

Hydrous mineral formation reaction between amorphous forsterite and water vapor in protoplanetary disks

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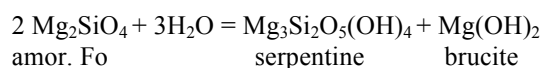
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Introduction

Several sources have been suggested as a source of terrestrial water; asteroidal water, cometary ice, disk gas and water molecules adsorbed on dust [e.g., 1]. Hydrous silicate dusts formed by gas-solid reaction in the solar nebula is also a possible carrier of water to the proto-Earth, but kinetic studies on hydrous mineral formation from crystalline magnesian silicates and water vapor have shown that the reaction is too sluggish to occur within the lifetime of protoplanetary disk [2, 3]. However, infrared observations and investigations of extraterrestrial materials show that both crystalline and amorphous silicate dust exist in protoplanetary disks. Amorphous silicates are thermodynamically unstable and may thus react with water vapor more rapidly than crystalline silicates. Moreover, hydrous phases may be formed from amorphous silicates as metastable phases at temperatures higher than their stable temperatures. In this study, in order to explore the possibility of hydrous mineral formation between amorphous silicates and water vapor in protoplanetary disks, we performed gas-solid reaction experiments between water vapor and amorphous forsterite.

Thermodynamics of hydrous mineral formation

Hydrous minerals that can be formed from crystalline forsterite are serpentine [$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$], and brucite [$\text{Mg}(\text{OH})_2$] [2, 3]. The expected reaction between amorphous forsterite (amor. Fo) and water vapor can also be expressed as follows;



With the standard Gibbs free energy for formation of amorphous forsterite [4], serpentine and brucite [5], a metastable phase boundary between amorphous forsterite and hydrous phases was obtained as a function of temperature and a partial pressure of H_2O (Fig. 1). The phase boundary between crystalline forsterite and hydrous phases is also shown in Fig. 1.

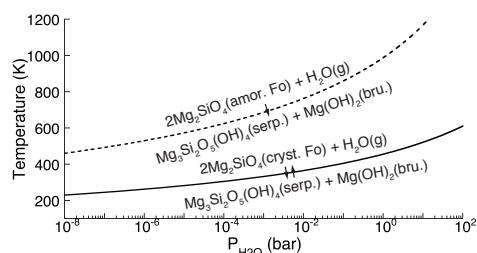


Fig. 1. –The metastable phase boundary between amorphous forsterite and hydrous phases (dotted curve) and a thermodynamic phase boundary between crystalline forsterite and hydrous phases (solid curve).

The metastable boundary between amorphous forsterite and hydrous phases is located $>200\text{K}$ above that for crystalline forsterite, indicating that amorphous forsterite could be hydrated at higher temperatures than crystalline forsterite.

Experiments

We conducted closed-system reaction experiments between amorphous forsterite and water vapor in sealed silica glass tubes at temperatures of 1023, 773, 723, 623, 523, 473 and 423 K and $P_{\text{H}_2\text{O}}$ of ~ 0 –50 bar for 2–694.5 hr. Water vapor pressures inside the glass tubes were controlled either by complete evaporation of pure water liquid (1–26 μL) for $P_{\text{H}_2\text{O}}=5$ –50 bar or by a $\text{Ca}(\text{OH})_2$ – CaO buffer for $P_{\text{H}_2\text{O}}<1.6$ bar. Amorphous forsterite powder, synthesized by a thermal plasma method, was provided by A. Tsuchiyama, Kyoto University. The amorphous powder was put in an inner silica glass tube (4 and 3 mm in outer and inner diameters) and placed in an outer silica glass tube (6 and 4 mm in outer and inner diameters) to prevent direct contact with liquid water or $\text{Ca}(\text{OH})_2$. The glass tubes were sealed in air for high $P_{\text{H}_2\text{O}}$ runs, while those were sealed in vacuum for low $P_{\text{H}_2\text{O}}$ runs. The experiments in glass tubes without water but with air were also done. The $P_{\text{H}_2\text{O}}$ in such experiments was at most 0.06 bar and regarded as $P_{\text{H}_2\text{O}}=0$ bar hereafter. Run products were analyzed with FT-IR (KBr pellet method; JSM FT/IR-4200), XRD (MX-Lab) and Raman spectroscopy (Acton SP-2750; Princeton Instruments, Inc.).

Results and Discussion

Infrared spectra of run products of 1023, 773, 623, 523 K are summarized with standards in Fig. 2. At 1023 K and $P_{\text{H}_2\text{O}}$ of 5–50 bar, amorphous forsterite turned into crystalline forsterite with 0.5-hr heating and no hydrous phase was observed (Fig. 2 a). Samples reacted at 773 K and $P_{\text{H}_2\text{O}}$ of 5–50 bar for 2 hr have small but sharp 2.7 μm absorption features (Fig. 2b). After further heating of 20 hr, the absorbance of 2.7 μm features decreased and these spectra changed into those of crystalline forsterite. These results clearly suggest the metastable formation of hydrous phase(s) at the temperatures above the thermodynamic boundary of hydrous phases. Samples reacted at 623 K and $P_{\text{H}_2\text{O}}$ of 5–50 bar for 24 hr also showed serpentine-like spectra with sharp 2.7 μm features (Fig. 2c). These hydrous phase(s) survived even after long-time heating of 336 hr. Both crystalline and amorphous forsterite were used as starting materials at 523 K and $P_{\text{H}_2\text{O}}$ of 5–42 bar, where both phases are expected to react into

serpentine + brucite. With 48-hr heating, only amorphous forsterite were hydrated and crystalline forsterite remained unchanged (Fig. 2d), implying that amorphous forsterite is hydrated more rapidly than crystalline forsterite.

