

OXYGEN ISOTOPE EXCHANGE BETWEEN AMORPHOUS FORSTERITE AND WATER VAPOR; AN EXPERIMENTAL STUDY. D. Yamamoto¹, M. Kuroda¹, S. Tachibana^{1,2}, N. Sakamoto¹ and H. Yurimoto^{1,3}, ¹Department of Natural History Sciences, Hokkaido University, Sapporo, Hokkaido 060-0810, Japan (daiki@ep.sci.hokudai.ac.jp), ²UTokyo Organization for Planetary Space Science, The University of Tokyo, Hongo, Tokyo 113-0033, Japan, ³Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, Sagami-hara, Kanagawa, 252-210, Japan.

Introduction: Oxygen isotopic compositions of various components in chondrites (e.g. CAIs, AOAs, chondrules and fine-grained matrix) show the evidence of isotopic mixing/exchange between ¹⁶O-rich and ¹⁶O-poor reservoirs in the early Solar System. The *Genesis* mission discovered that the oxygen isotopic composition of the Sun is similar to ¹⁶O-rich CAIs [1], suggesting that primary dust in the Solar System was ¹⁶O-rich and evolved to ¹⁶O-poor compositions through isotopic exchange with ¹⁶O-poor disk gas [2].

A large proportion of primitive Solar-System silicates dust would be amorphous [3], and oxygen isotopic exchange with disk gas would take place through thermal annealing in the early Solar System. However, it has been little known whether or not the oxygen isotopic exchange between amorphous silicates and water vapor occurred efficiently within the timescale of disk evolution. Here we experimentally investigated oxygen isotopic exchange between amorphous forsterite and water vapor in order to understand the oxygen isotopic exchange process in the early Solar System.

Experiments: Sub- μm -sized amorphous forsterite grains, synthesized by an induced thermal plasma method, were used as a starting material (average grain diameter ~ 80 nm; [4]). Oxygen-isotope exchange experiments between amorphous forsterite and H_2^{18}O vapor were carried out at 803–1073 K under disk-like low water-vapor pressures of 0.01–1 Pa using a gold-mirror vacuum furnace (Thermo-Riko GFA430VN) equipped with a gas flow system. H_2^{18}O vapor was provided from H_2^{18}O ice (97% ¹⁸O) kept at 243–253 K through the gas flow system. The water vapor pressure in the vacuum furnace was controlled by the balance between the flow rate and a pumping rate. We also annealed the starting material with isotopically normal water vapor of 1 Pa for comparison.

The run products were analyzed by a Fourier transform infrared spectrometer (JASCO FT-IR 4200) using a KBr pellet method. The existing phases were determined by an X-ray diffractometer (Rigaku SmartLab). Bulk oxygen isotope measurements were conducted for pelletized samples by secondary ion mass spectrometry (SIMS; Cameca ims-6f at Hokkaido University, Japan). For SIMS analysis, samples were shaped into pellets and sintered in a vacuum furnace in order to impede oxygen isotopic exchange during sintering.

Results and discussion: The Si-O stretching vibration absorption peak of amorphous forsterite at ~ 10 μm shifted to a higher wavelength with time for samples annealed with H_2^{18}O vapor of 1 Pa at 803–883 K (Fig. 1), whereas such a shift of peak position was not observed in the spectra of samples exposed to isotopically normal water vapor of 1 Pa at 853 K for 24 and 48 hr. This peak shift can be attributed to the replacement of oxygen from ¹⁶O to ¹⁸O, resulted in a lower vibration frequency (larger wavelength) of Si-O bonds, without crystallization. The isotopic exchange in the samples was confirmed by SIMS analysis. The SIMS analysis also showed that a relative peak shifts, expressed as a normalized wavenumber shift ($\Delta\kappa/\kappa_{\text{amor. Fo ref.}}(\%)$), of the 10- μm peak of amorphous forsterite can be used as an indicator of oxygen isotopic compositions of amorphous forsterite with $^{18}\text{O}/(^{18}\text{O}+^{16}\text{O}) < 0.4$.

At $P_{\text{H}_2\text{O}} \sim 0.01$ Pa, the reaction rates at 883 and 853 K inferred from $\Delta\kappa/\kappa_{\text{amor. Fo ref.}}$ were quite similar to each other. This little temperature dependence of the reaction rate implies that the supply of gaseous water is a rate-limiting step for isotopic exchange at lower $P_{\text{H}_2\text{O}}$ and higher temperatures. On the other hand, the reaction rate at 803 K under $P_{\text{H}_2\text{O}} \sim 0.01$ Pa was almost identical to that under $P_{\text{H}_2\text{O}} \sim 1$ Pa, suggesting that the rate-limiting step is not the supply of gas, but a different process that is not dependent on water vapor pressure.

At 953 K and $P_{\text{H}_2\text{O}} \sim 1$ Pa, crystallization of amorphous forsterite occurred. All typical peaks of crystalline forsterite shifted to higher wavelengths with peak broadening as crystallization proceeded. This can be interpreted as simultaneous crystallization and oxygen isotopic exchange; forsterite crystallized in the early stage kept its original normal oxygen isotopic compositions, while crystallization occurred from isotopically substituted amorphous forsterite in the late stage, resulting in the mixed broad infrared features of ¹⁸O-poor and ¹⁸O-rich crystalline forsterite.

