

## EVAPORATION IN EQUILIBRIUM, IN VACUUM, AND IN HYDROGEN GAS : Hiroko NAGAHARA, Geol. Inst., Univ. Tokyo, Hongo, Tokyo 113, Japan.

Evaporation experiments were conducted for SiO<sub>2</sub> in three different conditions; in equilibrium, in vacuum, and in hydrogen gas. Evaporation rate in vacuum is about two orders of magnitude smaller than that in equilibrium, which is consistent with previous works. The rate in hydrogen gas changes depending on hydrogen pressure. The rate at 10<sup>-7</sup> bar of hydrogen pressure is as small as that of free evaporation, but at 10<sup>-5</sup> bar of hydrogen pressure it is larger than that in equilibrium. In equilibrium and in vacuum, the evaporation rate is limited by decomposition of SiO<sub>2</sub> on the crystal surface, but it is limited by a diffusion process for evaporation in hydrogen gas. Therefore, evaporation rate of minerals in the solar nebula can be shown neither by that in equilibrium nor by that in vacuum.

The maximum temperature of the solar nebula at the midplane at 2-3 AU where chondrites are believed to have originated is calculated to be as low as 150K [1], 1500K [2], or in between them [3]. The temperature is, in any case, not high enough for total evaporation of the interstellar materials. Therefore, evaporation of interstellar materials is one of the most important processes for the origin and fractionation of solid materials. Fundamental process of evaporation of minerals has been intensively studied for these several years [4-8]. Those experiments were carried out either in equilibrium or in vacuum; however, evaporation in the solar nebula is in hydrogen (and much smaller amount of helium) gas. In order to investigate evaporation rate and compositional (including isotopic) fractionation during evaporation, vaporization experiments for various minerals in various conditions are conducted. At first, SiO<sub>2</sub> was adopted for a starting material, because thermochemical data and its nature of congruent vaporization are well known.

Experiments were carried out in a vacuum furnace system described by [4]. Capsule is either of Mo or of graphite with 1.5 or 3 mm inner diameter and 4 mm length. A capsule has two small orifices on sides and it is a Knudsen cell. Equilibrium vaporization experiments were carried out by using a capsule with a tight cap. Gas and solid are in equilibrium in the capsule, and equilibrium vapor pressure (Knudsen vapor pressure) was calculated from weight loss per time. The inside of the Knudsen cell is filled with intrinsic vapor from SiO<sub>2</sub> when a Mo-capsule is used, because Mo is not reactive with a silicate system. It is, however, not the case when a C-capsule is used: gas composition is affected by carbon vapor and  $f_{O_2}$  shifted to a lower value. Disequilibrium vaporization experiments were done by using a capsule without a cap, where generated gas is evacuated and does not condense again ("free evaporation"). Weight loss of the sample is converted to "Langmuir vapor pressure". Hydrogen gas was introduced to the chamber to investigate vaporization in a gas flow. The starting material is a single crystal of natural quartz. About 10mg of powdered sample was used for each experiment. Sample weight before and after experiment was precisely measured. Experimental temperature was 1600°C and 1700°C, the base pressure of the vacuum chamber was 10<sup>-11</sup>-10<sup>-9</sup> bar, and experimental duration ranged from 10 min to 1440 min. Hydrogen pressure was controlled by bleeding hydrogen gas through a micro-valve; high pressure above 10<sup>-5</sup> bar was not finely controlled because an ionic gauge does not work at high pressures.

After partial evaporation, residue remains to be SiO<sub>2</sub> in every experiment, suggesting that SiO<sub>2</sub> evaporates congruently which is consistent with previous works [6,9,10]. The results are summarized in Fig. 1. Weight loss is a linear function of time regardless of temperature and  $f_{O_2}$  (both in a Mo or C capsule) when evaporation is in equilibrium and in vacuum. Evaporation rate in a more reducing condition (in a C-capsule) is about 3.5 times more rapid than that in equilibrium (in Mo-capsule), which is always the case for evaporation of oxides and silicates which contain oxygen. In vacuum, evaporation rate is smaller than that in equilibrium by a factor of about 0.02, which coincides with literature data (0.011-0.015 at 1560-1685°C) [6]. This lowering of evaporation rate in vacuum compared to that in equilibrium may be due to formation of metastable gas species [6] or surface kinetics in solid such as crystallographic plane, purity, surface roughness, and porosity.

EVAPORATION OF SiO<sub>2</sub>: Nagahara, H.

In hydrogen gas, the evaporated fraction is not a linear function of time. In hydrogen gas, evaporated fraction becomes smaller than that in equilibrium, and the difference from equilibrium value becomes larger with time. At hydrogen pressure of 10<sup>-7</sup> bar, evaporation rate is nearly the same as that in vacuum, but is about 3-4 times larger at 10<sup>-5</sup> bar of hydrogen pressure. Contrary to higher total pressure, vaporization is more effective in hydrogen gas. This is because hydrogen is reactive with SiO<sub>2</sub>, and the possible reaction is SiO<sub>2</sub>(s)+H<sub>2</sub>(g)→SiO(g)+H<sub>2</sub>O(g).

