

**EXPERIMENTAL STUDY ON O-ISOTOPE EXCHANGE BETWEEN AMORPHOUS FORSTERITE DUST AND CARBON MONOXIDE GAS IN THE PROTOSOLAR DISK.** D. Yamamoto<sup>1,2\*</sup>, S. Tachibana<sup>2,1</sup>, N. Kawasaki<sup>3</sup>, M. Kamibayashi<sup>2</sup>, and H. Yurimomto<sup>3,1</sup>, <sup>1</sup>Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, Sagami-hara, Kanagawa 252-5210, Japan, <sup>2</sup>The University of Tokyo, Hongo, Tokyo 113-0033, Japan, <sup>3</sup>Department of Natural History Sciences, Hokkaido University, Sapporo, Hokkaido 060-0810, Japan. \*daiki@planeta.sci.isas.jaxa.jp, daiki@eps.s.u-tokyo.ac.jp

**Introduction:** Primitive Solar System materials exhibit mass-independent variation in oxygen isotopes. This variation is considered to be a result of oxygen isotope exchange between different oxygen isotope reservoirs, such as primitive solid materials and disk gas in the early Solar System [e.g., 1–4]. The self-shielding model predicts that <sup>16</sup>O-poor H<sub>2</sub>O gas and <sup>16</sup>O-rich CO gas were produced through isotopically selective photodissociation of CO [1, 5]. The oxygen isotope exchange between three major oxygen isotope reservoirs (primitive solid materials, H<sub>2</sub>O, and CO) would thus cause the oxygen isotope variation within extraterrestrial materials.

Amorphous silicate dust would have been present as dominant building block of solid materials in the early Solar System [e.g., 6]. We have experimentally determined oxygen isotope exchange kinetics between amorphous silicates and H<sub>2</sub>O gas to discuss the disk condition where the isotope exchange reaction occurs effectively [7, 8]. Although the gas phase isotope exchange kinetics between H<sub>2</sub>O and CO gas was discussed by [9], oxygen isotope exchange between amorphous silicates and CO gas has not yet been investigated. In this study, we performed oxygen isotope exchange experiments between amorphous silicate with forsterite (Mg<sub>2</sub>SiO<sub>4</sub>) stoichiometry (hereafter amorphous forsterite) and low pressure CO gas.

**Experiments:** About 30 mg of amorphous forsterite particles with an average grain diameter of 80 nm [7, 10] was used as the starting material for each experiment. Oxygen isotope exchange experiments between amorphous forsterite and <sup>18</sup>O-enriched carbon monoxide gas (CO; >95 atom% <sup>18</sup>O) were performed at 883K under low pressure CO gas condition ( $P_{CO} = 0.3$  Pa) using a gold-mirror vacuum furnace (Thermo-Riko GFA430VN) [7, 8, 10] equipped with a gas flow system. CO gas was supplied from a gas cylinder, and  $P_{CO}$  was controlled by the balance between the gas flow rate (0.65 cm<sup>3</sup> min<sup>-1</sup>) adjusted by a mass flow controller (Kofloc Model 3660) and the gas evacuation rate adjusted by a butterfly valve. The gas in the furnace was monitored by a quadrupole mass spectrometer (HORIBASTEC QL-SG01-065-1A).

The run products were analyzed by a Fourier-transform infrared spectrometer (JASCO FT-IR 4200) using a KBr pellet method. Oxygen isotope measure-

ments were conducted for pelletized samples by secondary ion mass spectrometry (SIMS; Cameca 1280-HR at Hokkaido University, Japan) using the analytical procedure reported by [4, 8]. For SIMS measurements, the pelletized samples were sintered in a vacuum by a vacuum furnace [11] at ~1100°C for 20–24 hours to prevent the oxygen isotope exchange between samples and the surrounding atmosphere during sintering [7, 8].

