

Research of Helium Isotopes in Taiwan: The Legacy of Dr. Tsanyao Frank Yang

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Helium isotope systematics is a powerful proxy to distinguish fluid origins and conveys fruitful geological information. In the past several decades, this robust isotope systematics had offered pivotal knowledge on many key issues in Earth and planetary sciences. It revealed essential geological information of Taiwan as well. Taiwan is located on the junction of two subduction systems-Ryukyu Arc and Luzon Arc. The geotectonic setting is complex and intriguing.

Dr. Tsanyao Frank Yang was the pioneer of gas geochemistry studies in Taiwan. He established the first gas geochemistry laboratory in National Taiwan University in 1998 and started exploring all possible research topics on and around this tectonic-active island. In the past two decades, his research covered volcanic/hydrothermal gas studies, volcanic activity monitoring, gas hydrate exploration, soil gas as a tool to locate fault traces, soil gas flux measurement, earthquake precursory, mud volcanoes, low-temperature geochronology and many more. He died of pancreas cancer in March 2015. He was a warm and enthusiastic mentor, a prolific scientist and a great friend. He will always be remembered.

Here we present Dr. Yang's achievement on helium isotopes studies in Taiwan throughout his research career. We integrate all the research results from his team and summarize the observations. We will show the distribution of helium isotope ratios in Taiwan and its implications on tectonic settings.

Keywords: Tsanyao Frank Yang, Taiwan, Helium isotopes

Volatile behaviors at an immature stage of subduction zone inferred from volcanic glasses in the Bonin fore-arc (IODP Expedition 352)

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IODP Expedition 352 was targeted to drill the entire magmatic sequence comprising the outer Bonin fore-arc to elucidate early subduction dynamics. During the expedition, a total of 1.22 km of igneous basement related to subduction initiation was cored from four sites (U1439, U1440, U1441, U1442). Two sites (U1440 and U1441) located nearer to the trench (stratigraphically lower and older sequence than U1439 and U1442), recovered igneous rocks at the basement that are mostly fore-arc basalts (FABs). From other two sites (U1439 and U1442) located ~15 km west from U1440 and U1441, boninites were recovered.

From all sites, we recovered fresh volcanic glasses manifest as chilled margins of pillow lavas, massive lavas, hyaloclastites and pyroclastic deposits. In order to constrain behaviors of volatiles at an immature stage of subduction zone, we analyzed volatile (H_2O , CO_2 , F, Cl, S) and P_2O_5 concentrations of 100 volcanic glasses (31, 23, 1 and 45 samples from U1439, U1440, U1441 and U1442, respectively) using SIMS (CAMECA IMS 1280-HR) at JAMSTEC.

Glasses from the boninite sites (U1439 and U1442) are higher in H_2O (~1.9 wt%) at the lower parts of the holes and slightly lower in H_2O (~1.6 wt%) at the upper parts of the holes and are remarkably in low CO_2 (< several ppm: below detection limit, DL) and S (7-130 ppm). Their F and Cl contents are 66-166 ppm and 357-981 ppm, respectively.

On the other hand, most glasses from the FAB sites (U1440 and U1441) have various H_2O contents (0.11-0.57 wt%) and measurable CO_2 contents (67-151 ppm) with high S contents (776-1250 ppm). Their F and Cl contents are 62-111 ppm and 101-597 ppm, respectively. Three highly evolved glasses (MgO 3.3 wt%) probably from the same glassy layer from U1440 are high in H_2O (0.80 wt%), F (300 ppm) and Cl (2900 ppm). We also found a boninitic glass between FAB lavas from U1440, in terms of H_2O (1.95 wt%), CO_2 (below DL) and S (301 ppm).

F/P ratios of glasses, which reflect their original source mantle, are 0.49 ± 0.03 (1 standard deviation) for boninites and 0.28 ± 0.02 for FABs. Since the F/P ratio of the depleted upper mantle (DM) is 0.27 ± 0.11 , those of FABs have not been influenced by subducting materials. However, 10-50 times higher Cl/K (0.6-4) and 2-4 times higher H_2O/F (24-56) ratios of FABs than those of DM indicate influx of a small amount of Cl-rich fluid to the mantle wedge at the very beginning of subduction formation. Boninites are highly enriched in H_2O (H_2O/F : 110-298), but not in Cl (Cl/K: 0.1-0.4) relative to FABs, indicating that contribution and composition of subducting materials have changed with time.