At 1073 K and $P_{\text{H}_2\text{O}} \sim 1$ Pa, an infrared spectrum of a run product showed several peaks of crystalline forsterite with normal oxygen isotopic compositions, suggesting that crystallization occurred prior to isotopic exchange with water vapor and the isotopic exchange is sluggish for crystalline forsterite.

Time evolution of oxygen isotopic compositions of amorphous forsterite at 803–883 K and $P_{\text{H}_2\text{O}} \sim 1$ Pa was

fitted with various reaction models, and we found that it follows the three dimensional diffusion equation in a sphere [5] as shown in Fig. 2, yielding the exchange rate (D) of $\ln(D) = -26.8 - 164 (kJ mol^{-1})/RT$. This supports that there is no P_{H_2O} dependence of the reaction rate at 803 K mentioned above.

Based on the experimental data, we estimated a timescale of oxygen isotopic exchange between amorphous forsterite (80 nm in diameter) and disk water vapor for the rate-limiting step of gas supply or diffusion. The reaction timescales for complete isotopic exchange are compared with timescales of crystallization of amorphous forsterite [6] and oxygen self-diffusion in crystalline forsterite [7] (Fig. 3). At $P_{H_2O} \sim 1$ and 10^{-4} Pa, oxygen isotopic exchange of amorphous forsterite would be controlled by diffusion at $< \sim 1200$ and $< \sim 780$ K, respectively. At temperatures above ~ 920 K ($P_{H_2O} \sim 1$ Pa) and ~ 850 K ($P_{H_2O} \sim 10^{-4}$ Pa), amorphous forsterite would crystallize rapidly, followed by oxygen isotopic exchange through diffusion into crystalline forsterite.

Because diffusive transport of oxygen (H_2O) occurs effectively in an amorphous state, amorphous forsterite dust could exchange oxygen isotopes within the disk lifetime if it was heated at temperatures higher than ~ 500 K. In other words, the original oxygen isotopic signature of amorphous forsterite (e.g. presolar signature) could be preserved only if the dust was kept at temperatures lower than ~ 500 K.

References: [1] McKeegan, K. D. et al. (2011) *Science*, 332, 1528–1532. [2] Yurimoto, H. & Kuramoto, K. (2004) *Science*, 305, 1763–1766. [3] Nuth III, J. A. et al. (2005) in *Chondrites and the Protoplanetary Disk*, 341, 675–700. [4] Koike, C. et al. (2010) *ApJ*, 709, 983–992. [5] Crank, J. (1975) *The Mathematics of diffusion*. Oxford Univ. Press. [6] Yamamoto, D. & Tachibana, S. in prep. [7] Jaoul, O. et al. (1980) *Earth Planet. Sci. Lett.*, 47, 391–397.

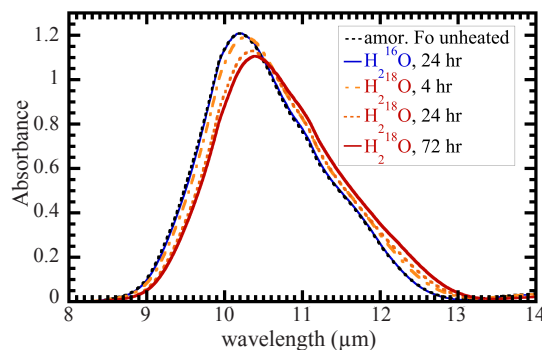


Fig. 1: Infrared spectra of samples exposed to $H_2^{18}O$ and $H_2^{16}O$ vapor at 853 K with a reference spectrum of the amorphous forsterite.

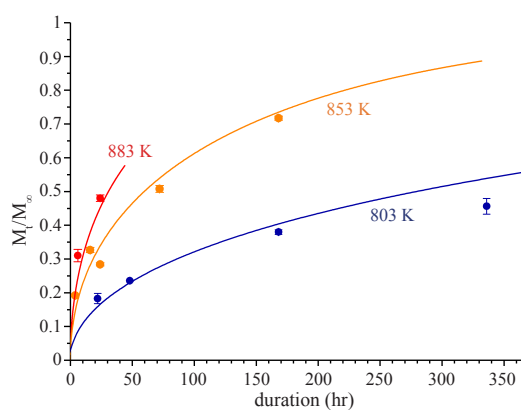


Fig. 2: Time evolution of the degree of oxygen isotopic exchange reaction at $P_{H_2O} \sim 1$ Pa. Best-fitted curves with the 3-D spherical diffusion [5] are also shown.

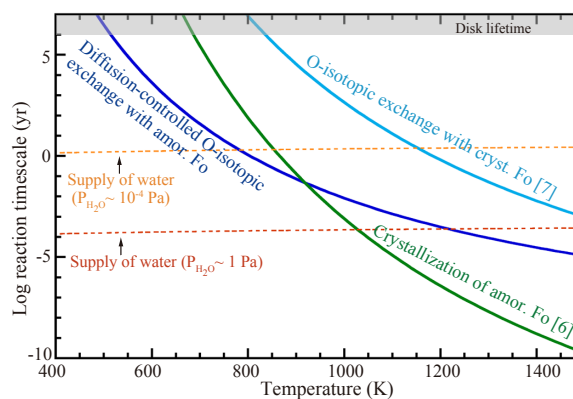


Fig. 3: Timescales of oxygen isotopic exchange of amorphous forsterite dust (80 nm in diameter) controlled by diffusion and the supply of gaseous water. Timescales of oxygen self-diffusion in crystalline forsterite and crystallization of amorphous forsterite are also shown for comparison.