

REACTION EXPERIMENTS OF FORSTERITE WITH SI-RICH GAS IN MOLECULAR-BEAM EPITAXY TYPE VACUUM FURNACE. H. Chiba¹, S. Tachibana¹, H. Nagahara¹, and K. Ozawa¹,

¹Department of Earth and Planetary Science, University of Tokyo, 7-3-1 Hongo, Tokyo 113-0033, Japan. tachi@eps.s.u-tokyo.ac.jp

Introduction: Magnesium and Si are the major rock-forming elements. Bulk Mg/Si ratios of chondrites and probably of terrestrial planets are not the same as the solar Mg/Si ratio (1.074; [1]), but show a variation ranging from lower to higher than the solar ratio [2-4]. This suggests that Mg/Si elemental fractionation between solid and gas occurred in the early solar system.

Elemental fractionation in the early solar system occurred as a result of chemical reactions that form chemical diversity between solid and gas and their physical separation. Equilibrium condensation calculation in the system of solar abundance indicates that a potential reaction capable of changing Mg/Si ratios of solid and gas is formation of enstatite (MgSiO₃) by a reaction between forsterite (Mg₂SiO₄) and Si-rich gas during cooling of the system. A large fraction of Mg-bearing gas condense into solids by formation of forsterite in the cooling system, and most of Si-bearing gas go into solids by formation of enstatite. The bulk Mg/Si ratio in condensates thus changes largely during formation of enstatite, and becomes close to the solar value after formation of enstatite. The Mg/Si fractionation in the early solar system should have occurred in the course of processes of forsterite condensation and enstatite formation. Note that it may have occurred during evaporation of enstatite and forsterite when the system was heated.

Reaction kinetics is a key factor to discuss the physical and chemical conditions, where Mg/Si fractionation occurred in the early solar system because the degree of fractionation largely depends on timescales of chemical reactions and physical separation process. For instance, maximum fractionation is expected when condensates separate from the system simultaneously with their formation due to rapid separation of solids.

Kinetics of enstatite formation: There have been experimental studies on reactions involving forsterite and enstatite (mostly on evaporation [e.g., 5-9]). There has been only one study on formation kinetics of enstatite [10], where diffusion-controlled formation kinetics of enstatite by a reaction between forsterite and Si-rich gas was obtained at 1650-1820 K. The reaction rates were extrapolated down to plausible enstatite-forming temperatures in protoplanetary disks and in a mass-loss wind from an evolved star to discuss enstatite formation [e.g., 10, 11]. However, it is not always valid to extrapolate the reaction kinetics obtained at higher temperatures to lower temperatures because a micro-

scopic reaction controlling an overall reaction may be different or even a different overall reaction may occur.

Here we report experiments on a reaction between forsterite and Si-rich gas at temperatures close to formation temperatures of enstatite in protoplanetary disks and circumstellar environments using a molecular-beam epitaxy (MBE) type vacuum furnace.

Experiments: The MBE-type furnace consists of a vacuum chamber equipped with a pumping system, a furnace with a tungsten-coil heater for gas generation, an infrared furnace for substrate heating, and a gas inlet system to introduce oxygen in the chamber.

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). Silica glass was heated at ~1650°C to generate Si-rich gas. In some runs, silica glass mixed with alumina was heated at ~1675°C, at which SiO₂-rich melt forms in the SiO₂-Al₂O₃ system, to increase the flux of Si-rich gas.

A chip of single crystal of forsterite (~4 x 4 x 0.5 mm) or a couple of chips of single crystal of forsterite (~4 x 2 x 0.5 mm) were put ~250 mm above the gas source, and heated at 900-1000°C, which is within the typical range of enstatite formation in protoplanetary disks, by an infrared furnace from behind. The temperature of the infrared heating system was calibrated against melting temperatures of silver (962°C) and sodium chloride (801°C). We covered the surface of forsterite opposite to the reaction surface with a platinum foil for effective heating by infrared light.

The pressure in the vacuum chamber during experiments was in the order of 10⁻⁴-10⁻⁵ Pa without oxygen flow. The experiment in the presence of oxygen flow was also carried out under a controlled total pressure of (4-7) x 10⁻⁴ 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 desired durations. 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. The surface of one sample was cut by a focused ion beam (FIB) method and the interface between forsterite and reaction product was observed transmission electron microscopy (TEM).

Results: The EDS and EBSD analyses of the surface of run products show that Si-rich amorphous oxide was formed in all the runs (Fig. 1).