Keywords: subduction zone, volatiles, IODP

Noble gas and halogen subduction processes constrained by the analysis of olivines from Izu-Mariana arc lavas

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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], mantle-derived xenoliths from Kamchatka and Luzon arcs [3], and in seafloor and forearc serpentinites [4] along with seawater-like heavy noble gases (Ar, Kr, and Xe) in the convecting mantle [5] strongly suggest the subduction of sedimentary-pore-fluid-like noble gases and halogens. The noble gas and halogen compositions of olivines in arc lavas of the Izu-Mariana subduction zone were determined to develop a better understanding of the processes that control the return of these volatile and highly incompatible elements into the mantle. Trace amounts of halogens (Cl, Br, and I) in the olivine samples were measured using a combination of neutron irradiation and noble gas mass spectrometry [6].

The $^3\text{He}/^4\text{He}$ ratios of samples are in the range of the mid-ocean ridge basalt (MORB) value. This is consistent with helium isotope ratios of the subduction zone mantle xenolith [3], which indicates a considerably low contribution to the mantle wedge beneath the arc of radiogenic ^4He in the subduction fluids observed in the Sanbagawa samples exhumed from depths in the range from 30 to 100 km [1,2]. In contrast, the $^{40}\text{Ar}/^{36}\text{Ar}$ ratios for each volcano (299-620) are significantly lower than the MORB source (up to 32,000 [5]), which indicates significant involvement of atmospheric Ar ($^{40}\text{Ar}/^{36}\text{Ar} = 296$) in the arc magmas. Systematically higher $^{40}\text{Ar}/^{36}\text{Ar}$ ratios in the rear arc than in the volcanic front suggest that subduction of seawater-derived Ar has a significant effect on the noble gas composition of the magma-generation region. Although the halogen compositions of most of the olivines are close to that of MORB-source mantle, some samples from the rear-arc regions show a significant contribution from pore-fluid-derived halogens. Combined with the noble gas results, halogen-poor fluid associated with atmospheric noble gases may be dominantly released from the subducting slab beneath the arc, while halogen supply from the subducted slab is limited to the magma generation region beneath some volcanoes in the rear arc. This implies the relative persistence of halogens in the subducting slab compared with noble gases.

A simple mass balance calculation of subducted and mantle-derived Ar isotopes reveals that higher subduction flux than that of seawater-derived Ar in the pore fluids of the subducting sediment/crust is required. Although the serpentinitized lithosphere in the subducting slab has been regarded as the best candidate for the carrier of seawater-derived Ar with high subduction flux [4], the ratios of halogens and noble gases to water of slab-derived fluids preserved in the fluid inclusions of subduction zone mantle peridotites are inconsistent with the ratios in serpentinites collected from the Earth's surface. This requires strong coupling behavior of halogens and noble gases with their host water during hydration of the subducting materials, release of aqueous fluids from subducted slab, and upward migration of the fluids in the mantle wedge. It remains unclear whether noble gases and halogens in the subducting materials are completely released beneath the Izu-Mariana rear arc. However, the presence of seawater-like noble gases in the convecting mantle [3] implies that a small portion of seawater-dissolved atmospheric noble gases may be transported to greater depths in the deeper mantle, and then incorporated into the mantle convection.

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Keywords: halogen, noble gas, subduction, mantle, volatile recycling

On the coexistence of high-Mg andesites and ultramafic volcanic rocks

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In order to understand the origin of magmas in the hydrous upper mantle, we have been investigating the phase relation and compositions of phases in the system peridotite-H₂O. Using X-ray radiography technique together with Kawai-type multi-anvil high-pressure apparatus (SPEED-1500, SPring-8, Japan), the second critical endpoint in the peridotite-H₂O system was determined to be at around 3.8 GPa and 1000 °C (corresponding to a depth of ~ 110 km) [1]. It is possible that two fluid phases (i.e., aqueous fluid and hydrous silicate melt) coexist up to 3.8 GPa. Above 3.8 GPa, however, hydrous silicate melt and aqueous fluid in upper mantle becomes indistinguishable from each other and the melting temperature of hydrous mantle peridotite can no longer be defined beyond this critical condition. Using the quenched recovered samples obtained by Mibe et al. [1], chemical compositions of aqueous fluid, silicate melt, and supercritical fluid magma in the vicinity of second critical endpoint were determined by the electron microprobe analyzer. In the run at 3.6 GPa, the composition of aqueous fluid was high-Mg andesitic, whereas the composition of hydrous silicate melt was komatiitic. Our experimental results indicate that high-Mg andesitic magma and komatiitic magma can be generated at the same time as the liquid-fluid immiscibility near the second critical endpoint in the peridotite-H₂O system. Some natural examples on the coexistence of high-Mg andesites and ultramafic volcanic rocks from various tectonic settings and locations around the world will also be presented.

