

EXPERIMENTAL STUDY ON HYDROUS MINERAL FORMATION REACTION BETWEEN AMORPHOUS FORSTERITE AND WATER VAPOR. D. Yamamoto¹, S. Tachibana¹, H. Nagahara², K. Ozawa² and A. Tsuchiyama³, ¹Department of Natural History Sciences, Hokkaido University, Sapporo, Hokkaido 060-0810, Japan (daiki@ep.sci.hokudai.ac.jp), ²Department of Earth and Planetary Science, The University of Tokyo, Hongo, Tokyo 113-0033, Japan, ³Department of Geology and Mineralogy, Kyoto University, Kyoto 606-8502, Japan

Introduction: Several sources have been suggested as the origin of terrestrial water such as hydrated asteroids, comets, disk gas and water molecules adsorbed on silicate grains [e. g., 1–4]. Hydrous silicate formed by a reaction between anhydrous silicate and water vapor can also be possible carrier of water to the rocky planet forming region inside the snowline because hydrous silicate are thermodynamically stable at ~250–225 K in protoplanetary disks [5]. However, kinetic studies on the reaction between anhydrous Mg-silicate and water vapor [5, 6] showed that hydrous silicate formation reaction is too sluggish to occur within the lifetime of protoplanetary disks. Infrared observations and investigations of extraterrestrial materials have shown that both crystalline and amorphous silicate dust exist as primary solid in protoplanetary disks. Amorphous silicates are thermodynamically unstable and may thus react with water vapor more effectively and/or rapidly than crystalline silicates. Moreover, hydrous phases may form from amorphous silicate as metastable phases at higher temperatures than their stability field [7]. In this study, in order to explore the possibility of hydrous mineral formation by the reaction between amorphous silicate and water vapor in protoplanetary disks, we performed closed-system gas-solid reaction experiments between amorphous forsterite and water vapor.

Experiments: Closed-system reaction experiments between amorphous forsterite and water vapor were conducted in sealed silica glass tubes at temperatures of 1023–423 K and water vapor pressures ($P_{\text{H}_2\text{O}}$) of ~0–50 bar for 0.5–694.5 hours. The starting material was 10–100 nm-sized amorphous forsterite powder synthesized by a thermal plasma method [8]. Amorphous forsterite, put into an inner silica glass tube (4 and 3 mm in outer and inner diameters, respectively) was placed in an outer silica glass tube (6 and 4 mm in outer and inner diameters, respectively). $P_{\text{H}_2\text{O}}$ inside the glass tubes were controlled either by complete evaporation of pure water liquid (1–26 μL) for $P_{\text{H}_2\text{O}} = 5\text{--}50$ bar or by a $\text{Ca}(\text{OH})_2\text{--CaO}$ buffer for $P_{\text{H}_2\text{O}} < 1.6$ bar. Pure water liquid injected into an alumina tube or reagent powder of $\text{Ca}(\text{OH})_2$ was put into the outer glass tube. The glass tubes were then sealed in air for high $P_{\text{H}_2\text{O}}$ run ($P_{\text{H}_2\text{O}} > 5$ bar), because water vapor in air is negligibly small ($P_{\text{H}_2\text{O}} < 10^{-1}$ bar), and in vacuum for low $P_{\text{H}_2\text{O}}$ runs ($P_{\text{H}_2\text{O}} < 1.6$ bar). The sealed glass tubes

were heated for a desired duration in a box furnace, and quenched in air. Crystalline forsterite, for comparison to amorphous reactant, was also used as a starting material for the runs at 523 K, where hydrous phases could be thermodynamically stable at an appropriate $P_{\text{H}_2\text{O}}$.

We also made heating experiments on amorphous forsterite at 953 K in vacuum ($P_{\text{H}_2\text{O}} < 10^{-8}$ bar) using a gold-image vacuum furnace (Thermo-Riko GFA430VN), where amorphous forsterite powder put in a silica-glass boat was directly exposed to vacuum.

Run products were analyzed with FT-IR (KBr pellet method; JSM FT/IR-4200), XRD (MX-lab), micro-Raman spectroscopy (Acton SP-2750).

Results and Discussion: Typical infrared spectra of run products heated at different temperature and $P_{\text{H}_2\text{O}}$ conditions are summarized in Fig. 1.

High $P_{\text{H}_2\text{O}}$ experiments. At 1023 K, amorphous forsterite transformed into crystalline forsterite with 0.5 hour heating at $P_{\text{H}_2\text{O}} = 5\text{--}50$ bar, and no hydrous phase was observed. In contrast, samples heated with no liquid water remained unchanged (Fig. 1a). This clearly indicates that water vapor promotes crystallization of amorphous forsterite at 1023 K. A similar effect of water vapor on crystallization of amorphous forsterite was confirmed at 953 K. FT-IR analyses of the samples heated for 2 hours at $P_{\text{H}_2\text{O}} = 50$ bar and in vacuum showed that the fraction of crystalline forsterite is almost unity in the sample heated at $P_{\text{H}_2\text{O}} = 50$ bar, while that is 0.02 in the sample heated in vacuum. We thus concluded that water vapor promotes crystallization of amorphous forsterite at temperatures ranging 953–1023 K.

Run products heated at 773 K and $P_{\text{H}_2\text{O}} = 5\text{--}50$ bar for 2 hours shows a small but sharp infrared absorption feature at 2.7 μm (Fig. 1b), which is due to stretching vibration of OH bond. After further heating for 20 and 47 hours, the absorption feature at 2.7 μm weakened and the overall spectral features changed to that resembling those of crystalline forsterite. The XRD pattern of sample heated at $P_{\text{H}_2\text{O}} = 50$ bar shows prominent peaks of crystalline forsterite with a small and broad reflection that is assigned to the crystallographic (002) plane of chrysotile or the (001) plane of lizardite. The micro-Raman spectrum of the same sample clearly shows the coexistence of serpentine and crystalline forsterite. These results suggest that hydrous phase(s) temporarily formed in a short-time duration eventually

dehydrated to form crystalline forsterite at 773 K in the presence of water vapor.

