O goes into the deep mantle and the deep mantle is in the reduced state, however, H2O might be not stable and would be decomposed.

Thus, some active elements would change their chemical from depending on the redox state, which would surely control the cycle of volatiles in the Earth's interior. Although the deep mantle is inferred to be less oxidized than the upper mantle, we have no good knowledges about their state. Based on such information from noble gas isotopes, kimberlites and E-chondrites, I have suggested a possibility that the deep mantle might be more reduced than what has been conjectured so far based on C-chondrires (1). Further, significant depletion of of H, C, N, S relatived to Si in the earth compared to chondrite values might be related to the cycle behavior of these elements controlled by the redox state. However, we have no sufficient data on the chemical properties of such elements at high pressures under the reduced state. To promote our proper understanding of the cycle of volatiles in the Earth's interior, we should pay more attention to the issues mentioned here.

(1) I. Kaneoka, Presented at the session 04a, Goldschmidt Conference, Yokohama, 2016.

Keywords: volatiles, cycle, redox state, deep mantle, chemical form

In situ optical study of H_2O-CO_2-CO system at high pressures

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Externally heated diamond anvil cell (DAC) technique provides optical access to the sample, homogeneously heated to high temperatures, and is widely used for *in situ* observations and spectroscopic measurements. Nevertheless, the pressure range achievable with the conventional externally heated hydrothermal DAC is limited by low resistance of diamond anvils to thermal stress at high temperatures. In this study we used a modified external heating system combined with the lever type DAC (Whale cell) in order to reach simultaneous high temperatures and high pressures for *in situ* measurements.

Visual observations and Raman spectroscopy were carried out for $C_2H_2O_4$ composition in the temperature range to 720 degree C and pressure range to 6.4 GPa. Above 105 degree C and 1 GPa a dissociation of starting material with the formation of CO_2 solid, H_2O and CO fluid phases was observed. At temperatures above 377 degree C and pressures above 2 GPa a polycrystalline phase was stable, which transformed to a solid carbon phase above 565 degree C and 5.5 GPa. Raman spectra of the solid carbon phase contain two broad peaks, consistent with the *D* breathing mode and *G* bond-stretching mode of C atoms. Therefore, solid phases are stable in this system in the broad region of temperatures and pressures. Obtained results have interesting implications for transportation mechanism of water and CO_2 into the Earth’s interior in cold subduction zones.

Keywords: Externally heated diamond anvil cell, Raman spectroscopy, C-O-H fluid

Investigation of H-D isotope effect in a hydrous mineral using neutron diffraction

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The isotope fractionation factor is important to discuss the origin of minerals and rocks because it is affected by the environment of where the mineral is formed. Hydrogen and deuterium is known to have a large isotope fractionation that comes from a different in mass. Based on experiments at ambient pressure, Graham et al (1980) indicated the importance of O-H...O geometry on D/H isotope fractionation showing that the mineral with shorter O...O distance of hydrogen bond tends to deplete in deuterium. This result suggests the importance of pressure effect on hydrogen isotope fractionation because the pressure changes the O...O distance in minerals significantly.

In this study, we investigated the evolution of hydrogen bond geometry in distorted rutile type mineral guyanite (CrOOH) under pressure using neutron diffraction. This mineral is known to have a large difference in the unit cell volume between CrOOH and CrOOD at ambient pressure. However the previous X-ray diffraction study (Sano-Furukawa et al., 2012) has indicated that this volume difference merges at around 5 GPa. We attempt to explain the cause of the phenomena from the crystallographic view.

Neutron diffraction experiment was conducted at the PLANET beamline in J-PARC by using Paris-Edinburgh press. We observed the change in deuterium distribution from order to disorder at around 3~5 GPa. In the presentation, the relation between the change of hydrogen bond geometry and reduced partition function ratio will be discussed.

