A KINETIC STUDY ON HYDROUS MINERAL FORMATION REACTION BETWEEN AMORPHOUS FORSTERITE AND WATER VAPOR IN PROTOPLANETARY DISKS.

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Introduction: Hydrous silicates formed by a reaction between anhydrous silicate and water vapor are one of the possible water carriers to the rocky planet forming region because hydrous silicate are thermodynamically stable at ~250−225 K in protoplanetary disks [1]. Prinn and Fegley (1989) [1] modeled hydrous silicate formation in protoplanetary disk by the Simple Collision Theory (SCT) with the activation energy of MgO hydration, which yielded ~70 kJ/mol. They concluded that the reaction between anhydrous crystalline Mg-silicate and water vapor is too sluggish to occur within the disk lifetime.

Infrared observations and investigations of extraterrestrial materials have shown that both crystalline and amorphous silicate dust exist as primary solid in protoplanetary disks [e.g. 2]. Amorphous silicates are thermodynamically unstable and may thus react with water vapor more effectively and/or rapidly than crystalline silicates. In this study, in order to explore the possibility of hydrous mineral formation by the reaction between amorphous silicates and water vapor and the stability of hydrous minerals in protoplanetary disks, we performed hydrous mineral formation reaction experiments between amorphous forsterite and water vapor and dehydration experiments of serpentine in vacuum.

Experiments: *Hydrous mineral formation reaction experiment.* Gas-solid reaction experiments were carried out using an autoclave at temperatures of 323−373 K and water vapor pressure (P_{H2O}) of ~0.1−1 bar for 0.5−60 hours. The starting material was 10–100 nm-sized amorphous forsterite powder synthesized by a thermal plasma method [3]. The sample and water were put separately in the autoclave without direct contact.

Dehydration experiments. Dehydration experiments of serpentine were carried out at 898−723 K for 5 minutes−12 hours using a gold-image vacuum furnace (Thermo-Riko GFA 430VN). We used grounded natural antigorite serpentine (Nagatoro, Saitama prefecture, Japan) as a starting material. The sample was weighted before and after heating and the extent of dehydration was determined by the weight loss of sample.

Run products from both experiments were analyzed with FT-IR (KBr pellet method) and XRD (SmartLab, Rigaku).

Results: *Hydrous mineral formation reaction experiments.* Infrared spectra of run products heated at 373 K and P_{H2O} of ~1 bar are shown in Fig. 1. The 10

μm feature attributed to Si-O stretching vibration gradually changed from a broad feature of amorphous forsterite to some sharp features with time. We also found the gradual development of ~2.7 μm feature, which is assigned to free -OH stretching vibration. The XRD pattern of run products changed the original halo peak of amorphous forsterite to those of serpentine polymorphs and brucite. Quantitative analysis of the serpentinization degree was made based on the spectra fitting of the 10 μm feature and the development of the free -OH stretching vibration band. The time evolution of serpentinization derived from the spectral evolution at ~10 μm and ~2.7 μm can be fitted with the Johnson-Mehl-Avrami (JMA) equation (Fig. 2) and the equation of interface-controlled reaction.
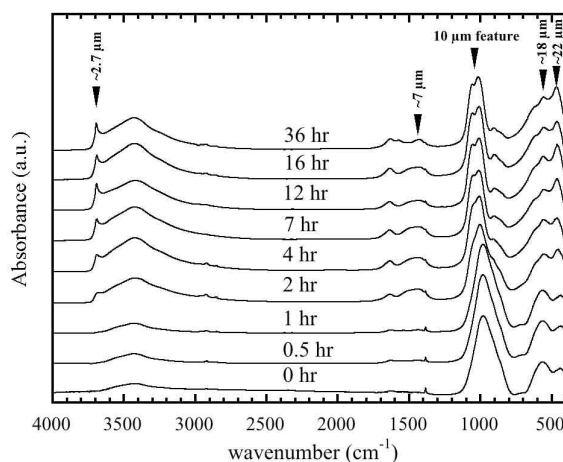

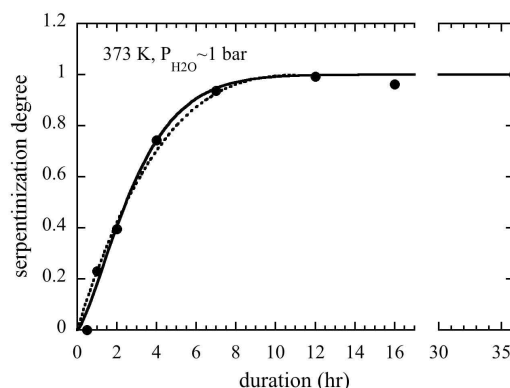Fig. 1. Infrared spectra of run products heated at 373 K and P_{H2O}~1 bar for different durations.

Fig. 2. Serpenitinization degree estimated from the spectral fitting at 10 μm versus heating duration at 373 K and P_{H2O}~1 bar. The fitting curves with a JMA equation (solid curve) and an interface-controlled reaction (dotted curve).

Experimental data was fitted well with the JMA equation with Avrami exponent n~1 and the equation of interface-controlled reaction, suggesting that hydrous mineral formation is controlled by an interface reaction between amorphous forsterite and hydrous phases. The activation energy of the rate constant for serpentinization are ~21 kJ/mol and ~16 kJ/mol for the spectral evolution at ~10 and ~2.7 μm, respectively.