**Results and Discussions:** The main gas species in the furnace during the experiments was C<sup>18</sup>O, and the partial pressure of H<sub>2</sub><sup>18</sup>O was more than three orders of magnitude lower than  $P_{CO}$  ( $< \sim 1 \times 10^{-4}$  Pa). All the experimental conditions and results of the oxygen isotope measurements are summarized in Table 1. Infrared absorption spectra of the samples heated with C<sup>18</sup>O gas for 3–24 hours have broad peaks centered at ~10 and 18 μm attributed to Si-O stretching and O-Si-O bending vibration of amorphous forsterite [7, 10], respectively, and no appearance of new peaks was observed (Fig. 1). This suggests that the samples remained amorphous within 24 hours at 883 K, which is consistent with our previous studies [7, 10]. While the oxygen isotope composition [<sup>18</sup>O/(<sup>18</sup>O+<sup>16</sup>O)] ( $f^{18}O$ ) of the starting material was 0.0020 (the terrestrial ratio),  $f^{18}O$ 's of the amorphous samples heated with C<sup>18</sup>O gas increased with time (Table 1). The errors of  $f^{18}O$  estimated by multiple measurements become increased with increasing degree of oxygen isotope exchange (Table 1), which may be due to the presence of particle size distribution of the starting material. The size distribution of the starting material could result in different degrees of isotope exchange depending on the grain size [7, 8, 10].

Temporal change of  $f^{18}O$  in the heated samples relative to that of the starting material ( $\Delta f^{18}O = f^{18}O_{\text{sample}} - f^{18}O_{\text{std.}}$ ) is shown in Fig. 2. The modeled curve of  $\Delta f^{18}O$  of amorphous forsterite heated with H<sub>2</sub><sup>18</sup>O gas of 0.3 Pa (97 atom% <sup>18</sup>O) at the same experimental temperature [7] is also shown for comparison. The  $f^{18}O$  of the amorphous forsterite heated with C<sup>18</sup>O gas increased linearly with time, and the reaction time-scale is about one order of magnitude smaller than that with H<sub>2</sub>O gas at the same T-P condition [7, 8]. This change of  $\Delta f^{18}O$  cannot be explained by the reaction with H<sub>2</sub><sup>18</sup>O in the furnace because the partial pressure

of  $\text{H}_2^{18}\text{O}$  was  $\sim 3 \times 10^{-4}$  of  $P_{\text{CO}}$ . We thus conclude that the oxygen isotope exchange occurred between amorphous forsterite and  $\text{C}^{18}\text{O}$  gas. The slow isotope exchange reaction with CO gas could be due to ineffective oxygen isotope exchange reaction between dissolved CO molecules and structural oxygen atoms.

In spite of the slow isotope exchange rate of amorphous forsterite with CO gas, the isotope exchange timescale for  $\sim 0.1 \mu\text{m}$ -sized amorphous forsterite dust with CO gas is 4–5 orders of magnitude shorter than the timescale of gas phase isotope exchange between CO and  $\text{H}_2\text{O}$  gas at 883 K in the protosolar disk [9]. This implies that amorphous forsterite dust would control oxygen isotope compositions of CO and  $\text{H}_2\text{O}$  gas at temperatures where the gas phase isotope exchange reaction would be ineffective because amorphous forsterite dust exchanges oxygen isotopes with both CO ( $^{16}\text{O}$ -rich) and  $\text{H}_2\text{O}$  gas ( $^{16}\text{O}$ -poor).

**References:** [1] Yurimoto H. and Kuramoto K. (2004) *Science* 305, 1763–1766. [2] McKeegan K. D. et al. (2011) *Science* 332, 1528–1532. [3] Yurimoto H. et al. (1998) *Science* 282, 1874–1877. [4] Kawasaki N. et al. (2018) *Geochim. Cosmochim. Acta* 221, 318–341. [5] Lyons J. R. & Young E. D. (2005) *Nature* 435, 317–320. [6] Nuth J. A. et al. (2005) In *Workshop on chondrites and the Protoplanetary Disk ASP Conference Series* 341, 675–700. [7] Yamamoto D. et al. (2018) *Astrophys. J.* 865, 98 (14pp). [8] Yamamoto D. et al. (2019) *Meteorit. & Planet. Sci.* 1–12. [9] Alexander C. M. O'D. (2004) *Geochim. Cosmochim. Acta* 68, 3943–3969. [10] Yamamoto D. and Tachibana. S. (2018) *ACS Earth & Space Chem.* 2, 778–786. [11] Kamibayashi M. et al. (2018) *LPS XXXIX*, abstract #2432.