Keywords: hydrogen bond, neutron diffraction, hydrous mineral

Fluorine and chlorine fractionation during magma ocean solidification: Implications for the origin and abundance of terrestrial halogens

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The isotopic compositions of terrestrial volatiles, such as hydrogen, nitrogen, and chlorine, are very similar to that of volatile-rich CI-CM type carbonaceous chondrites [e.g, 1, 2], suggesting that terrestrial volatile elements may have been mainly derived from these types of asteroids during the formation of the Earth. However, the abundance pattern of volatiles in the silicate Earth is different from carbonaceous chondrites [e.g., 1]. More specifically, super-chondritic H/N, Ar/Xe, and F/Cl ratios of the Earth have been reported [e.g., 1]. The simplest explanation for these observations is that terrestrial volatiles were delivered and fractionated during the main accretion phase. If this is the case, elucidating the fractional processes of volatiles in terrestrial planets is a key to understanding the origin of volatiles in terrestrial planets.

In this study, we focus on the super-chondritic F/Cl ratio of the Earth. The super-chondritic F/Cl ratio of the Earth indicates the selective loss of chlorine and the preferential retention of fluorine. Previous experimental studies have shown that fluorine and chlorine are moderately to highly lithophile under high pressure and high temperature conditions [3, 4, 5]. This indicates that fluorine and chlorine would have been partitioned into mantle during core-mantle separation. Thus, fluorine and chlorine fractionation would have occurred during magma ocean solidification and/or subsequent degassing processes. In order to test the former case, we experimentally investigate the solubility of fluorine and chlorine in mantle minerals at the transition zone and lower mantle conditions.

Starting materials were composed of high-purity oxides (SiO_2, Al_2O_3, CaO, MgO, FeO) and iron metal (Fe) with enstatite chondritic proportion [e.g., 6]. Fluorine and chlorine were added to the mixture as CaF_2 and $FeCl_2$, respectively. The starting materials were encapsulated into a graphite capsule. The experiments were performed at 18-25 GPa and 2123-2273 K using the multi-anvil press at Ehime University. The elemental compositions and phase assemblies of recovered samples were determined by raman spectroscopy, microfocused X-ray diffractometry, and electron microprobe analyzer. The abundances of fluorine and chlorine in minerals were determined by nano-scale secondary ion mass spectrometry at Atmosphere and Ocean Research Institute.

The preliminary experimental results show that the solubility of fluorine in $MgSiO_3$ majorite is approximately one order of magnitude higher than that of chlorine. Although we did not investigate the mineral-melt partition coefficients for fluorine and chlorine, the experimental results show that the crystallization of majorite in a deep magma ocean might have increased F/Cl ratios of the solid mantle. If the compatibility of fluorine and chlorine with other mantle minerals is similar to the case of majorite, the degassing of volatiles with high F/Cl ratios from the mantle after the escape of chlorine-rich primordial atmospheres might have yielded the current abundance pattern of terrestrial halogens. This hypothesis is consistent with the recent proposed scenario for explaining terrestrial super-chondritic Ar/Xe ratio [7].

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Keywords: Halogen, Magma ocean

Volatile element transport within a closed system constrained by halogens and noble gases in mantle wedge peridotites

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Halogen and noble gas systematics are powerful tracers of volatile recycling in subduction zones. The presence of noble gases and halogens with seawater and sedimentary pore-fluid signatures in exhumed mantle wedge peridotites and eclogites from the Sanbagawa-metamorphic belt, southwest Japan [1,2], and in seafloor and forearc serpentinites [3] along with seawater-like heavy noble gases (Ar, Kr, and Xe) in the convecting mantle [4] strongly suggest the subduction of sedimentary-pore-fluid-like noble gases and halogens.

