

EXPERIMENTAL STUDY OF REACTION BETWEEN FORSTERITE AND SI-RICH GAS. H. Chiba¹, S. Tachibana¹, and H. Nagahara¹, ¹Department of Earth and Planetary Science, University of Tokyo (7-3-1 Hongo, Tokyo 113-0033, Japan, toboeallnight@gmail.com)

Introduction: Solid-gas reactions may have played an important role in the chemical fractionation in space. Magnesium and silicon are the major rock-forming elements, and the Mg/Si ratio is almost unity in the solar system elemental abundance [1].

According to equilibrium condensation models for the solar abundance, most of Mg and Si condense as forsterite (Mg_2SiO_4), which reacts with Si-rich gas to form enstatite at lower temperatures [e.g., 2, 3]. This solid-gas reaction determines the extent of Mg/Si fractionation since the atomic ratio of Mg/Si in the solid changes from 2 of forsterite to 1 of enstatite, and may have caused the Mg/Si fractionation recorded in chemical groups of chondrites.

It is thus important to understand the enstatite-forming reaction between forsterite and Si-rich gas. Imae et al. [4] have carried out reaction experiments between forsterite and Si-rich gas with a double capsule technique, where a chip of forsterite in a Mo capsule was put in a larger Mo capsule containing cristobalite. The double capsule was heated in vacuum at 1378-1550°C, and forsterite in the inner capsule was reacted with Si-rich gas generated from cristobalite. The reaction products were polycrystalline clinoenstatite, and the thickness of the reaction layer reached up to $\sim 20 \mu\text{m}$. They extrapolated reaction rates down to plausible enstatite-forming temperatures in the early solar system to discuss enstatite formation. Their reaction rates were applied for formation of silicates in a mass-loss wind from an evolved star as well [5].

However, it is always dangerous to extrapolate the reaction kinetics obtained at higher temperatures to lower temperatures because a microscopic reaction controlling an overall reaction may be different or even a different overall reaction may occur.

Here we report our preliminary results on reaction experiments between forsterite and Si-rich gas at temperatures close to those in protoplanetary disks and circumstellar environments using a new equipment.

Experiments: Reaction experiments were carried out in a newly developed vacuum furnace (Fig. 1), designed based on a molecular beam epitaxy system used in the field of semiconductor industry.

The furnace consists of a vacuum chamber equipped with a pumping system, a furnace with a tungsten-coil heater for gas generation, a infrared fur-

nace for substrate heating, and a gas inlet system to introduce oxygen in the system.

A chip of synthesized single crystal of quartz was heated by a tungsten-coil heater at $\sim 1650^\circ\text{C}$ to generate Si-rich gas. The temperature of the tungsten-coil furnace was calibrated against a melting point of platinum (1768°C) and an eutectic point of Rh-C (1657°C).

A chip of single crystal of forsterite ($\sim 4 \times 4 \times 0.5 \text{ mm}$) was put $\sim 250 \text{ mm}$ above the gas source, and heated at ~ 800 or $\sim 900^\circ\text{C}$ by an infrared furnace from behind, of which temperature was calibrated against melting temperatures of silver (962°C) and sodium chloride (801°C). Because forsterite is almost transparent to infrared light, we covered the surface of forsterite opposite to the reaction surface with a platinum foil and further with a graphite plate for effective heating by infrared light.

The pressure in the vacuum chamber during experiments was 1.2×10^{-4} - $2.0 \times 10^{-5} \text{ Pa}$. The experiment in the presence of oxygen flow was also carried out under a controlled total pressure of $\sim 7 \times 10^{-4} \text{ Pa}$. The mean free path of gaseous molecules is longer than several meters under such pressure conditions, and thus molecular beam conditions were reached during experiments.

The gas source and a substrate were cooled rapidly after heating of <10 and 48 hours. The substrate was observed with a field-emission scanning microscopy (FE-SEM, JSM-7000F), and the surface chemical composition and crystallinity were determined by energy-dispersive X-ray spectroscopy (EDS) and electron backscatter diffraction (EBSD) equipped with FE-SEM.

Results: The reacted surface of forsterite looked almost the same as the starting material, regardless of experimental conditions (Fig. 2).

The EDS analyses at the accelerating voltages of 3-5 kV, which was lower than the typical accelerating voltage to determine the chemical compositions of the area very close to the sample surface, indicated that the surface of forsterite was covered with a very thin reaction layer consisting of silicon and oxygen regardless of experimental conditions (Fig. 3). Although we could not determine thicknesses of the layer, this observation is consistent with the expected thickness of the reaction layer estimated from the gaseous flux onto the forsterite substrate ($\ll 1 \mu\text{m}$). We have not been able to determine precise Si/O ratios of the reaction

products, but there seemed to be no significant difference in the Si/O ratios for run products formed in the presence or absence of oxygen flow. No magnesium was detected although it should be present if enstatite was formed.

