

**KINETICS OF EVAPORATION OF MgO, SiO<sub>2</sub>, AND Mg<sub>2</sub>SiO<sub>4</sub>, AND THEIR EFFECT ON ISOTOPE MASS FRACTIONATIONS: A. Hashimoto, Harvard-Smithsonian Center for Astrophysics, Cambridge MA 02138, USA**

Understanding the kinetics of evaporation and condensation will provide the key to answering two questions: (1) Did chondrite components (such as CAI's) form as condensates from the gas, or as evaporation residues from precursor solid materials? (2) Did they form under near-equilibrium conditions, or far from equilibrium? I have carried out experimental studies of evaporation kinetics in a vacuum (to eliminate the effect of vapor recondensation) [1]. The vacuum evaporation rates ( $J_L$ ) of solid oxides at various temperatures have been measured. Each of these can be compared to  $J_e$ , the equilibrium incident rate at which molecules would impinge on the solid oxide surface from a vapor in equilibrium with it, which can be calculated from its equilibrium vapor pressure [2].  $J_e$  expresses the theoretical maximum evaporation rate, because the evaporation rate cannot exceed the recondensation rate at equilibrium, by definition. Therefore the ratio  $J_L/J_e$ , which is termed the *evaporation coefficient*  $\alpha_v$ , cannot exceed unity.

This abstract discusses the kinetics of evaporation of Mg<sub>2</sub>SiO<sub>4</sub> (forsterite), the most abundant mineral in meteoritic and rocky planetary matter. Since forsterite is compounded of MgO and SiO<sub>2</sub>, it was logical to study these simple oxides first. Experiments showed  $\alpha_v$  to be 0.12-0.22 for MgO (periclase) at 1600-1900°C (consistent with the data of [3]), and  $\alpha_v = 0.011-0.015$  for SiO<sub>2</sub> (high cristobalite) at 1560-1685°C. In both cases  $\alpha_v$  increased with temperature; there is a linear relationship between  $1/T$  and  $\log \alpha_v$ . The fact that  $\alpha_v \ll 1$  indicates that evaporation takes place at far lower rates than the theoretical maximum evaporation rate, and implies that a substantial activation energy barrier is attached to one of the elementary rate processes involved in evaporation.

In the above derivation of  $\alpha_v$ 's, all the gaseous species of Si were included in calculating  $J_e$ . SiO(g) is the dominant Si species in equilibrium with SiO<sub>2</sub>(s), and contributes the most to  $J_e$ . However, if only SiO<sub>2</sub>(g), a relatively minor molecule in the equilibrium system, is taken into account in calculating  $J_e$ ,  $\alpha_v^-$  becomes 0.7-0.9, almost unity. ( $\alpha_v^-$  is used to distinguish the evaporation coefficient for this hypothetical system from the normal  $\alpha_v$ .) Furthermore, the experimentally derived activation enthalpy,  $\Delta H_v^* = 138.0 \pm 13.7$  (2 $\sigma$ ) kcal/mol, and activation entropy,  $\Delta S_v^* = 38.3 \pm 7.2$  (2 $\sigma$ ) cal/mol K, agree closely with the calculated thermodynamic enthalpy of vaporization ( $\Delta H_v^0 = 139.7 \pm 8.0$ ) and entropy of vaporization ( $\Delta S_v^0 = 39.6 \pm 0.8$ ) for the reaction SiO<sub>2</sub>(s)  $\rightarrow$  SiO<sub>2</sub>(g) at the average experimental temperature. This implies that SiO<sub>2</sub> (high cristobalite) actually evaporates as SiO<sub>2</sub>(g), which only later decomposes into SiO(g) and O(g). This, however, is not the case for the evaporation of MgO (periclase), because  $J_e$  for MgO(g) is much smaller than  $J_L$  (*i.e.*,  $\alpha_v^- > 1$ , which violates the condition  $\alpha_v^- \leq 1$ ). Therefore periclase probably evaporates *via* the decomposition reaction MgO(s)  $\rightarrow$  Mg(g) + O(g) and/or O<sub>2</sub>(g), with a significant activation energy barrier involved.

Forsterite was found to evaporate congruently at the experimental temperatures (1600-1800°C). Equilibrium calculations from literature thermodynamic data also indicate that the vapor produced from forsterite should have forsterite stoichiometry. Though these two results agree, their meanings are different. During kinetically controlled (vacuum) evaporation, the fastest reaction path among all possible competing reactions determines the evaporation rate, and for forsterite this happens to involve the evaporation of stoichiometric forsterite. At equilibrium, the vapor has a composition that minimizes the free energy of the whole system. Because the evaporation was stoichiometric,  $\alpha_v$ 's for the MgO and SiO<sub>2</sub> components are equal, and were found to be 0.09-0.14.  $\alpha_v$  increases with temperature. As before, all the vapor

