

## Accurate measurement of H<sub>2</sub>O concentration and speciation in silicate glasses using FTIR spectroscopy

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Accurate measurement of H<sub>2</sub>O 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 H<sub>2</sub>O-rich vapour. Fourier Transform Infrared (FTIR) spectroscopy can be used to find not only the overall H<sub>2</sub>O concentration (H<sub>2</sub>O<sub>t</sub>) of silicate glasses, but also the individual concentrations of the two H<sub>2</sub>O species: molecular H<sub>2</sub>O (H<sub>2</sub>O<sub>m</sub>), 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 H<sub>2</sub>O<sub>t</sub> molar absorptivity coefficient when using the 3500 cm<sup>-1</sup> H<sub>2</sub>O<sub>t</sub> absorbance peak to find H<sub>2</sub>O<sub>t</sub> and OH (indirectly as [OH] = [H<sub>2</sub>O<sub>t</sub>] - [H<sub>2</sub>O<sub>m</sub>]) concentrations, and in particular how this can be used to reconstruct the original H<sub>2</sub>O 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<sup>-1</sup> and ~1600 cm<sup>-1</sup>, and demonstrate how the 1830 cm<sup>-1</sup> peak can be used to correct FTIR imaging of H<sub>2</sub>O concentrations in samples of varying glass thickness, and how the superposition of the 1630 cm<sup>-1</sup> H<sub>2</sub>O<sub>m</sub> and 1600 cm<sup>-1</sup> silicate peaks may result in overestimation of H<sub>2</sub>O<sub>m</sub> concentration in thick and/or H<sub>2</sub>O<sub>m</sub>-poor samples.

Keywords: FTIR spectroscopy, H<sub>2</sub>O speciation, volcanic glass

## アパタイトの水素拡散実験：含水量の影響

## 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  $\text{H}_2\text{O}$  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.,  $\text{H}_2\text{O}$ : ~800ppm [3]) in order to estimate the hydrogen diffusivity of Imilchil apatite.

Apatite crystal from Imilchil, Morocco ( $\text{H}_2\text{O}$ : ~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  $^2\text{H}$  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  $^2\text{H}$  concentration of the samples obtained by Cameca ims 4f-E7 secondary ion mass spectrometry (SIMS) at LPS Kyoto University.

The depth profiles of  $^1\text{H}$  and  $^2\text{H}$  close to the surface region in Imilchil apatite show that the  $^1\text{H}$ - $^2\text{H}$  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  
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 H<sub>2</sub>O 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 H<sub>2</sub>O/Ce with 1/Ce and F/Nd with 1/Nd are best explained by mixing of the melts with different H<sub>2</sub>O/Ce and F/Nd. In these plots, the MIs with radiogenic Pb tend to have low H<sub>2</sub>O/Ce (50-100) and low F/Nd (20-40), implying that the melt derived from the HIMU reservoir had lower H<sub>2</sub>O/Ce (~200) than and similar F/Nd (~20) to the ordinary mantle peridotite.

キーワード：揮発性元素、海洋島玄武岩、マントル循環

Keywords: Volatile, Ocean island basalts, Mantle recycle

## ヨウ素に富むハロゲンの沈み込みとマントルのI/Cl比

## 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 <sup>36</sup>Ar 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/H<sub>2</sub>O ratios in natural serpentine in seafloor serpentinites [1] and the amount of water subducted within the hydrous slab mantle [6], and (ii) halogen/<sup>36</sup>Ar ratios in natural serpentine [1] and the subduction flux of <sup>36</sup>Ar. The <sup>36</sup>Ar 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 <sup>36</sup>Ar/<sup>3</sup>He ratio in MORB source [4] and the <sup>3</sup>He 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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キーワード：沈み込み、ハロゲン、マントル

Keywords: Subduction, Halogen, Mantle

MORB-like and radiogenic/nucleogenic noble gas components in southern Patagonian subcontinental lithospheric 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  $13.66 \pm 0.37$ ) 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.

キーワード : noble gas、mantle xenolith、Patagonia、subduction、subcontinental lithospheric mantle  
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