Hydrogen diffusion experiment of fluorapatite under water vapor conditions

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Apatite [$Ca_5(PO_4)_3$(F, Cl, OH)] contains highly volatile elements such as F, Cl, and OH in the anion sites, making it a useful recorder of volatile components and water in fluids and magmas in the Earth and extraterrestrial bodies (e.g., [1]). Many studies in the past decade have sought to explore the origin and evolution of water in planetary bodies based on the water contents and hydrogen isotopic compositions of apatite (e.g., [2][3]). However, without an understanding of hydrogen diffusivity in apatite, it is difficult to estimate whether original hydrogen isotopic compositions from crystallization are preserved, or the subsequently modified by reactions with water after crystallization. Therefore, it is necessary to understand the hydrogen diffusivity in apatite during water–rock interactions. Recently, hydrogen diffusion coefficient of fluorapatite parallel to the *c*-axis was reported [4]. Here we report hydrogen diffusivity of the anisotropy and the water content dependence of hydrogen diffusion to compare with that of *c*-axis [4].

In order to investigate the water content dependence of hydrogen diffusion, natural fluorapatite crystals that have different water content (from Durango, ~500 ppm H_2O [2] and Morocco, ~4000 ppm H_2O [5]) were used for diffusion experiment. To investigate the anisotropy of hydrogen diffusion in apatite, Durango apatite crystals were cut in two directions for the crystallographic *c*-axis (parallel or normal to the *c*-axis). Hydrogen diffusion experiments using these natural fluorapatites were carried out under a saturated D_2O/O_2 vapor flow at temperatures of 500–700 ˚C. Diffusion depth profiles for ^1H and ^2D were measured using secondary ion mass spectrometry (CAMECA ims 4f-E7 SIMS), indicating that ^2D diffusion occurred by an exchange reaction between the original ^1H and ^2D during annealing. Hydrogen diffusion coefficients were obtained by the fitting of diffusion profiles of ^2D using Fick’ s second law; they followed an Arrhenius-type relationship.

Hydrogen diffusion in Durango apatite normal to the *c*-axis is approximately five times faster than that of along to the *c*-axis. Variation in water content of apatite would not lead to large changes in the hydrogen diffusivity. The similarities of the activation energy for hydrogen diffusion in apatite and hydrous minerals suggest that hydrogen in apatite lattice is transported via the Grotthuss mechanism like other hydrous minerals [6]. Hydrogen diffusion coefficients in apatite are several orders of magnitude greater than those of other elements. This study indicates that the hydrogen isotopic compositions of apatite are readily affected by the presence of water vapor through the H–D exchange reaction without changing the total water content in the crystal. Hydrogen diffusion of apatite crystals would play an important role to determine the hydrogen isotopic compositions of apatite in extraterrestrial bodies.

References

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