In order to determine how volatiles are carried into the mantle wedge and how the subducted fluids modify halogen and noble gas compositions in the mantle, we analyzed halogen and noble gas compositions of mantle peridotites containing H_2O-rich fluid inclusions collected at volcanic fronts from two contrasting subduction zones (the Avacha volcano of Kamchatka arc and the Pinatubo volcano of Luzon arcs) and orogenic peridotites from a peridotite massif (the Horoman massif, Hokkaido, Japan) which represents an exhumed portion of the mantle wedge [5].

The halogen and noble gas signatures in the H_2O-rich fluids are similar to those of marine sedimentary pore fluids and forearc and seafloor serpentinites. This suggests that marine pore fluids in deep-sea sediments are carried by serpentine and supplied to the mantle wedge, preserving their original halogen and noble gas compositions.

On the other hand, the measured Cl/H_2O and $^{36}Ar/H_2O$ in the peridotites are higher than those in sedimentary pore fluids and serpentine in oceanic plates. The halogen/noble gas/H_2O systematics are interpreted within a model where water is incorporated into serpentine in a closed system formed along fracture zones developed at the outer rise, where oceanic plates bend prior to entering subduction zones, preserving Cl/H_2O and $^{36}Ar/H_2O$ values of sedimentary pore fluids. Dehydration–hydration process within the oceanic lithospheric mantle maintains the closed system until the final stage of serpentine dehydration. The sedimentary pore fluid-like halogen and noble gas signatures in fluids released at the final stage of serpentine dehydration are preserved due to highly channelized flow, whereas the original Cl/H_2O and $^{36}Ar/H_2O$ ratios are fractionated by the higher incompatibility of halogens and noble gases in hydrous minerals. The fluids are supplied to the mantle wedge beneath volcanic fronts and trapped as fluid inclusions in mantle wedge peridotites.

Some studies have argued that the sources of trace elements and water are decoupled in subduction zone magmas and that the major source of water is serpentine. Halogen and noble gas signatures found in the peridotites investigated here reveal that serpentine supplies a significant amount of water to the mantle wedge beneath volcanic fronts, and that this water is not strongly decoupled from these two groups of elements. The seawater-like noble gases in the convecting mantle [4] can be also explained by deeper subduction and/or involvement of the noble gas signatures observed in this study, to the convecting mantle.

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Keywords: halogen, noble gas, mantle, subduction, slab fluids

Systematics of volatile elements in melt inclusions from the proto-Izu-Bonin-Mariana arc (30-40 Ma)

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IODP Expedition 351 “Izu-Bonin-Mariana (IBM) Arc Origins” drilled at Site U1438 in the Amami Sankaku Basin, about 100 km west of the Kyushu-Palau Ridge, a remnant of the IBM arc. We recovered 1611-m-long cores composed of 150-m of igneous basement (Unit 1), which were formed when subduction initiated at ~52 Ma, and 1461-m of sediments (Units I, II, III and IV), which were deposited immediately after subduction initiation (Fig. **a**). We focused on Unit III (30-40 Ma) and have already analyzed the major elements and volatile elements (S and Cl) of more than 300 melt inclusions from Unit III with electron probe microanalyzers and have discussed the causes for temporal changes in volcanism of the proto-IBM arc (Brandl et al., 2017; Hamada et al., under review).

In order to extend our previous studies, we analyzed the concentrations of four volatile elements (H_2O, S, Cl, F) and P_2O_5 of a sub-set of 56 representative melt inclusions by Secondary Ion Mass Spectrometry (SIMS) at the Kochi Institute for Core Sample Research of JAMSTEC. Quantification of volatile elements was based on callibration lines and volatile standards by Shimizu et al. (2017). Generally, abundances of volatile elements increase from 40 Ma to 30 Ma (Figs. **b-e**), along with incompatible elements such as K_2O and P_2O_5 (Fig. **f**). As a result, the ratios of volatile elements to incompatible elements, such as F/K_2O and Cl/K_2O, are almost constant from 40 Ma to 30 Ma, irrespective of the rock series (low-K series or medium-K series) and chemical groups (clusters) of melt inclusions assigned by Hamada et al. (under review) (Figs. **g** and **h**). Because frontal-arc volcanoes and rear-arc volcanoes of the IBM arc are characterized by low-K series rocks and medium-K series rocks, respectively, these results suggest that (i) the volcaniclastics that accumulated at Site U1438 originate from both frontal-arc volcanism and rear-arc volcanism, and that (ii) volcanism around Site U1438 shifted from frontal-arc to rear-arc volcanism over time.