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Keywords: high pressure and high temperature

Redox dehydration melting of mantle transition zone deduced from the H₂O storage capacity

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Knowledge of the H₂O storage capacities of minerals forming mantle peridotite provides essential constraints on estimation of H₂O content and the onset of hydrous partial melting in the mantle. In the mantle transition zone, wadsleyite can store significant amount of H₂O in their crystal structures under extremely high oxygen fugacity. However, the H₂O storage capacity has not been determined under the low oxygen fugacity predicted from the mantle transition zone⁷. Here we report that the H₂O storage capacity of wadsleyite in equilibrium with the peridotite assemblage under lower oxygen fugacity is much smaller than that under higher one. Very low H₂O storage capacity of wadsleyite can attribute to the low H₂O activity in the melt. Considering the more reducing state in the deep mantle, dominant speciation of volatile phases is not H₂O but H₂. Low H₂O activity in the reduced deep mantle requires that H₂O storage capacity in the Earth's mantle is much smaller than that predicted from the maximum H₂O concentration determined under the high oxygen fugacity. The hydrated and oxidised subducted slab will induce "redox dehydration melting" through decrease of oxygen fugacity by the surrounding reduced mantle transition zone. H₂O in the generated melt will be reduced to hydrogen through the oxidation of iron-bearing minerals. Fe-H melt or FeH_x trapping the released hydrogen would become the main carrier of hydrogen into the deep mantle.

Keywords: redox condition, water storage capacity, dehydration

Noble gas incorporation into the deep Earth

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The present state of the Earth evolved from energetic events that were determined early in the history of the solar system. A key process in reconciling this state and the observable mantle composition with models of the original formation relies on understanding the planetary processing that has taken place over the past 4.5Ga and the range of most relevant P-T conditions governing primary segregation and mixing. Recent developments with the laser-heated diamond anvil cell have made possible extension of the conventional pressure limit for solubility and partitioning experiments as well as the direct study of volatile trace elements. In particular, selected results of liquid-liquid, metal-silicate (M-Sil) partitioning are presented for several noble gas and molecular elements in a synthetic chondritic mixture, spanning a wide range of atomic number - helium to iodine. The application of these methods is new and allows extension of geochemical studies performed in larger-volume apparatus. Not only is the attainment of uniform and equilibrium mixing important in this small-sample environment (perhaps 10-100 micrometers in linear dimension depending on the pressure), but also the microanalysis of quenched samples to determine the distribution of minor and trace elements. Systematic results on the solubility of He, Ne and Ar suggests that their incompatibility in solid silicate and metallic phases may not have been as great as previously thought -- and hence are candidates for storage in the deep Earth. Helium solubility in the metal phase relative to that of the silicate suggests the core should be considered a deep Earth reservoir for example. If the core is a reservoir, then the mechanisms for interaction with the lower mantle become important requiring examination of the processes of material exchange at the core-mantle boundary. The interpretation of the results depended on precise microanalysis of LHDAC samples, and the application of UV laser ablation, mass-spectrometric techniques that provided for the first time a spatially resolved depth profile in samples. Attention needs to be paid to the likely mode of solubility - entrapment versus bonded and non-bonded host environments for example - and we attempt to consider the real implications for the Earth in either case.

Keywords: Noble gases, Laser-heated diamond-anvil cell, core-mantle, element partitioning, solubility

Hydrous bridgmanite: Water storage capacity in the lower mantle

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Recently hydrous ringwoodite was found in a natural diamond inclusion, which includes ~1.5 wt% H₂O. In addition, the experimental studies show that wadsleyite and ringwoodite, which are the most abundant minerals in the mantle transition zone, can contain water up to 2.2-2.7 wt% [e.g. Inoue et al., 1995, 1998, Kohlstedt et al., 1996]. These results show that the mantle transition zone is a strong water reservoir in the Earth's interior, and at least locally, hydrous. On the other hand, the water storage capacity in the lower mantle is a matter of debate.

We have been conducting the study for the stability and water solubility of hydrous and nominally anhydrous minerals, and the recent target is the effect of Al. In this process, we found that Al-bearing bridgmanite (Mg-silicate perovskite) can contain significant amount of water. The possible H substitution mechanism can be proposed by means of chemical compositional relationship between Mg, Si, Al and H. In addition, we clarified the possible H position in the bridgmanite by means of the powder neutron diffraction analysis in J-PARC, together with the single crystal X-ray structural analysis in PF. This shows that the significant amount of H (water) can be stored in the Earth's lower mantle.