species were included in calculating  $J_e$ . Based on the reaction kinetics observed for pure MgO and SiO<sub>2</sub> oxides, the dominant reaction path is postulated to be  $Mg_2SiO_4 \rightarrow 2Mg(g) + SiO_2(g) + 2O(g)$  (or O<sub>2</sub>). Taking into account only Mg(g), SiO<sub>2</sub>(g), and O(g) in  $J_e$ ,  $\alpha_V = 0.4-0.6$ , again close to unity. However, in this case  $\Delta H_V^*$  (136.6±1.9) and  $\Delta S_V^*$  (37.3±1.0) for the evaporation of the SiO<sub>2</sub> component from forsterite do not agree with  $\Delta H_V^0$  (124.8±1.6) and  $\Delta S_V^0$  (32.7±0.2) for SiO<sub>2</sub>(g) in the above reaction. If the SiO<sub>2</sub> component evaporates as SiO<sub>2</sub>(g), as it appears to from high cristobalite, then an additional activation energy ( $\approx \Delta H_V^* - \Delta H_V^0 = 12$  kcal/mol) must be involved for SiO<sub>2</sub>(g) to evaporate from forsterite, unlike the case for high cristobalite.

The experimental temperature ranges may be higher than the temperatures at which evaporation and condensation occurred in the primitive solar nebula. Since the  $1/T - \log \alpha_V$  plot is linear, it is easily extrapolated to lower temperatures, where  $\alpha_V$  decreases.  $\alpha_V$  for forsterite is  $\sim 0.12$  at 1700°C,  $\sim 0.04$  at 1400°C. Thus at 1400°C forsterite evaporates  $\sim 25$  times more slowly than it would if  $\alpha_V$  were 1; it is more refractory than such a material that has a similar equilibrium vapor pressure but a larger  $\alpha_V$ . (It might be the case, for example, that forsterite evaporates at the same rate as some intrinsically much more refractory mineral whose  $\alpha_V \approx 1$ . If evaporation were interrupted, both materials would still be found in the residue, making it appear that they are equally refractory. If the process continued to equilibrium, however, this could entail complete evaporation of the forsterite but not the more refractory mineral.)

Isotopic mass fractionations of Mg, Si, and O can be modelled on the basis of the evaporation kinetics described above. According to the absolute rate theory, at high temperatures, where the system approaches classical behavior, isotopic fractionation is controlled only by the transfer rate of reacted molecules from the transition state to the product [4]. When evaporation kinetics are controlled by desorption, this transfer rate corresponds to the desorption rate of molecules from the substrate (*i.e.*, unvaporized residue), which is proportional to the inverse square root of the reduced mass of the molecule and substrate. Since the substrate is  $\sim$ infinitely massive compared to a vapor molecule leaving the surface, the reduced mass is just the mass of the molecule. Because forsterite evaporates congruently (*i.e.*, Mg, Si, and O have the same volatility), the degree of isotope mass fractionation of Mg, Si, and O depends only on the masses of vapor molecules containing each element. Therefore Mg isotope fractionation (in  $\delta$ ) should be larger than that of Si by a factor  $[\ln(25/24)^{1/2}]/[\ln(61/60)^{1/2}] = 2.47$ , if the above discussion is correct and Mg and Si evaporate as Mg(g) and SiO<sub>2</sub>(g). The mass fractionation of oxygen isotopes should be a weighted mean of SiO<sub>2</sub> (M=60), O (16), and O<sub>2</sub> (32) fractionations. All these predictions need to be experimentally tested: meanwhile, however, it is interesting to apply them to FUN inclusions, in which large O, Mg, and Si isotope fractionations have been observed [5]. Data points in a plot of  $\delta^{29}Si$  vs.  $\delta^{25}Mg$  [ $\delta^{29}Si$  normalized by  $\ln(61/60)^{1/2}$ , rather than  $\ln(45/44)^{1/2}$ , and  $\delta^{25}Mg$  normalized by  $\ln(25/24)^{1/2}$ ] have been found to fall near a straight line with a slope of 1 [6], consistent with the vaporization of forsterite as Mg(g), SiO<sub>2</sub>(g) and O(g) (or O<sub>2</sub>) molecules. This tends to suggest that FUN inclusions are residues produced by kinetically-controlled evaporation.

**REFERENCES:** [1] Hashimoto, A. (1988) *Lunar Planet. Sci. XIX*, 459-460. [2] Langmuir, I. (1913) *Phys. Rev.* 2, 329-342. [3] Sasamoto, T. *et al.* (1974) *Yogyo-Kyokai-shi* 82, 603-610. [4] Melander, L. (1960) *Isotope Effects on Reaction Rates*, Ronald Press, 1-181. [5] Clayton, R. N. *et al.* (1985) in *Protostars & Planets II*, Univ. Arizona Press, 755-771. [6] Clayton, R. N. *et al.* (1987) Talk presented at the 18th Lunar Planet. Sci. Conf.