Samples heated for 24 hours at 623 K and $P_{\text{H}_2\text{O}} = 5\text{--}50$ bar show serpentine-like spectra features with sharp $2.7\ \mu\text{m}$ absorption (Fig. 1c). The spectral features became closer to those of serpentine with further heating, and samples heated for 432 hours show the spectra most closely resembling serpentine (Fig. 1c). In XRD pattern of sample heated at $P_{\text{H}_2\text{O}} = 50$ bar for 24 hours, two broad peaks that can be assigned to the reflection from the (002) plane of chrysotile or from the (001) plane of lizardite, and that from the (004) plane of chrysotile appeared. The presence of brucite was clearly confirmed by micro-Raman spectroscopy with the detection of Raman-shift peak at $3650\ \text{cm}^{-1}$. These lines of evidence indicate that hydrous mineral formation proceeded at least after 432 hours heating at 623 K.

Only amorphous forsterite transformed into hydrous phase(s) and crystalline forsterite remained unchanged at 523 K and $P_{\text{H}_2\text{O}} = 30$ bar for 24 hours, implying that hydrous minerals formed from amorphous forsterite more rapidly than from crystalline forsterite.

Low $P_{\text{H}_2\text{O}}$ experiments. Run products heated at 823 K and $P_{\text{H}_2\text{O}} = 1.6$ bar for 141 hours and at 773 K and $P_{\text{H}_2\text{O}} = 0.6$ bar for 20 hours showed only crystallization of amorphous forsterite. Further experiments at lower temperatures for longer duration are surely needed.

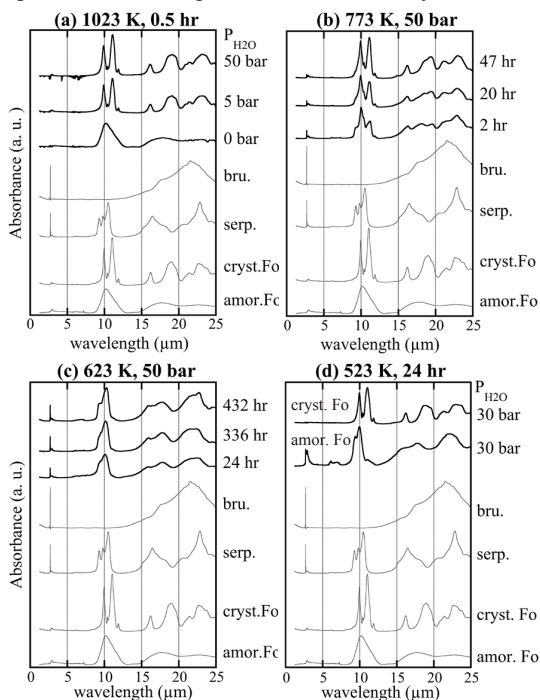


Fig. 1. Infrared spectra of run products (thick curves) heated at (a) 1023 K, (b) 773 K, (c) 623 K and (d) 523 K with references (amor. Fo: amorphous forsterite; cryst. Fo: crystalline forsterite; serp.: chrysotile serpentine; bru.: brucite).

Summary: The present experimental results are summarized in Fig. 2., and we conclude that hydrous mineral formation from amorphous forsterite and water vapor occurs via a metastable reaction at temperatures higher than the thermodynamically stable field for hydrous phases at $P_{\text{H}_2\text{O}}$ of $5\text{--}50$ bar. We also found that the hydrous minerals form more rapidly from amorphous forsterite than from crystalline forsterite. Although further experiments at lower $P_{\text{H}_2\text{O}}$ conditions are needed for extrapolation to disk conditions, hydrous minerals may form from amorphous forsterite grains by a reaction with water vapor in protoplanetary disks within their lifetime.

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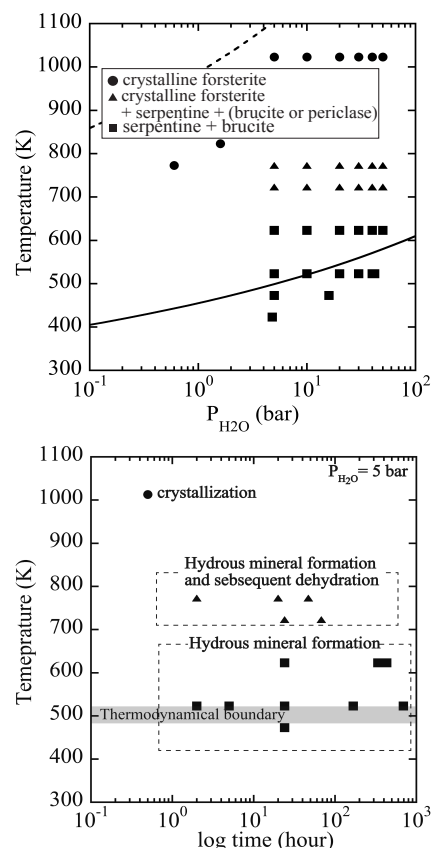


Fig. 2. Phases obtained in the reaction experiments. *Top.* Run products shown with temperature and $P_{\text{H}_2\text{O}}$ conditions. A thermodynamic boundary of hydrous phases and a metastable boundary between amorphous forsterite and hydrous phases [7] are also shown. *Bottom:* Run products at $P_{\text{H}_2\text{O}} = 5$ bar shown with temperature and duration.