Because of the H in the bridgmanite, the physical properties of the bridgmanite can be changed. The information is very important to discuss the water content and the composition in the lower mantle. We have also conducted the equation of state and the ultrasonic wave velocity measurements of hydrous bridgmanite in BL04B1, SPring-8 to determine the elastic wave velocities and the elastic properties under high pressure and temperature condition. In this talk, I will introduce about our "hydrous bridgmanite" project.

Keywords: hydrous bridgmanite, lower mantle, Synchrotron X-ray in situ experiment, neutron diffraction, elastic property

Formation of a hydration zone at the bottom of the lower mantle

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One of the major water carriers into the lower mantle is delta-AlOOH-phase H $\text{MgSiO}_2(\text{OH})_2$ solid solution (aluminous phase H) [1]. Our experiments revealed that the solid solution containing water can be stable to the core-mantle boundary region, 120 GPa and 2500 K [2, 3], which is the condition along the normal mantle geotherm. The core-mantle boundary is the region with a large temperature gradient, thus dehydration or dehydration melting is inevitable at the core-mantle boundary. There are three possibilities on the roles of this hydrous phase at the core-mantle boundary region: First, the reaction of this hydrous phase with the metallic core to introduce hydrogen into the core. Second, dehydration melting at the core-mantle boundary which might create a partial molten low velocity zone at the core-mantle boundary. Third, formation of a hydrated zone at the base of the lower mantle by supplying fluid dehydrated at the hot core-mantle boundary. Here, we consider a possible role of this hydrous phase for formation of a hydration region at the base of the lower mantle, the third process listed above.

Ohira et al. [2] revealed that hydration of aluminous bridgmanite creates delta-AlOOH phase and MgSiO_3 bridgmanite containing smaller amount of Al_2O_3 . This hydration reaction can occur by supplying fluid dehydrated at the hot core-mantle boundary. Mashino et al. [4] measured the sound velocity of delta-AlOOH at high pressure and revealed that both V_p and V_s of this phase is greater than the major transition zone minerals such as ringwoodite and majorite, whereas the velocities are lower than bridgmanite at the bottom of the lower mantle. Drop of sound velocities can be expected by formation of delta-AlOOH phase by consuming Al_2O_3 in bridgmanite at the base of the lower mantle. Decrease of the sound velocity can be accounted for the low velocity nature at the core-mantle boundary. Thus, the bottom of the lower mantle may be a second largest water reservoir next to the mantle transition zone.

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Keywords: Lower mantle, Core-mantle boundary, delta-AlOOH, Phase H, Hydration, Low velocity region

Global water cycle constrained by the evolution of dynamic hypsometry

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The presence of liquid water on the surface is one of the important characteristics that make the Earth a unique planet, and it is usually considered to be critical for a planet to be habitable. Also, surface water is often believed to be essential for the operation of plate tectonics, which in turn enables the return of surface water to the planetary interior. The amount of surface water is thus a time-dependent variable that is controlled by the dynamics of Earth's interior. The Earth not only has surface water but also has just a right amount of it to allow the subaerial exposure of continental crust, which is important for the modulation of the atmospheric composition as well as various biogeochemical cycles. To better understand the role of water in the Earth history, therefore, we need to decipher how the distribution of water between the surface and the deep interior has changed with time and how it has affected the surface environment. In this contribution, we focus on reconstructing the history of surface water by assembling relevant observational constraints and theoretical considerations. It is now possible to derive a fairly robust constraint on the history of surface water, at least back to around 3 Ga, by examining the constancy of continental freeboard in light of the evolution of dynamic hypsometry. We also discuss its implications for the coevolution of Earth's interior and surface environment.

Keywords: oceans, mantle convection, plate tectonics

Global fluxes of fluorine and sulfur efficiently released at mid-ocean ridges

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Fluorine and sulfur are major components of high temperature volcanic gases, and significantly affect surface environments due to high chemical activity. Therefore their fluxes between the mantle and surface environments are important to elucidate evolutionary histories of Earth's atmosphere and ocean. We estimated fluorine and sulfur fluxes at mid-ocean ridges (MOR) based on chemistry of submarine vent fluids and MORB vesicles which may reflect components efficiently released from magmas through upward propagation of film ruptures by bubble expansions during decompression[1]. Fluorine flux was constrained by two methods as follows:

1) Multiplication of fluorine concentrations in submarine hydrothermal fluids and the fluid flux at MOR may provide an estimate of fluorine flux at MOR. A worldwide vent chemistry research[2] suggested that vent fluids are depleted in fluorine (<0.74 ppm F) relative to seawater (1.29 ppm F). The global flux of vent fluids of $(8.0 \pm 2.1) \times 10^{15}$ g/y was calculated using a numerical Bayesian inversion procedure to explain the relationship between compositions of hydrothermal fluids and altered sheeted dikes[3]. This value is not consistent with the flux of $(3.1 \pm 0.7) \times 10^{16}$ g/y obtained based on the ^3He concentration of $(1.7 \pm 0.2) \times 10^{-14}$ mol/g (1σ) in 10 high temperature ($>200^\circ\text{C}$) hydrothermal fluids at EPR and MAR[4], and the MOR ^3He flux of (527 ± 102) mol/y[5]. These two fluid fluxes, when multiplied by the maximum fluorine concentration of 3.88×10^{-8} mol/g, provides fluorine fluxes ranging from 3.1×10^8 mol/y to 1.2×10^9 mol/y with an average of $(7.6 \pm 4.5) \times 10^8$ mol/y.

2) Multiplication of F/ ^3He ratios in MORB vesicles and ^3He flux will provide another fluorine flux. We analysed eight MORB vesicles ($13^\circ\text{N}, 17^\circ\text{S}$ on EPR; $15^\circ\text{N}, 30^\circ\text{N}, 37^\circ\text{N}$ on MAR; $24^\circ\text{S}-25^\circ\text{S}$ on CIR) with a crushing technique extracting fluorine and helium simultaneously[6]. Fluorine was extracted into alkaline solution and measured by an ion chromatography (ICS-2100; Thermo Fisher Scientific Inc.), while helium was measured by a noble gas MS (VG5400; Waters Corp.), both housed at AORI. F/ ^3He ratios in vesicles range from 2.0×10^5 to $<2.8 \times 10^7$ with an average of $(1.2 \pm 0.5) \times 10^6$ (1σ), providing a global fluorine flux of $(6.4 \pm 3.1) \times 10^8$ mol/y by multiplying the MOR ^3He flux.

One might calculate a weighted mean of two MOR fluorine fluxes to be $(6.8 \pm 2.5) \times 10^8$ mol/y. However it should be noted that the actual MOR fluorine flux may be lower than this flux because the applied fluorine concentration in hydrothermal fluids is an upper limit, and seawater contamination was not deconvolved for MORB vesicles. We also note that this flux is much lower than flux (1.13×10^{12} mol/y) estimated using the F/ CO_2 ratio in the MORB source and CO_2 flux from the mantle[7], implying that the most part of fluorine resides in the melt and is not released immediately after the oceanic crust production.

Sulfur flux, together with carbon, will be estimated based on chemistry of vent fluids and MORB vesicles, which is similar approach as for fluorine. In addition, comparing MOR and arc fluxes, the global cycles of fluorine, sulfur, and carbon will be discussed in the presentation.

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Keywords: fluorine flux, sulfur flux, carbon flux, mid-ocean ridge basalt, hydrothermal fluid, volcanic gas

Redistribution of noble gases during magma ocean crystallization

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Recent measurements of Xe isotopes place the formation of high $^3\text{He}/^4\text{He}$ mantle to within the first 80 Ma of solar system history. This timeframe coincides with Earth's accretion, leading to the hypothesis that a magma ocean concentrated materials that now comprise the high $^3\text{He}/^4\text{He}$ source. We have initiated an experimental study to better constrain the distribution of noble gases within the solid Earth during magma ocean crystallization and the petrogenesis of high $^3\text{He}/^4\text{He}$ mantle. We report the Ar contents of minerals (bridgmanite, periclase) and liquids (silicate and Fe metallic melts) salient to magma ocean crystallization that were synthesized in the presence of Ar-rich fluids at high pressure. Our initial experiments are conducted with Ar because it is the middle noble gas, so its behavior is most representative of the bulk elemental group. Experiments were conducted using laser-heated diamond anvil cells (DAC) and multi-anvil (MA) apparatus and were analyzed by microprobe and laser ablation techniques.

