

THE EFFECT OF WATER VAPOR ON EVAPORATION KINETICS OF FORSTERITE. S. Inada¹ and S. Tachibana¹, ¹Department of Earth and Planetary Science, The University of Tokyo (7-3-1 Hongo, Tokyo 113-0033, Japan).

Introduction: Water vapor is a major oxidant in gas-solid reactions in the early Solar System. A wide variety of oxidation states among chondrites or chondritic components indicates that the redox state of the Sun's protoplanetary disk varied within the chondrite forming region, which could have been caused by heterogeneous water vapor distribution in the disk due to accretion and sublimation of icy dust/pebbles [e.g., 1, 2]. Such heterogeneous distribution of water vapor also explains the oxygen isotope evolution of dust in the inner Solar System [3].

Water vapor may affect the evaporation kinetics of minerals and melts that was responsible for elemental and isotopic fractionation processes in the early Solar System. An evaporation flux under low pressure conditions (J_{vap}) has conventionally been described using Hertz-Knudsen (HK) equation [e.g., 4, 5]:

$$J_{vap} = \frac{\gamma P^{eq}}{\sqrt{2\pi mRT}}, \quad (1)$$

where m and P^{eq} are the mass and the equilibrium vapor pressure of evaporating gas species, R is the gas constant, T is temperature, and γ is the evaporation coefficient defined as a ratio of a measured flux to the ideal flux ($0 < \gamma \leq 1$).

Several experiments on evaporation of forsterite (Mg_2SiO_4), a major magnesium silicate, in low-pressure H_2 gas found that P_{H_2} dependence of evaporation rates is attributed to the change of P^{eq} (eq. (1)) [e.g., 6]. The effect of water vapor on evaporation of forsterite was investigated for the Mg_2SiO_4 - H_2 - H_2O system based on the HK equation [7]. It was predicted that the evaporation occurs either (1) in the free evaporation-dominated (FED) regime, where the effects of H_2 and H_2O are ignored, under the low P_{H_2} and P_{H_2O} condition, (2) in the hydrogen reaction-dominated (HRD) regime, where the evaporation rate increases proportionally to $P_{H_2}^{1/2}$, in the protoplanetary disk-like P_{H_2} condition [7], or (3) in the H_2 - H_2O buffer-dominated (HBD) regime, where the evaporation rate depends on P_{H_2}/P_{H_2O} under the oxidizing or low temperature conditions.

However, evaporation of forsterite in the HBD regime has not been experimentally confirmed yet. Moreover, the validity of the HK equation, given from the detailed balance between evaporation and condensation at equilibrium, under disequilibrium conditions is not necessarily guaranteed [8].

In this study we present preliminary results of evaporation experiments of forsterite in the presence of both H_2 and H_2O . We also propose a reaction model that

reasonably explains previous and present experiments and leads to derivation of the HK equation under disequilibrium.

Methods:

Experiments. The starting material was a single crystal of forsterite cut into rectangular parallelepipeds with the size of $\sim 1 \times 6 \times 6$ mm, the largest face parallel to (010). Evaporation experiments were carried out in a vacuum furnace (background pressure $\sim 10^{-4}$ Pa) at 1600 and 1350 K. Hydrogen gas was introduced into the furnace and its pressure was kept at 1 Pa by adjusting the flow rate. Water vapor was introduced into the furnace by passing H_2 gas ~ 1 cm above liquid water in the gas supply line. The P_{H_2}/P_{H_2O} ratio of the gas was controlled by changing the water temperature at room temperature ($P_{H_2}/P_{H_2O} = 224 \pm 7$) or $10^\circ C$ ($P_{H_2}/P_{H_2O} = 429 \pm 8$).

Weight losses of the samples were measured after the experiments to obtain evaporation rates.

Reaction model. The absolute reaction rate of evaporation as an elementary step was derived using the transition state theory and compared to the HK equation.

Results:

Experiments. Forsterite evaporated congruently without leaving any evaporation residue as in [6]. Weight losses of heated samples increased linearly with heating duration, suggesting that evaporation obeys a linear rate law (Fig. 1). The evaporation rates at 1 Pa hydrogen gas (no water vapor) were obtained from multiple experiments under the same condition, and were calculated to be $(1.13 \pm 0.06) \times 10^{-5}$ and $(6.5 \pm 0.2) \times 10^{-8}$ mol m^{-2} s^{-1} at 1600 and 1350 K, respectively, corresponding to the activation energy of 370 ± 6 kJ/mol. These results are consistent with previous studies [5, 6]. Experiments in 1 Pa of the H_2 - H_2O mixture at 1350 K yielded the evaporation rates of $(6.7 \pm 0.5) \times 10^{-9}$ and $(7.4 \pm 0.6) \times 10^{-9}$ mol m^{-2} s^{-1} at P_{H_2}/P_{H_2O} of 224 ± 7 and 429 ± 8 , respectively. These evaporation rates are smaller than the evaporation rate at 1350 K and 1 Pa of H_2 (Fig. 2).