Volatiles in silicic (dacitic~rhyolitic) melt inclusions (Cluster 6 melt in Figs. **g** and **h**) seem to behave differently from those dissolved in mafic melts. Fluorine concentration of silicic melt inclusions (600-800 ppm) does not increase with increasing K_2O (Fig. **g**). Silicic melt inclusions mainly occur at ~30 Ma, the upper level of Unit III, which corresponds to the timing just before the arc rifting and back-arc opening of the IBM arc from ~25 Ma. These silicic melts may be a products of fractional crystallization or may be crustal anatexis (Ikeda and Yuasa, 1989). With respect to the occurences of extremely Cl-rich melt inclusions (Cluster 2 melt inclusions in Figs. **g** and **h**), we discuss two possibilities for their origin: one is that they are the “halogen-rich andesite melts” as proposed by Straub and Layne (2003) for the IBM arc; the other is brine assimilation in a submarine hydrothermal system. No F enrichment is observed for extremely Cl-rich (Cluster 2) melt inclusions, and they cannot be “halogen-rich andesite melts” (Straub and Layne, 2003). Therefore, brine assimilation likely explains the origin of extremely Cl-rich melt inclusions.

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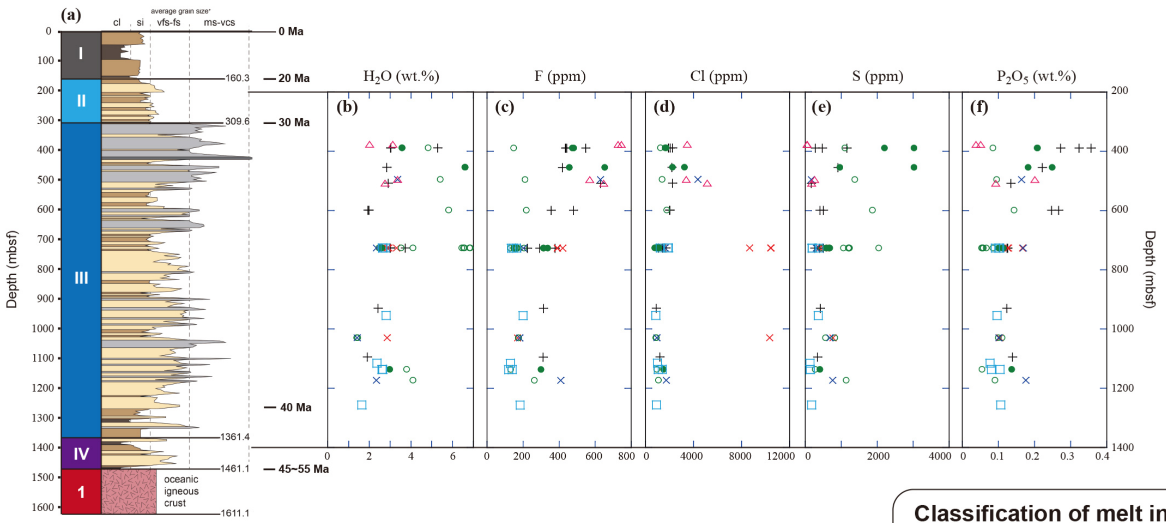
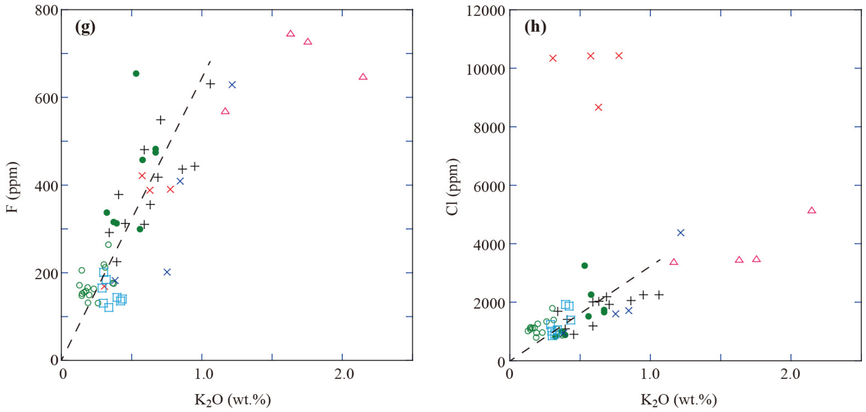
Keywords: IODP, Izu-Bonin-Mariana arc, Amami Sankaku Basin, Melt inclusion, SIMS