The Ar contents of the large majority of bridgmanite and periclase analyses in the MA experiments were at or below the WDS detection limit. Detection limits are calculated from counting statistics and nominally approached 20 ppm Ar for longer duration analyses. Saturation of an Ar-rich fluid in the MA experiments was confirmed by high Ar concentration blebs throughout the recovered samples. Laser ablation analyses on a MA experiment yielded highly variable Ar concentrations in bridgmanite, ranging from 450 to 10 ppm. Given the observation of Ar-rich blebs in the MA experiments, we interpret the lower range in Ar concentration as our current best estimate of Ar solubility in bridgmanite. The Ar contents of samples from DAC experiments were more variable, but large areas of laser-heating spots on bridgmanite contain Ar contents at or below the detection limit by EDS microprobe (~100 ppm Ar). Bridgmanite disproportionated to (Mg,Fe)O and SiO₂ in some higher temperature heating spots. These phases also had undetectable Ar concentrations. In a parallel series of experiments, we have also quantified the concentration of Ar dissolved into silicate and Fe metallic liquids at 15 GPa using a DAC. Preliminary measurements by EDS yield Ar concentrations of 4000 ppm for the silicate liquid and Ar concentrations below detection in the Fe metallic liquid. This concentration is similar to previous determinations of Ar solubility in silicate liquids at transition zone pressures.

Our results imply that noble gases are strongly concentrated in silicate liquids over minerals and liquid Fe during magma ocean episodes. High $^3\text{He}/^4\text{He}$ mantle is associated with unradiogenic noble gas signatures. Given this, we suggest that the petrogenesis of high $^3\text{He}/^4\text{He}$ mantle is related to the fractionation of a silicate liquid during a magma ocean episode.

Keywords: noble gases, magma ocean, volatiles

Accurate measurement of H₂O concentration and speciation in silicate glasses using FTIR spectroscopy

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Accurate measurement of H₂O concentration and speciation in silicate glasses is important not only for studies of erupted glasses that use the volatile record to reconstruct eruption processes, but also for studies that use experimental glasses to find e.g. the partition coefficients of other volatiles that partition into H₂O-rich vapour. Fourier Transform Infrared (FTIR) spectroscopy can be used to find not only the overall H₂O concentration (H₂O_t) of silicate glasses, but also the individual concentrations of the two H₂O species: molecular H₂O (H₂O_m), and dissociated hydroxyl groups (OH). Here we discuss key developments and refinements of FTIR methodology with respect to finding the water contents of silicate glasses. Firstly, we demonstrate the importance of using a species-dependent H₂O_t molar absorptivity coefficient when using the 3500 cm⁻¹ H₂O_t absorbance peak to find H₂O_t and OH (indirectly as [OH] = [H₂O_t] - [H₂O_m]) concentrations, and in particular how this can be used to reconstruct the original H₂O contents of glasses that have since undergone secondary hydration at low temperature. Secondly, we discuss the strong dependence on glass composition of 'silicate peaks' at ~1830 cm⁻¹ and ~1600 cm⁻¹, and demonstrate how the 1830 cm⁻¹ peak can be used to correct FTIR imaging of H₂O concentrations in samples of varying glass thickness, and how the superposition of the 1630 cm⁻¹ H₂O_m and 1600 cm⁻¹ silicate peaks may result in overestimation of H₂O_m concentration in thick and/or H₂O_m-poor samples.

Keywords: FTIR spectroscopy, H₂O speciation, volcanic glass

Hydrogen diffusion experiment in apatite: Effect of different water content

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The calcium phosphate apatites, with general formula $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$, are very common accessory minerals in the terrestrial samples. Since apatite has F, Cl and OH in anion site, there are many studies to discuss about volatile components and water with apatite [1]. Apatite is also major components on extraterrestrial samples, chondrites, achondrites, Moon and Mars [2]. Therefore, apatite is generally recognized as a ubiquitous mineral in our solar system. Recently, there are many studies focusing on the origin and evolution of water in the Earth and solar system based on hydrogen isotopic compositions of apatite (e.g., [3] [4]). However, it is unclear whether the hydrogen isotopic compositions of apatites correspond to the magmatic water in the apatite crystallization or the diffused hydrogen from external water after apatite crystallization by hydrothermal metamorphism.

Hydrogen diffusion in apatite has been recently reported that hydrogen diffusion is caused by hydrogen exchange reaction between the original OH and the diffused hydrogen from water [5]. The H_2O concentration in apatite might be possible to control the hydrogen diffusivity. In this study, we performed hydrothermal diffusion experiment with higher water content of Imilchil apatite than that of Durango apatite (e.g., H_2O : ~800ppm [3]) in order to estimate the hydrogen diffusivity of Imilchil apatite.

Apatite crystal from Imilchil, Morocco (H_2O : ~10000 ppm) (e.g., [6]) was used for hydrogen diffusion experiment in this study. Specimens were cut along to *c*-axis and polished with several grades of diamond. Since apatite originally has hydrogen as OH, we chose $^2\text{H}_2\text{O}$ as diffusion source and ^2H was used as a tracer of hydrogen diffusivity in apatite [5]. Specimens were annealed under the same conditions of [5]. H-diffusion coefficients in the samples were determined using depth profiles of ^2H concentration of the samples obtained by Cameca ims 4f-E7 secondary ion mass spectrometry (SIMS) at LPS Kyoto University.