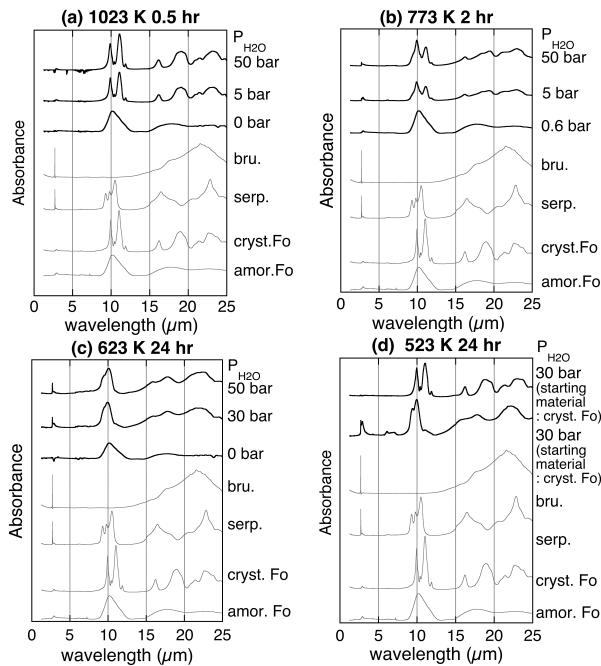


Fig. 2 –Infrared spectra of run products (thick curves) heated at 1023, 773, 623 and 523 K and P_{H_2O} of 0–50 bar with standard samples (thin curves).

The sample heated at 773 K and P_{H_2O} of 50 bar for 2 hr showed only an XRD pattern of crystalline forsterite in spite of the detection of 2.7 μm in infrared features. This may be because the abundance of hydrous phase(s) is too small to be detected with XRD (Fig. 3). The sample heated at 623 K and P_{H_2O} of 50 bar for 24 hr showed an XRD pattern similar to serpentine with a small peak of brucite (001). The small intensity of brucite peak may be due to its low mass fraction and low crystallinity.

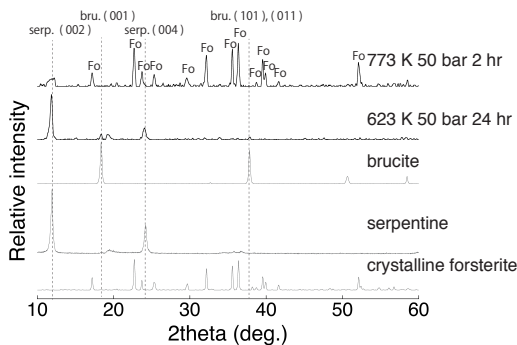


Fig. 3 –XRD patterns of run products and standards.

The presence of brucite was clearly confirmed by micro-Raman spectroscopy. We obtained Raman spectra at a high-frequency region (3164.60–3819.15 cm^{-1}) with the grating of 1200 lines/mm, where Raman peaks assigned to OH stretching vibrations in hydrated phase are present. The samples heated at 523 K and P_{H_2O} of 42 bar for 2 hr and at 623 K and

P_{H_2O} of 50 bar for 24 hr showed two peaks at 3651, 3694 cm^{-1} and 3650, 3697 cm^{-1} respectively. The peak positions of brucite and serpentine obtained from standard samples are 3649 cm^{-1} and 3696 cm^{-1} . Although there are slight differences in peak positions between run products and standards, which might be due to the low crystallinity of run products, the micro-Raman spectroscopy showed the presence of brucite in run products, and also indicated that two phases exist with a molar ratio of $\sim 1:1$.

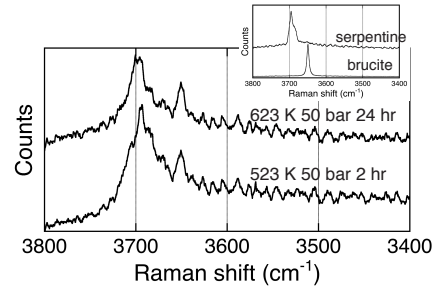


Fig. 4 –Raman spectra of run products heated at 523 K and P_{H_2O} of 50 bar for 2 hr and at 623 K and P_{H_2O} of 50 bar for 24 hr.

The experimental results are summarized in Fig. 5. and we concluded that hydrous mineral formation from amorphous forsterite and water vapor occurs as a metastable reaction at temperatures higher than the thermodynamic boundary of hydrous phases at P_{H_2O} of 5–50 bar. We also found that the hydrous mineral formation from amorphous forsterite occurs with a faster rate than from crystalline forsterite. This implies that hydrous minerals may be formed from amorphous forsterite grains by gas-solid reaction in protoplanetary disks within their lifetime.

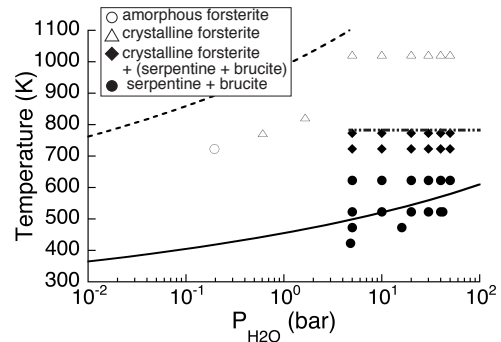


Fig. 5 –Summary of experimental results. Hydrous mineral formation boundary of amorphous forsterite (dash-dotted line) may exist between the metastable phase boundary between amorphous forsterite and hydrous phases (dotted curve) and a thermodynamic phase boundary between crystalline forsterite and hydrous phases (solid curve).

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