Dehydration experiments. Infrared spectra of samples heated at 723 K for 0.25−12 hr in vacuum are shown in Fig. 3. With dehydration, the relatively sharp features at ~10, 16, 18 and 22 μm originated from Si-O stretching vibration and O-Si-O vending vibration modes became broaden and the peak intensity of 2.7 μm feature attributed to the free –OH stretching mode of
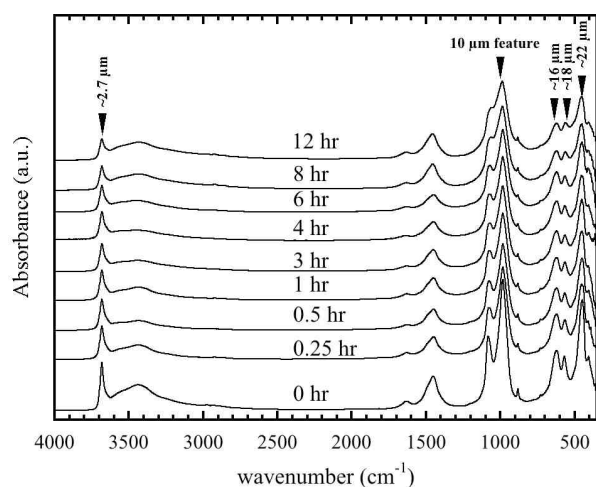

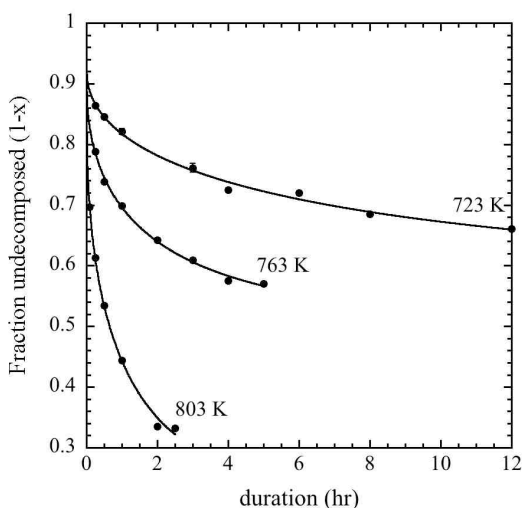Fig. 3. Infrared spectra of run products heated at 723 K for different durations in vacuum.

Fig.4. Time evolution of dehydration fraction of serpentine at 723, 763 and 803 K. The fitted curves were obtained based on the three-dimensional diffusion controlled reaction model (modified Jander equation).

serpentine decreased. This indicates the loss of hydroxyl group accompanied with the formation of disordered structure by dehydration. The weight loss of samples was converted into the degree of dehydration regarding the weight loss of samples (~13.5 %) heated at 898 K for 3−4 hr as complete dehydration. Note that the weight loss of ~13.5 % is almost consistent with the weight fraction of water in stoichiometric serpentine.

The three-dimensional diffusion controlled reaction can provide the best fit of time evolution of dehydration of serpentine in vacuum (Fig. 4), and the rate constant k at 723−803 K followed an Arrhenius relationship with activation energy of ~112 kJ/mol and a frequency factor of ~$5.0 \times 10^2 \, s^{-1}$.

Discussion: We apply the activation energy of hydration of amorphous forsterite to the SCT model [1] to determine the time scale of hydrous mineral formation from amorphous forsterite. This timescale is compared with the dehydration time scales of serpentine (this study) and brucite [4] and the crystallization timescale of amorphous forsterite [5] in the solar nebula [Fig. 5]. The comparison indicates that amorphous forsterite could be hydrated to form serpentine and brucite within the lifetime of solar nebula (<10Myr [6]) at total pressure of solar nebula of 10^{-3} bar, which will be discussed in more detail at the conference.

References: [1] Prinn, R. G. & Fegley, B. J. (1989) In *Origin and Evolution of Planetary and Satellite Atmospheres*, 78–136. [2] Henning Th. (2010) *Annual Review of Astronomy and Astrophysics*, 48, 21–46. [3] Koike, C. et al. (2010) ApJ, 709, 983–992. [4] Gordon, R. S. & Kingery, W. D. (1967) J. Am. Ceram. Soc., 50, 8–14. [5] Yamamoto, D. & Tachibana, S. Metsoc, 78, 5247. [6] Pascucci, I. & Tachibana, S. (2010) Protoplanetary Dust, 263–298.
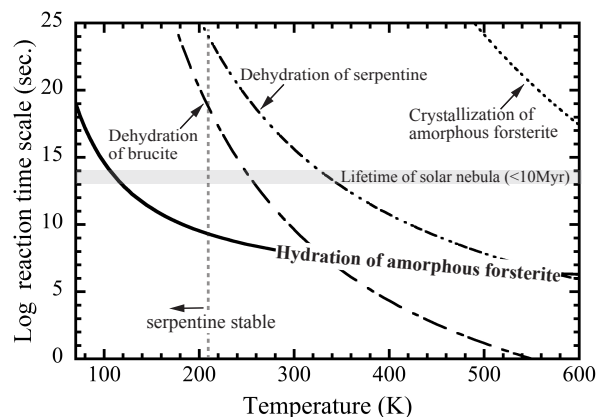

Fig. 5. Time scales of hydrous mineral formation from amorphous forsterite, dehydration of serpentine and brucite [5] and crystallization of amorphous forsterite [6] in the solar nebula with a total pressure of 10^{-3} bar.