

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 CO₂ 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 ¹³⁰Xe) 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/fissionogenic xenon isotopes, whose ratios are typical of plume-derived reservoirs. The Xe contribution, coming from the spontaneous fission of ²⁴⁴Pu, is 2.26±0.28 %. The Xe contribution from spontaneous fission of ²³⁸U 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°C (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-SO₄ 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°C) gas vents. In 2015-2016 we measured fluxes of SO₂ 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, CO₂, 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 SO₂, CO₂ 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 SO₂) 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 CO₂/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 SO₂), 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/³He ratios, and radiogenic isotope signatures to distinguish between various arc, back-arc, and hotspot affinities in the region. Along the NWLSC elevated ³He/⁴He 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, ³He/⁴He - C/³He 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% H₂O, 1200 ppm CO₂, 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 CO₂ content was possibly 3–4 times higher because the majority of the original CO₂ can be lost to a shrinkage bubble (e.g., Wallace, 2015). The $\delta^{34}\text{S}$ 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 $\delta^{34}\text{S}$ 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 S²⁻ 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 CaSO₄. 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 H₂O-CO₂-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, SO₄²⁻ ion, gypsum (CaSO₄·2H₂O) and anhydrite (CaSO₄) were found in the fluid inclusions. Kumagai et al. (2014, Contrib Mineral Petrol) reported a possible presence of Mg-sulfate hydrate in CO₂-H₂O-Cl fluid inclusions in the Ichinomegata lherzolite xenoliths sampled in a rear arc side of northeastern 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 Fe³⁺/Fe²⁺ 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 sulfate 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 CO₂-rich melt in the asthenosphere evidenced by petit-spot

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Carbon dioxide (CO₂)-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 CO₂ and 1% of H₂O (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 CO₂-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, CO₂ and H₂O 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 CO₂-rich silicate melt are produced in the asthenosphere because of the existence of CO₂-rich fluid or carbonate. Based on solidus for the peridotite–CO₂–H₂O system at approximately 3 GPa, the CO₂-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) CO₂-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 CO₂-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 CO₂. For future studies, geochemistry of petit-spot lavas could contribute to quantitative determination of amount of CO₂ 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. H₂O 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, hawaiiite, trachyte, and phono-tephrite 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 eclogite at 3 to 5 GPa under slightly hydrous conditions. Under active shield 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 acidic rocks found from south flank of Kilauea by Sisson et al (2002). This model can also explain why alkali acidic magma (mugearite, hawaiiite) 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 $1-3 \times 10^{11} \text{ kg yr}^{-1} H_2O$ and $2-4 \times 10^9 \text{ kg yr}^{-1} Cl$, 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 $F [ppm] = (477 \pm 7) \times H_2O [wt.\%] + (47 \pm 2)$. This F-H₂O mantle array represents melting of mantles ranging from a near-dry depleted MOR mantle (DMM: H₂O = 100ppm; H₂O/F=10) to a hydrous primitive mantle (PM: H₂O = 750ppm; H₂O/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 (H₂O-enrichment) in arcs, negatively (H₂O-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-H₂O 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 $^3\text{He}/^4\text{He}$ 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, CO_2 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 CO_2 bubbles due to the decrease of solubility of CO_2 in a magma with the decreasing pressure. While in the reduced state, CO_2 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, SO_2 is degassed easily at a shallow depth from a magma. In the reduced state, S reacts easily with metal elements such as Fe or Cu and forms sulfide minerals like FeS, FeS_2 or CuS. When sulfide minerals are formed, they remain at a depth without forming volatiles. H_2S also works as volatiles, but its chemical behavior in volcanic gas would be different from that of SO_2 .

N exists generally as N_2 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 oxidized state. Furthermore, in a much reduced state, N would exist as NH_3 and it might be not easy to be degassed from a deep mantle.

In the case of H, H_2O is most common form at a shallow depth in the oxidized state. When recycled H_2O goes into the deep mantle and the deep mantle is in the reduced state, however, H_2O might be not stable and would be decomposed.

Thus, some active elements would change their chemical form 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-chondrites (1). Further, significant depletion of H, C, N, S related 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.

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

***In situ* optical study of H₂O-CO₂-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 C₂H₂O₄ 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 CO₂ solid, H₂O 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 CO₂ 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