No enstatite was found even at the interface between forsterite and surface deposit (Fig. 2), suggesting that no reaction occurred between forsterite and Si-rich gas in the present experiments. No crystallization of Si-O rich amorphous layer occurred either.

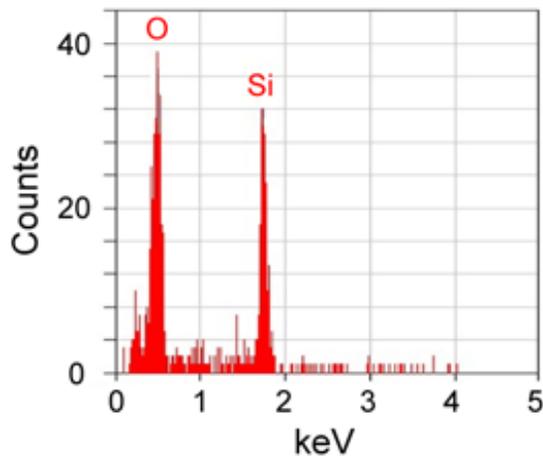


Fig. 1. An EDS spectrum of the reaction layer heated at $\sim 900^\circ\text{C}$ for 48 hours. The spectrum was obtained with an accelerating voltage of 5 kV to obtain characteristic X-rays only from the thin reaction layer.

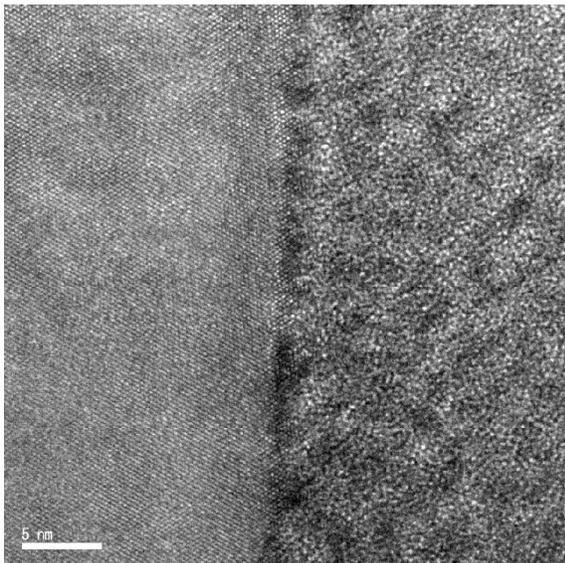


Fig. 2. The interface between forsterite (left) and surface deposit formed at $\sim 1000^\circ\text{C}$ for 48 hours (right). The deposit was Si-rich amorphous oxide. No crystalline phase was found at the interface. The scale bar is 5 nm.

Discussion: The present results are inconsistent with previous experiments, where enstatite formed [10]. The difference between this study and [10] is the temperature for reaction. The temperature range in this study is within the plausible range for enstatite formation in protoplanetary disks and even higher than that for mass-loss winds from evolved stars. Although the data we obtained are still preliminary, the present study implies that formation of enstatite via a reaction between forsterite and Si-rich gas under realistic temperature conditions is kinetically less favored and that Si-rich amorphous oxide forms instead.

If this is the case, enstatite may form either by direct condensation from gas [e.g., 12] or by crystallization at the interface between forsterite and condensed Si-rich amorphous oxide due to annealing. We are currently working on annealing experiments of run products to test the latter possibility. We expect to report on the results at the conference.

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] Lodders, K. (2003) *Ap. J.* **591**, 1220-1247. [5] Hashimoto, A. (1990) *Nature* **347**, 53-55. [6] Nagahara, H. and Ozawa, K. (1996) *GCA* **60**, 1445-1459. [7] Tsuchiyama, A. et al. (1998) *Mineral. J.* **20**, 113-126. [8] Tachibana, S. et al. (2002) *GCA* **66**, 713-728. [9] Takigawa, A. et al. (2009) *Ap. J.* **707**, L97-L101. [10] Imae, N. et al. (1993) *EPSL* **118**, 21-30. [11] Ferrarotti, A. S. and Gail, H. -P. (2001) *A&A* **371**, 133-151. [12] Kozasa, T. and Hasegawa, H. (1987) *Prog. Theor. Phys.* **77**, 1402-1410.

This work is supported by Grant-in-Aids for Scientific Research (16104007), and the authors thank T. Kogure for his help with use of FIB and observation with TEM.