Classification of melt inclusions by Hamada *et al.* *(under review)*

+ **Cluster 1 melt inclusions**
(Medium-K tholeiitic series rocks)

× **Cluster 2 melt inclusions**
(Extremely high-Cl melt inclusions)

○ **Cluster 3 (low-K) melt inclusions**
(High-S melt inclusions)

● **Cluster 3 (medium-K) melt inclusions**
(High-S melt inclusions)

× **Cluster 4 melt inclusions**
(High-Cl melt inclusions)

□ **Cluster 5 melt inclusions**
(High-Mg calc-alkaline andesites)

△ **Cluster 6 melt inclusions**
(Dacitic~rhyolitic melt inclusions)

Fluid-fluxed melting of the mantle as the cause of intraplate magmatism over a stagnant slab: implications from Fukue Volcano Group, SW Japan

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The Pacific Plate subducting from the Japan Trench has accumulated in the mantle transition zone beneath NE Asia, and intraplate magmatism has been active above the stagnant Pacific slab. Since the discovery of a remnant of the Pacific slab in the mantle transition zone (Fukao et al., 1992), slab stagnation and its relationship with intraplate magmatism has received growing attention. In particular, electric conductivity observations have suggested a remarkably hydrous mantle transition zone beneath NE China (e.g., Kelbert et al., 2009), and experimental, seismic, and numerical studies have indicated that dehydration of the stagnant slab plays a significant role in magma genesis (e.g., Ohtani and Zhao, 2009). In this study, a petrological and geochemical study was carried out on basalts from a monogenetic volcano (Akashima Volcano) in the Fukue Volcano Group, SW Japan, to clarify the role of deep dehydration of the stagnant Pacific slab in the magmatism.

Akashima is a small volcanic island (0.52 km^2), located southeast of Fukue Island, which is at the southwestern end of the Goto Islands. The eruption products (46.8–51.0 wt.% SiO_2) consist of a low-Si group (< 48.4 wt.%) and a high-Si group (> 48.8 wt.%), and the former predates the latter. The modal abundance of phenocrysts is typically ˜5% olivine for the low-Si group. Some samples additionally contain small amounts (< 0.5%) of plagioclase phenocrysts. The products of the high-Si group typically contain ˜5% olivine and ˜10% plagioclase phenocrysts. The low-Si samples have higher TiO_2 and rare-earth element concentrations, and higher $^{87}Sr/^{86}Sr$ ratios and lower $^{143}Nd/^{144}Nd$ and $^{206}Pb/^{204}Pb$ ratios than the high-Si samples.

