

EFFECT OF WATER FUGACITY FOR OXYGEN SELF DIFFUSION IN GEHLENITE

S. Ishikubo¹, S. Tachibana^{2,3}, N. Kawasaki¹, D. Yamamoto¹, M. Kuroda¹, and H. Yurimoto^{1,3}, ¹Natural History Sciences, Hokkaido University, Sapporo 060-0810, Japan (shogo@ep.sci.hokudai.ac.jp) ²UTokyo Organization for Planetary Space Science, The University of Tokyo, Hongo, Tokyo 113-0033, Japan. ³ISAS/JAXA, Sagami-hara, Kanagawa 252-210, Japan.

Introduction: Calcium-aluminum-rich refractory inclusions (CAIs) are the oldest objects in the Solar System, and exhibit oxygen isotopic variations among different minerals [1]. A mechanism to produce mineralogical-controlled oxygen isotopic variations is the diffusive oxygen isotope exchange between CAI-constituting minerals and oxygen bearing gas species (e.g., H₂O) in the protosolar disk or on parent bodies after the CAI formation. The oxygen self-diffusion coefficients in melilite have been experimentally determined using isotopically labelled CO₂ and/or CO [2, 3], but the combination of oxygen diffusivity in melilite and those in other CAI constituting minerals cannot explain the mineralogical-controlled oxygen isotope distributions observed in CAIs. However, oxygen self-diffusion in CAI-constituting minerals could be variable under hydrous conditions as in the case of some silicate minerals [4]. Especially, melilite may be highly enhanced with increasing water fugacity compared with other CAI minerals to form the oxygen isotope distribution in CAIs. In order to examine the effect of water fugacity on oxygen self-diffusion in melilite, we conducted oxygen diffusion experiments in gehlenite (Ca₂Al₂SiO₇) in the presence of water vapor.

Experiments: Oxygen self-diffusion experiments in a single crystal of gehlenite, synthesized by the Czochralski pulling method by M. Morioka, U. Tokyo, were conducted at 800, 850, and 900°C and water vapor pressure (P_{H₂O}) of 0.3 and 0.01 Pa for 24 and 120 hr. A gold-mirror vacuum furnace equipped with a gas flow system for water vapor (Thermo- Riko GFA 430VN) [5, 6] was used for the experiments under the low P_{H₂O} conditions, inferred in protoplanetary disks. ¹⁸O enriched water (97-atom% ¹⁸O) was used as a source of water vapor. The P_{H₂O} in the furnace (0.3 and 0.01 Pa) was controlled by adjusting a flow rate of H₂¹⁸O vapor and a gas evacuation rate. The melilite crystals showing smooth cleavage surfaces ((001) plane; 2 mm × 10 mm) were used for the experiments. The observations of crystal surfaces were made with a field-emission scanning electron microscope with EDS (energy dispersive X-ray spectroscopy) and EBSD (electron backscatter diffraction) (FE-SEM-EDS-EBSD; JEOL JSM-7000F) and depth profiles of ¹⁶O, ¹⁸O and ²⁸Si along the [001] axis were obtained by secondary ion mass spectrometry (Cameca ims-1280HR) at Hokkaido University.

Results & Discussion: No reaction products were observed on the surface of run products, and the surface remained gehlenite. The depth profiles of oxygen isotopes show that the sample surface is enriched in ¹⁸O due to oxygen isotope exchange with H₂¹⁸O vapor. The ¹⁸O fraction decreases with depth from the surface, and it drops down to that of the terrestrial value at the depths of ~100 nm and ~150 nm at 800 and 900°C, respectively. No significant P_{H₂O} dependences of the depth profiles of oxygen isotopes were observed. The observed ¹⁸O profiles were fitted with a one-dimensional diffusion equation in a semi-infinite medium with a constant surface concentration [7]. The obtained self-diffusion coefficient of oxygen along the [001] axis is about one order of magnitude smaller than that in [2] at 800–900°C with a similar activation energy (~200 kJ/mol). The smaller oxygen self-diffusion coefficient in the present study could be due to the difference in the point defect concentration within the crystals. Present results show that oxygen self-diffusion in melilite is not enhanced in the presence of water vapor, at least at the disk-like P_{H₂O} of 0.01-1 Pa, and that the diffusion coefficient of oxygen self-diffusion in melilite obtained under dry conditions are applicable for discussion on oxygen isotope evolution for CAI constituting minerals in the protosolar disk.

References: [1] Clayton R. N. (1993) *Annual Review of Earth Planetary Sciences* 21:115-149. [2] Yurimoto H. et al. (1989) *Geochimica et Cosmochimica Acta* 53:2387-2394. [3] Ryerson F. J. and McKeegan D. K. (1994) *Geochimica et Cosmochimica Acta* 58:3713-3734. [4] Stephen C. E. et al. (1988) *Contributions to Mineralogy and Petrology* 100:490-495. [5] Yamamoto D. and Tachibana S. (2018) *ACS Earth and Space Chemistry* 2:778-786. [6] Yamamoto D. et al. (2018) *The Astrophysical Journal* 865:98 (14pp). [7] Crank J. (1956) *The Mathematics of diffusion*. 2nd edition Oxford:Oxford University Press.