The depth profiles of ^1H and ^2H close to the surface region in Imilchil apatite show that the ^1H - ^2H exchange reactions control the diffusion mechanism, which is consistent with that of Durango apatite [5]. H-diffusion coefficients of Imilchil apatite are higher than those of Durango apatite by a factor of about 2. The activation energy of hydrogen diffusion in Imilchil apatite is consistent with that of Durango apatite, which is similar to that of OH-bearing silicate minerals (e.g., [7]). Hydrogen diffusion coefficients are several orders of magnitude faster than that of other elements (e.g., O and Sr, [8]; Mn and U, [9]). As results, this study indicates that the effect of hydrogen diffusion in apatites during hydrothermal geological events should be considered to estimate the origin of magmatic water from hydrogen isotopic compositions of apatite crystals.

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Keywords: apatite, hydrogen, diffusion, SIMS

Volatile element compositions of HIMU basalts; a study of Raivavae in the South Pacific

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Volatile budget in the mantle reservoirs have been poorly constrained because of limited number of studies thus far on volatile concentrations in the mantle-derived ocean island basalts (OIBs). We present preliminary results of in-situ geochemical analyses on the olivine-hosted melt inclusions (MIs) from Raivavae Island in the South Pacific to provide new constraints on volatile composition in the HIMU mantle reservoir that is considered to have formed by storage of ancient subducted slabs in the mantle. Raivavae is unique in that the basalts are classified into two groups in terms of Pb isotopes, suggesting that the basalts with radiogenic Pb isotopes involve more recycled slab materials in the source than those with less-radiogenic Pb isotopes. The MIs analyzed in this study were chosen from the two basalt groups. Volatiles together with major and trace elements and Pb isotopes were measured on the same MI through a series of analyses using SIMS, EPMA, and LA-ICP-MS. We prepared two sample sets; these were the natural MIs with crystalline phases inside and the homogenized glassy MIs that were reheated on the heating stage. The natural MIs show larger variation in volatile and trace element compositions than the homogenized MIs owing to the heterogeneous distribution of crystalline phases. This was confirmed by mapping of the volatiles in the natural MIs, where dendritic clinopyroxenes are depleted in volatiles while H₂O and F are concentrated in amphiboles that occur in some MIs. Most MIs have Pb isotope compositions indistinguishable from their host basalts, but one MI has Pb isotope compositions close to that from another group, suggesting an episodic cross-talk of the melts between the two groups. The MIs with less-radiogenic Pb exhibit larger variations in volatile and trace element compositions than the MIs with radiogenic Pb. Notably, some MIs with less-radiogenic Pb isotopes are associated with highly depleted incompatible element composition. Such compositions have never been observed in any bulk rocks on the island. Nevertheless, all the MIs, including the unusually depleted MIs, display broad correlations between volatiles and trace elements with similar incompatibility. Linear variations of H₂O/Ce with 1/Ce and F/Nd with 1/Nd are best explained by mixing of the melts with different H₂O/Ce and F/Nd. In these plots, the MIs with radiogenic Pb tend to have low H₂O/Ce (50-100) and low F/Nd (20-40), implying that the melt derived from the HIMU reservoir had lower H₂O/Ce (~200) than and similar F/Nd (~20) to the ordinary mantle peridotite.

Keywords: Volatile, Ocean island basalts, Mantle recycle

Subduction of iodine-rich halogens and the I/Cl ratio in the mantle

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Volatiles are continuously expelled from the mantle via volcanic activity, whilst being simultaneously transported into the Earth at subduction zones. Since the addition of even small amounts of volatiles may induce major changes in the chemical and physical properties of mantle rocks, understanding volatile recycling processes is critical for understanding mantle heterogeneity and its temporal evolution. Halogens and noble gases are powerful tracers of volatile recycling in subduction zones [1-3]. The subduction of sedimentary pore fluid-derived halogens and noble gases (i.e., sourced from seawater trapped in pores of marine sediments) via the hydrous mineral serpentine has been proposed based on sedimentary pore fluid-like halogen and noble gas signatures in seafloor and forearc serpentinites [1], mantle peridotites from the Sanbagawa metamorphic belt, Japan [2], and mantle xenoliths from volcanic fronts [3]. These subducted halogens can be readily identified by their I/Cl ratios, which are several orders of magnitude higher than those of seawater and depleted MORB mantle (DMM). Non-radiogenic, heavy noble gas compositions in the convecting mantle are similar to those in seawater and sedimentary pore fluids, indicating the 90% of ³⁶Ar in the convecting mantle was originally derived from these sources [4]. Conversely, halogen elemental ratios in mantle xenoliths from intraplate settings (Europe and North America) can be accounted for by fractionation from a DMM-like composition, obviating the need for subduction [3]. Because Re-Os model ages of the subcontinental lithospheric mantle in these localities are around 1.6 Ga [5], the DMM-like halogen signatures of the mantle must have remained constant for at least 1.6 Gyrs.