The low-Si samples have distinct incompatible element concentrations and Sr, Nd, and Pb isotopic compositions from those of the high-Si samples. This observation suggests that the low-Si and high-Si magmas were not produced by a series of magmatic processes. The most magnesian samples in each group are primitive (> 8 wt.% MgO), and therefore, both the low-Si and high-Si magmas originated from different source mantle materials. The H_2O contents of the primary magmas were estimated as ˜2 wt.% for both the low-Si and high-Si groups. Analyses using multicomponent thermodynamics suggested that the low-Si and high-Si primary magmas were generated at ˜2.5 GPa and 1345ºC and at ˜1.8 GPa and 1285ºC, respectively. The melting pressure of ˜2.5 GPa for the low-Si magma suggests its generation in the asthenospheric mantle. On the other hand, the melting pressure of ˜1.8 GPa for the high-Si magma coincides well with the depth of the asthenosphere–lithosphere boundary at 60–65 km (˜1.8 GPa) beneath Fukue Island (Zhu et al., 2006). Therefore, the high-Si magma is considered to have been generated by interaction of the low-Si magma with the SCLM.

The H_2O/Ce ratios of the primary low-Si magma of ˜650 is higher than the range of 100–250 for normal MORB (Michael, 1995), and is closer to the range found in subduction zone magmas (800–10000; Ruscitto et al., 2012). This observation suggests that the source mantle of the Akashima magma is significantly hydrous compared with the normal asthenospheric mantle. The mantle potential temperature for the low-Si Akashima magma, calculated as ~1300ºC, is within the range for subduction zone magmas (1150–1350ºC; Lee et al., 2009). Therefore, the Akashima magma may have been generated primarily by melting of the ambient asthenospheric mantle at ~2.5 GPa, triggered by an influx of fluids originating from dehydration of the stagnant Pacific slab, similar to the case of the Chugaryong Volcano in Korea (Sakuyama et al., 2014). The water storage capacity of the upper mantle is significantly lower than that of the underlying mantle transition zone. Therefore, the release of fluids from the mantle transition zone to the upper mantle may suggest that the transition zone beneath Akashima was locally saturated with water.

Keywords: Intraplate magmatism, Mantle transition zone, Water, Stagnant slab

Temporal variation of He isotopes in fumarolic gases at Mt. Hakone, Japan

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Volcanic and seismic activity was intensified at Mt. Hakone in 2015. Earthquake swarm activity was observed in the end of April 2015, which was followed by small eruptions at the Owakudani geothermal area from June to July. Eruptions and seismic activity had been frequently observed till about October 2015, and the activity became calm in the end of the year. From May 2015, we have been investigating ^{3}He/^{4}He ratios in fumarolic gases collected at two sites in the Owakudani geothermal area, located at Mt. Kamiyama which is one of the central cones of Hakone caldera. One fumarolic gas (T) is located near the parking of the geothermal area, and another fumarolic gas (S) is located on the north flank of Mt. Kamiyama, 500m far from the fumarole T. Helium isotopes in collected gases were measured with Helix-SFT or VG5400 mass spectrometer housed at Atmosphere and Ocean Research Institute. ^{3}He/^{4}He ratios in samples were calibrated against atmospheric value (R_a: ^{3}He/^{4}He = 1.38x10^{-6}). Since He isotopes are useful magmatic fluid tracers, temporal variations of ^{3}He/^{4}He ratios may provide information about volcanic activity. ^{3}He/^{4}He ratios at two fumaroles slightly increased until August 2015, also after the small eruptions from June to July. The corrected ^{3}He/^{4}He ratio at the fumarole T increased from 6.53 R_a (June) to 6.72 R_a (August), while that of the fumarole S increased from 6.57 R_a (May) to 6.76 R_a (August) in 2015. After that, the ratios at two fumaroles started to decrease. Corrected ^{3}He/^{4}He ratios at fumarole T and S decreased to 6.37 R_a (October 2016) and 6.45 R_a (September 2016), respectively. These variations may reflect hydro-volcanic activity at Mt. Hakone. At Mt. Ontake, the magmatic high He isotopic ratio was supplied into geothermal systems associated with excess water vapor which could have provided the driving force for the 2014 eruption (Sano et al., 2015). There is a possibility that elevation of He isotopic ratios may be related to vapor accumulation and potential activation of Mt. Hakone, while decrease in the ratios may reflect inactivation. We will also present N and Ar isotope data, and discuss gas geochemistry along the volcanic activity of Mt. Hakone.