Reaction model. Based on the transition state theory, the rate of the reaction $A \rightarrow B$ is expressed as follows:

$$J = \left(\frac{k_B T}{2\pi m} \right)^{\frac{1}{2}} \frac{Q_{TS}}{Q_A} \exp\left(-\frac{E^+}{k_B T}\right) [A], \quad (2)$$

where number densities of the condensed phase (A) and the transition state (TS) are given as $[A]$ and $[TS]$. Q_X is a partition function of X , E^+ is the energy difference between A and TS , and k_B is the Boltzmann constant.

Using the equilibrium relation between A and B , eq. (2) is expressed by:

$$J = \left(\frac{k_B T}{2\pi m}\right)^{\frac{1}{2}} \frac{Q_{TS}}{Q_B} \exp\left(-\frac{E^-}{k_B T}\right) [B]^{eq}, \quad (4)$$

where E^- is the energy difference between B and TS , and $[B]^{eq}$ is the number density of B equilibrated with A . When B is vapor, $[B]^{eq}$ corresponds to P^{eq} in the HK equation (eq. (1)), and the HK equation is derived from the transition state theory. Comparison of eq. (4) with eq. (1) shows that the evaporation coefficient γ is given by:

$$\gamma = \frac{Q_{TS}}{Q_B} \exp\left(-\frac{E^-}{k_B T}\right). \quad (5)$$

The same expression was used for the condensation coefficient in previous studies [9, 10], and the detailed balance of evaporation and condensation can be achieved at equilibrium.

We also found that the evaporation rate cannot be expressed by the HK equation when the speciation of TS is different from that of B in the vapor phase, which will be discussed in detail somewhere else.

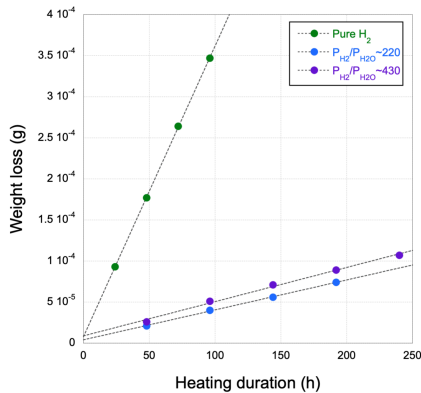


Fig. 1. Weight losses of the forsterite samples heated at 1 Pa of H_2 - H_2O gas or pure H_2 at 1350 K plotted against heating duration (closed circles). Linear regression is shown with dotted lines.

Discussion:

Evaporation kinetics. The present experiments confirmed for the first time that water vapor suppresses evaporation of forsterite in the predicted HBD regime. The evaporation rates at 1350 K with P_{H_2}/P_{H_2O} of ~ 220 and ~ 430 are close to each other and correspond to the evaporation coefficients of ~ 0.015 and ~ 0.008 , respectively (Fig. 2). These estimated evaporation coefficients are similar to but slightly smaller than that obtained in the HRD regime (~ 0.024), and may suggest smaller (P_{H_2}/P_{H_2O}) dependence than that predicted for the HBD regime [8]. If this is the case, the evaporation behavior of forsterite in the HBD regime may not be simply expressed by the HK equation, which should be confirmed by further experiments.

Implications for evaporation of forsterite in protoplanetary disks. It is not clear that evaporation of forsterite obeys the HK equation in the HBD regime [7], but the present study showed that water vapor suppresses the evaporation rate in the HBD regime. When P_{H_2O} in protoplanetary disks is enhanced by a factor of ten [1] from that for the system of solar abundance ($P_{H_2}/P_{H_2O} \sim 2 \times 10^3$ [11]), evaporation of forsterite is expected to occur in the HBD regime at temperature up to ~ 1600 K under the total pressure of ~ 10 Pa. The suppressed evaporation in the presence of water vapor extends the timescale of elemental and isotopic fractionation. If evaporation of CAI melts and chondrule melts also obey the evaporation in the HBD regime, the evaporative elemental and isotopic fractionation would have been suppressed under the enhanced P_{H_2O} condition.

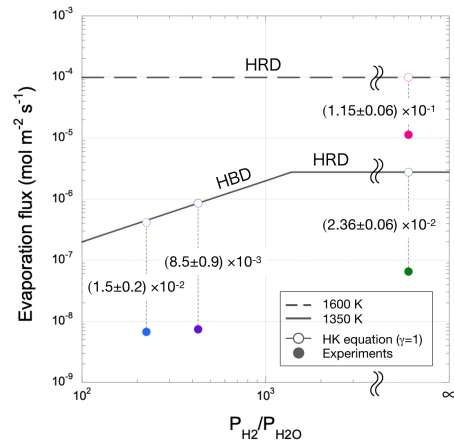


Fig. 2. Evaporation fluxes of forsterite heated at 1 Pa of H_2 - H_2O gas or pure H_2 at 1600 and 1350 K (closed circles). The ideal evaporation fluxes ($\gamma=1$) in the evaporation regimes of HRD (1600 and 1350 K) and HBD (1350 K) are shown with dashed and solid lines, respectively, and open circles represent those predicted for the experimental conditions. The evaporation coefficient (γ) for each experimental condition is shown in the figure.

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