The EBSD analyses showed that the reaction layers heated at $\sim 900^\circ\text{C}$ for 48 hours were not crystalline, which means that the product is amorphous. The reaction layer formed at $\sim 800^\circ\text{C}$ for shorter duration (<10 hours) sometimes showed the EBSD pattern for the (100) surface of forsterite, which was the original surface of the substrate most likely because the layer was very thin.

All lines of evidence indicate that the solid-gas reaction between forsterite and Si-rich gas at ~ 800 - 900°C did not form enstatite, but Si-rich amorphous oxides. However, it should be noted that only the surfaces of a few run products were analyzed in the present study and that we cannot exclude a possibility of crystallization at the interface between forsterite and amorphous condensates, especially samples heated for 48 hours. Analyses of cross sections of run products will be performed in a future study.

Implication for enstatite formation in space:

Magnesium-free amorphous silicates formed on the surface of forsterite at 1070-1170 K and 10^{-4} - 10^{-5} Pa in the present study is inconsistent with μm -thick polycrystalline enstatite layers formed in experiments at higher temperatures [4]. This difference is considered to be caused by the difference of reaction temperatures (and may be pressure).

Experimental conditions in the present study, such as temperature and pressure, are close to the formation conditions of enstatite in a mass-loss wind from AGB stars [5]. Our preliminary results thus implies that enstatite formation by solid-gas reactions between forsterite and Si-rich gas cannot be expected in a mass-loss wind and that enstatite may be formed either by direct kinetic condensation from gas [6] or by crystallization at the interface between forsterite and condensed Si-rich amorphous due to annealing.

References: [1] Anders, E. and Grevesse, N. (1989) *GCA* **53**, 197-214. [2] Grossman, L. (1972) *GCA* **37**, 1119-1140. [3] Wood, J. A. and Hashimoto, A. (1993) *GCA* **57**, 2377-2388. [4] Imae, N. et al. (1993) *EPSL* **118**, 21-30. [5] Ferrarotti, A. S. and Gail, H. -P. (2001) *A&A* **371**, 133-151. [6] Kozasa, T. and Hasegawa, H. (1987) *Prog. Theor. Phys.* **77**, 1402-1410.

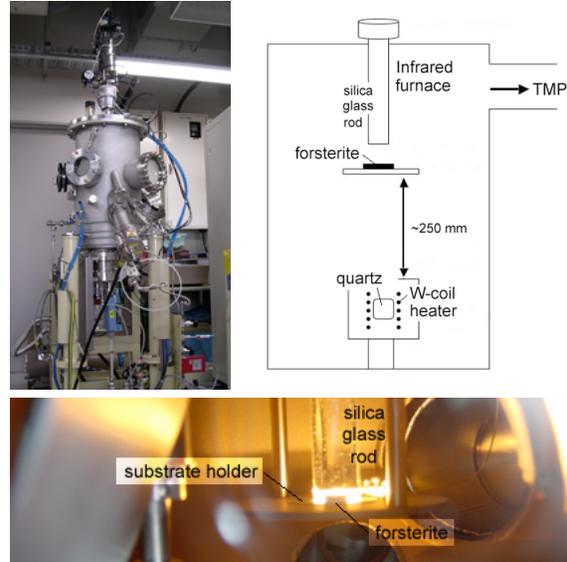


Figure 1: (upper left) The new vacuum furnace used in the present experiments. (upper right) Schematic illustration of the vacuum chamber. (bottom) A substrate holder heated by the infrared furnace.

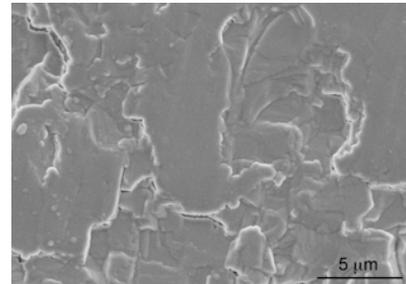


Figure 2: An SEI image of the surface of forsterite reacted with Si-rich gas at $\sim 900^\circ\text{C}$ for 48 hours without an oxygen flow.

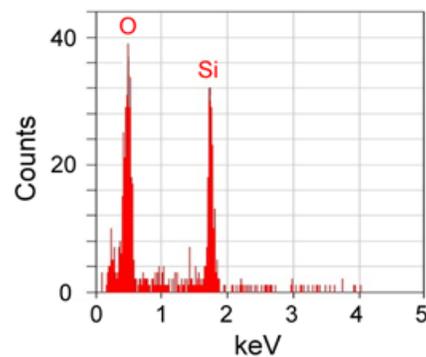


Figure 3: An EDS spectrum of the reaction layer heated at $\sim 900^\circ\text{C}$ for 48 hours. The spectrum was obtained with an accelerating voltage of 5 kV.