Keywords: Mt. Hakone, Volcanic gas, Helium isotope

Geochemistry of olivine melt inclusions in Pitcairn Island basalts: A multiple-instrument approach

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Ocean island basalts (OIBs) provide essential information on evolution of the Earth’ s mantle, because OIBs are sourced from plumes from the deep mantle that include recycling materials. OIBs at the Pitcairn Island show distinct geochemical characteristics from other OIBs with their enriched isotopic signatures, so called enriched mantle 1 (EM1) component. This particular feature could have been caused by the involvement of recycled materials including chemically differentiated oceanic plate slab or delaminated continental lithosphere and lower crust (e.g., Eisele et al., 2002). In order to understand behavior of volatile elements during mantle recycling, we analyzed H_2O, CO_2, F, S, and Cl in the olivine-hosted melt inclusions in the Pitcairn OIBs using a secondary ion mass spectrometry (SIMS). Major and trace elements, and Pb isotope compositions were also determined on the same melt inclusions with an electron probe micro analyzer (EPMA) and a laser ablation-inductively coupled plasma-mass spectrometer (LA-ICP-MS). Most of the olivine-hosted melt inclusions contain microcrystals due to slow cooling after emplacement of the host lavas. In the preliminary study, we found that measured element concentrations were blurred by the microcrystals. Therefore, we homogenized the melt inclusions by a heating and quenching method. Homogenization experiment was performed in a $CO_2 + H_2$ atmosphere using an electric furnace. For the first step, liquidus temperature of the melt inclusions was explored by altering the furnace temperature at every 25 ˚C between 1100 ˚C and 1350 ˚C. We found that the liquidus temperature was between 1150 ˚C and 1175 ˚C. All the olivines were then heated just above the liquidus temperature at 1150 ˚C or 1175 ˚C for 10 minutes and quenched. Previous studies showed that H_2O may be diffused out from a melt inclusion through host olivine during homogenization. In order to assess the effect on H_2O diffusion, we also heated naturally homogeneous melt inclusions in a pyroclastic rock and compared H_2O concentrations before and after heating. In this presentation, effects of homogenization on volatile compositions will be discussed. After corrections for the effects of post-entrapment crystallization, concentrations of the volatile elements together with the major and trace elements, and Pb isotopes in the melt inclusions are used to explore volatile contents in the source mantle of the Pitcairn OIBs.

Volatiles in olivine-hosted melt inclusions in HIMU basalts from Raivavae, South Pacific

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Volatile cycle in the mantle has been poorly constrained because of limited number of studies thus far on volatile compositions in the mantle-derived ocean island basalts. We performed in-situ geochemical analyses on the olivine-hosted melt inclusions (MI) from Raivavae Island in the South Pacific. MIs were homogenized on the heating stage before chemical analyses. Compositions of major elements, trace elements, volatile elements, and Pb isotopes were determined by the combination of analytical techniques using EPMA, LA-ICP-MS, and SIMS. Carbon dioxide is distributed in both glasses and shrinkage bubbles in MI. We measured CO_2 density in bubbles using micro Raman spectrometry and determined the volume ratio between bubbles and MI applying micro X-ray CT technique to calculate CO_2 in bubbles, which is added to CO_2 in glasses measured with SIMS to determine the total CO_2 in MI.
The basalts from Raivavae are classified into two groups in terms of Pb isotopes. Most MI in less radiogenic-Pb basalts have similar Pb isotopic compositions to host basalts. MI in radiogenic-Pb basalts generally exhibit radiogenic (HIMU) character, but they show larger isotopic variation than the host basalts. It is notable that small number of MI have different Pb isotope ratios from host basalts, suggesting mingling of radiogenic melts and less radiogenic melts during olivine crystallization. Despite some exceptions, MI with radiogenic Pb isotopes are characterized by lower SiO_2 and higher CaO, La/Yb, and Nd/Hf than MI with less radiogenic Pb. These facts suggest that the radiogenic-Pb (HIMU) melts were formed by low-degree partial melting of carbonated source. MI with radiogenic Pb clearly show elevated Cl/Nb and F/Nd relative to MI with less radiogenic Pb. Enrichment of Cl and F in radiogenic-Pb melts implies that these elements have been transported into the mantle via subduction of hydrothermally altered oceanic crusts. The correlation of H_2O/Ce and CO_2/Nb with Pb isotopes is somewhat blurred, probably owing to degassing and diffusive loss of CO_2 and H_2O. However, MI with the most radiogenic Pb have the lowest H_2O/Ce and the highest CO_2/Nb, which may also reflect the feature of the basalt source.

