

Relationship between oxygen diffusivity and Ca/Ti ratio in perovskite

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<**Introduction**> Calcium-aluminum-rich inclusions (CAIs) in carbonaceous chondrites are composed of refractory minerals, such as mellilite, spinel, and perovskite and believed to be the first solid in the early solar system. Previous studies reported heterogeneous oxygen (O)-isotopic compositions among the CAI minerals (Clayton et al. 1973). The O-isotopic compositions are considered to be a marker of O-isotopic composition in the solar nebula (Yurimoto et al. 1998; Itoh and Yurimoto 2003; Park et al. 2012). However, it is unclear that the heterogeneous O-isotopic composition is resulted from whether environment where the mineral crystalized or diffusion during heating event after the crystallization. To discuss this issue, investigation of O-diffusivity of minerals is necessary.

Perovskite crystals show several order of larger O-diffusion coefficients than other CAI minerals (Gautason and Muehlenbachs 1993; Ryerson and McKeegan 1994; Sakaguchi and Haneda 1996). Thus, their O-isotopic compositions can provide us an important key to understand O-diffusivity of CAI minerals and thermal histories of CAIs. Diffusivity of solids is influenced by impurity in the sample (e.g. Sakaguchi et al. 2010). In this study, we performed O-diffusion experiments perovskite with different Ca/Ti ratio to understand O-diffusivity in perovskite.

<**Experimental**> Polycrystalline perovskite samples were prepared by a conventional sintering technique. High-purity reagent-grade powders of CaCO₃ and TiO₂ were used as the starting materials. These powders were mixed as Ca/Ti=0.098-1.002 by ball milling with PSZ balls. The powders were pressed as a sheet and were sintered at 1350 degC for 2 h in the atmosphere. Then, perovskite samples with different Ca/Ti ratio were obtained. Different of Ca/Ti ratio of the samples from initial value due to a contamination of ZrO₂ from PSZ balls was calibrated within the error of ~0.001. The samples were polished by a chemical mechanical polishing and then were annealed under ¹⁸O₂ gas at 750-1000 degC for 20 min~several hours. O-diffusion coefficients in the samples were determined using depth profiles of ¹⁸O concentration of the samples obtained by secondary ion mass spectrometry (SIMS) (Cameca ims-4f). Distributions of ¹⁸O ions in cross section of the samples were observed using high spatial-resolution ion image obtained by NanoSIMS (Cameca NanoSIMS 50).

<**Results and discussion**>Ca-rich sample and Ti-rich sample showed different O-diffusivity. In Ti-rich sample, two contributions to the O-diffusion mechanism are observed in depth profiles of ¹⁸O concentration obtained from Ti-rich perovskite samples. One starts near surface (diffusion I) and the other starts from about a few 100 nm depth (diffusion II) of the sample. In Ca-rich perovskite samples, only one diffusion mechanism was observed. O-diffusion coefficients (D) in Ca-rich samples were larger than that of Ti-rich samples, in both diffusion I and II. D value of 950 degC in the Ti-rich sample (Ca/Ti=0.098) was 7x10⁻¹³cm²/s (diffusion I) and 1x10⁻¹¹cm²/s (diffusion II), whereas the value of a Ca-rich sample (Ca/Ti=1.002) was 8x10⁻¹⁰cm²/s.

High resolution ¹⁸O concentration image of Ti-rich samples showed decrease of ¹⁸O concentration around the grain boundaries, indicating formation of blocking layer for O-diffusion. Such blocking layer has also been reported in BaTiO₃ with perovskite structure (Watanabe et al. 2014).

This study revealed difference of O-diffusivity in perovskite by slight change of Ca/Ti ratio and larger O-diffusivity of Ca-rich perovskite than Ti-rich perovskite. Larger O-diffusion coefficients of perovskite than that of other CAI minerals suggested that perovskite record the final thermal process, which the CAI experienced. This study suggests that shorter timescale required for change of O-isotopic composition for Ca-rich perovskite than previously considered. We will also discuss defect chemistry and mechanism of the O-diffusion in this presentation.

Keywords: perovskite, oxygen diffusivity