In order to investigate vaporization rate and fundamental process controlling evaporation, the relationships are shown in logarithmic scale in Fig. 2. Equilibrium evaporation rate and free evaporation rate have slope of 1 in the figure, showing that evaporation rate is limited by decomposition of SiO<sub>2</sub> at the surface of the crystal. The reaction is, thus, SiO<sub>2</sub>(s) → SiO(g)+1/2O<sub>2</sub>(g). On the contrary, evaporation rates in hydrogen gas have slope of 1/2. Slope of 1/2 represents that the process is controlled by diffusion. Possible diffusion processes are (1) formation of SiO+H<sub>2</sub>O layer on the surface of the solid, (2) diffusion of hydrogen in solid SiO<sub>2</sub>, and (3) formation of amorphous SiO<sub>2</sub> layer on the solid surface. The possibility (1) is implausible, because the mean free paths in the experimental conditions is about 3m at 10<sup>-5</sup> bar and 300m at 10<sup>-7</sup> bar, which are far beyond the size of the experimental chamber. The generated SiO+H<sub>2</sub>O layer should be evacuated away in a second and it can not be a rate limiting factor. The possibility (2) may be implausible, because hydrogen diffusion in SiO<sub>2</sub> is more rapid than oxygen by 3 to 8 orders of magnitude [11]. If the data of [11] is extended to the present experimental temperatures, hydrogen diffusion distance is in the order of grain size of the present work, and it can not be a rate limiting factor. Thus the possibility (3) is the only possible explanation, although the presence of amorphous material on the surface has not been probed with the X-ray technique.

The present study suggests that evaporation rate of minerals in hydrogen gas is neither of that in equilibrium, that in vacuum, nor that in between them. The evaporation rate depends on hydrogen gas pressure. Further experimental determination for meteoritic minerals will be necessary for the discussion of evaporation of minerals in the solar nebula.

REFERENCES: [1] Wood, J.A. and Morfill, G.E. in *Meteorites and the Early Solar System* (eds., Kerridge, J.F. and Matthews, M.S.) pp.329-347, [2] Boss, A.P. (1992) *LPS XXII* 141-142, [3] Cameron, A.G.W. (1985) in *Protostar and Planets II* (eds., Black, D.C. and Matthews, M.S.) pp.1073-1099, [4] Nagahara, H. *et al.* (1992) *LPS XXII* 959-960, [5] *ibid.* 961-962, [6] Hashimoto, A. (1990) *Nature* **347** 53-55, [7] Davis, A. *et al.* (1990) *Nature* **347** 655-657, [8] Uyeda, C. *et al.* (1991) *EPSL* **107** 138-147, [9] Sata, T. *et al.* (1978) *Rep. Res. Lab. Eng. Mate. Tokyo Inst. Tech.* **3**, 666-764, [10] Mysen, B.O. and Kushiro, I. (1988) *Amer. Mineral.* **73** 1-19, [11] Dennis, P.F. (1984) *J. Geophys. Res.* **89** 4047-4058; Kronenberg, A. K. *et al.* (1986) *J. Geophys. Res.* **91** 12723-12744.

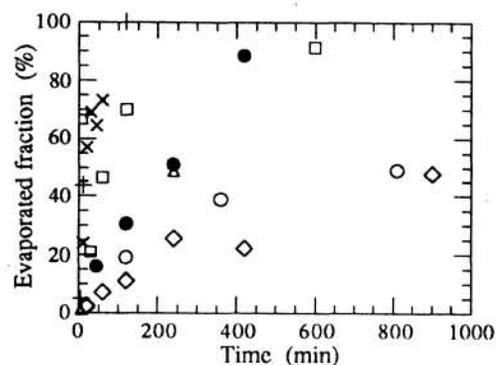


Fig. 1 Evaporated fraction of SiO<sub>2</sub> as a function of time. Solid circle: 1600°C equilibrium, cross: 1600°C equilibrium in C-capsule, diamond: 1600°C free evaporation, circle: 1600°C in 10<sup>-7</sup> bar hydrogen gas, square: 1600°C in 10<sup>-5</sup> bar hydrogen gas, plus: 1700°C equilibrium in C-capsule, triangle: 1700°C free evaporation.

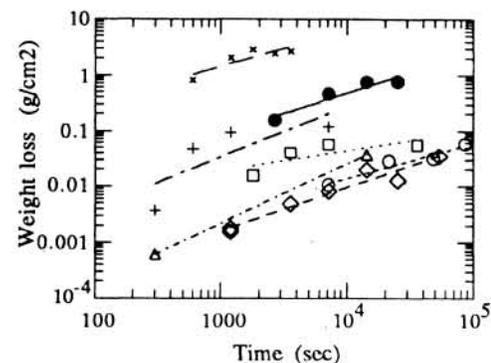


Fig. 2 Log-log relationship of weight loss and time. Symbols are the same as those in Fig. 1. Equilibrium and free evaporation rates have slope of 1, and the rates in hydrogen gas have slope of 1/2.