Here, we use a box model to estimate the halogen subduction fluxes required to have maintained this I/Cl ratio in the mantle over the past 1.6 Gyr. These modeled halogen fluxes are compared with those estimated from (i) halogen/H₂O ratios in natural serpentine in seafloor serpentinites [1] and the amount of water subducted within the hydrous slab mantle [6], and (ii) halogen/³⁶Ar ratios in natural serpentine [1] and the subduction flux of ³⁶Ar. The ³⁶Ar subduction flux has been constrained from its concentration in the convecting mantle and its outgassing flux at mid-ocean ridge systems, which is estimated from the ³⁶Ar/³He ratio in MORB source [4] and the ³He outgassing flux from mid-ocean ridges [7], respectively.

Our data show that the estimated subduction flux of iodine carried by the hydrous slab mantle is too high to keep the I/Cl ratio in the mantle constant over the investigated time period. The present-day DMM-like I/Cl ratio can only be preserved if halogens are not efficiently released from subducting slabs and consequently do not become incorporated into the convecting mantle. In contrast, subducted noble gases should be incorporated into the convecting mantle in order to account for its seawater-like noble gas signature [4]. As such, we interpret that noble gases are readily expelled from subducting slabs at upper-mantle depths due to their high volatilities, whereas halogens are not, and so are transported to significantly greater depths in the Earth.

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Keywords: Subduction, Halogen, Mantle

MORB-like and radiogenic/nucleogenic noble gas components in southern Patagonian subcontinental lithospheric mantle

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Southern Andean Patagonia is one of the few sites where interactions between oceanic and continental lithosphere due to the subduction of an active spreading ridge beneath continent can be investigated. In order to characterize the noble gas composition of Patagonian subcontinental lithospheric mantle (SCLM) we analyzed noble gas and lithophile (Sr-Nd-Pb) isotopes of mantle xenoliths from Pali-Aike Volcanic Field and Gobernador Gregores in southern Patagonia.

Noble gas composition of the mantle xenoliths reflects three-component mixing between air, SCLM and MORB-like. Pali-Aike mantle xenoliths represent the intrinsic local SCLM reservoir with higher $(U+Th+K)/(^3He, ^{22}Ne, ^{36}Ar)$ ratios than MORB source. This mantle reservoir is characterized by radiogenic $^3He/^4He_{AVERAGE} = 6.87 \pm 0.04 R_A$ and nucleogenic mantle neon with $^{21}Ne/^{22}Ne$ average of 0.090, with $^3He/^{22}Ne$ ratios (up to 13.66 ± 0.37) higher than depleted MORBs (8.31-9.75). $^{40}Ar/^{36}Ar$ ratios vary from near-atmospheric ratio (510) up to 16400, with mantle $^{40}Ar/^{36}Ar$ reaching 54000. Mantle $^{129}Xe/^{132}Xe$ reach up to 1.11, whereas $^{136}Xe/^{132}Xe$ up to 0.40. Gobernador Gregores mantle xenoliths represent the SCLM metasomatized by MORB-like component with $^3He/^4He_{AVERAGE} = 7.24 \pm 0.09 R_A$, slightly less nucleogenic mantle neon with $^{21}Ne/^{22}Ne = 0.065$, $^3He/^{22}Ne = 8.39 \pm 0.14$, and $^{40}Ar/^{36}Ar$ ratios usually less than 4000.

Based on these new data, we conclude that the highly radiogenic/nucleogenic signature of Pali-Aike mantle xenoliths compared to the MORB source represents an intrinsic feature of the SCLM reservoir beneath southern Patagonia. This signature could have been homogenized during the last 14 Ma, after rapid the passage and northward migration of the Chile Triple Junction and its slab window at this latitude. On the other hand, the less radiogenic/nucleogenic MORB-like component identified in Gobernador Gregores mantle xenoliths can be explained by recent metasomatism of the SCLM due to the asthenospheric mantle upwelling in response to the opening of a slab window beneath Patagonia because of South Chile Ridge subduction.

Keywords: noble gas, mantle xenolith, Patagonia, subduction, subcontinental lithospheric mantle