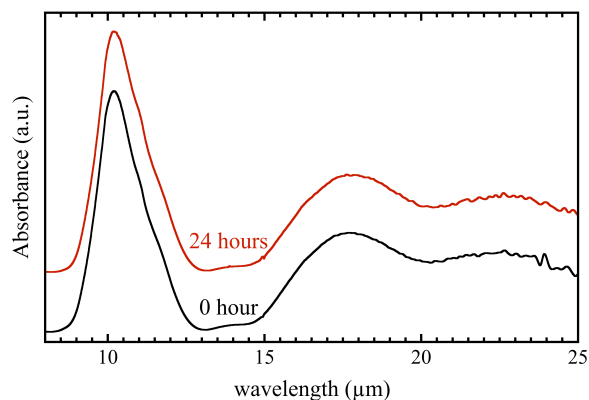
**Table 1:** O-isotope compositions of amorphous forsterite along with duration at 883 K and  $P_{\text{CO}} = 0.3 \text{ Pa}$ .

Duration (hour)	$f^{18}\text{O}^a$
0 <sup>b</sup>	$0.0020 \pm 0.00001$
3	$0.0103 \pm 0.0018$
4	$0.0114 \pm 0.0023$
4	$0.0097 \pm 0.0020$
7	$0.0145 \pm 0.0059$
16	$0.0368 \pm 0.0118$
20	$0.0441 \pm 0.0142$
24	$0.0514 \pm 0.0153$

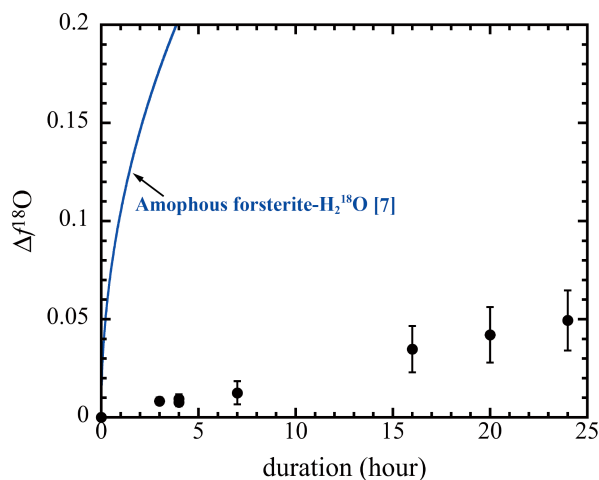
<sup>a</sup>Oxygen isotope compositions ( $^{18}\text{O}/(^{18}\text{O}+^{16}\text{O})$ ) of samples.

Errors represent the  $1\sigma$  standard deviations.

<sup>b</sup>The starting material sintered in a vacuum.



**Fig. 1:** Infrared absorption spectra of amorphous forsterite used as the starting material (black curve) and the sample heated with  $\text{C}^{18}\text{O}$  gas at 883 K for 24 hours (red curve). The spectrum of the run product is arbitrarily shifted in the vertical direction.



**Fig. 2:** Temporal change of  $\Delta f^{18}\text{O}$  ( $=f^{18}\text{O}_{\text{sample}} - f^{18}\text{O}_{\text{std.}}$ ) for amorphous forsterite heated with  $\text{C}^{18}\text{O}$  gas of 0.3 Pa (black circles) at 883 K with the modeled curve of  $\Delta f^{18}\text{O}$  for amorphous forsterite heated with  $\text{H}_2^{18}\text{O}$  gas of 0.3 Pa at the same temperature (blue solid curve [7]). Errors are  $1\sigma$  standard deviations.