Keywords: Volatile, Ocean island basalts, Melt inclusion

Determination of water content of natural talc: application to a recipe for hydrogen manometry

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Hydrogen manometry is a conventional yet powerful, absolute technique for the determinations of water contents of rocks and minerals. The concentration of water in a stoichiometric pure talc was determined by the hydrogen manometry technique so that accuracy of this technique was assessed. The talc sample was from Haicheng mine, China. Bulk chemical composition of the talc sample is ($Mg_{2.930}$, $Fe_{0.001}$) ($Si_{4.003}$, $Al_{0.002}$) on the anhydrous 11 oxygen basis (Matsumura Sangyo Co., Ltd., pers. comm.), which is nearly identical to that of the ideal talc $Mg_3Si_4O_{10}(OH)_2$. Powder X-ray diffraction also shows that the sample consists thoroughly of talc, free from any possible impurity.

About 20 mg of the <38um size fraction of the talc sample was loaded in a Pt crucible and sealed in a quartz-glass reaction vessel. The reaction vessel was then connected to a high vacuum line, and the Pt crucible was heated to 1000 ˚C at the rate of ~1 ˚C/sec using an induction furnace to let the talc sample completely degassed. Degassing was monitored with a Pirani gauge. Degassing from the talc started at around 500 ˚C and ended by 800 ˚C. During the degassing, the released gas was continuously sublimated using liquid nitrogen, so that the gas pressure buildup in the vacuum line was kept not to exceed 10 Pa. The H_2O was cryogenically purified using an acetone - solid CO_2 mixture slurry, and then converted to H_2 gas in a deleted uranium furnace at 700 ˚C. The H_2 gas was transferred into a calibrated volume with a Toepler pump, and the pressure of the H_2 gas was determined. Complete thermal decomposition of the talc to enstatite + amorphous silica was confirmed by X-ray diffraction of the residue after degassing. Repeated measurements of the talc sample yielded H_2O content of 4.71 ±0.05 wt%. This value agrees with 4.75 wt% H_2O of the ideal talc $Mg_3Si_4O_{10}(OH)_2$ within analytical uncertainty.

The gas pressure buildup in the vacuum line could reach an order of kilopascal (one hundred times more than that in the present study) if the released H_2O gas was not continuously sublimed during the degassing process. Clog et al. (2012; Geochim. Cosmochim. Acta 83, 125-137) showed that at high temperatures under such high H_2O gas pressure, a large fraction of the H_2O gas (up to 20%) is retained in the coexisting Pt alloy, which results in a poor yield of the gas in the hydrogen manometry. Diffusion flux of H_2O (H) into Pt metal is proportional to square root of the pressure of surrounding H_2O gas. Results of the present study suggest that holding H_2O gas pressure at less than 10 Pa is a key to have accurate data from the hydrogen manometry.

Keywords: water, hydrogen manometry, talc