

## Hydrogen diffusion experiment in apatite: Effect of different water content

\*Yoshinori Higashi<sup>1</sup>, Shoichi Itoh<sup>1</sup>, Ken Watanabe<sup>2</sup>, Isao Sakaguchi<sup>2</sup>

1. Graduate School of Science, Kyoto University, 2. National Institute for Materials Science

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.

## References

- [1] McCubbin and Jones (2015) *Elements*, 11, 183-188.
- [2] Webster and Piccoli (2015) *Elements*, 11, 177-182.
- [3] Greenwood et al. (2011) *Nature Geosci.*, 4, 79-82.
- [4] Usui et al. (2015) *Earth Planet. Sci. Lett.*, 410, 140-151.
- [5] Itoh et al. (2015) *Goldschmidt abstract*, 2015 1394.
- [6] Barnes et al. (2013) *Chemical Geology*, 337-338, 48-55.
- [7] Graham (1981) *Contrib. Mineral. Petrol.*, 76, 216-228.
- [8] Farver and Giletti (1989) *GCA*, 53, 1621-1631.
- [9] Cherniak (2005) *Chemical Geology*, 219, 297-308.

Keywords: apatite, hydrogen, diffusion, SIMS