# KINETICS AND MECHANISMS OF VOLATILIZATION OF SiC AND SiO$_2$ IN THE SOLAR NEBULA;

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SUMMARY. We determined the evaporation rates of SiC and SiO$_2$ in H$_2$-CO$_2$ and in noble gas-H$_2$-CO$_2$ gas mixtures. The evaporation rate of SiO$_2$ in H$_2$-CO$_2$ with log f_{O_2} = IW - 2.8 is close to that for SiC, but the rate increases significantly as log f_{O_2} is decreased from IW - 3 to IW - 6. In contrast, rates for SiC are independent of f_{O_2} of the gas. Dilution by He has a negligible effect on the evaporation rates of SiC and SiO$_2$, but reaction rates in Ne- and Ar-bearing gas mixtures are slower. These effects are interpreted in terms of the dependence of diffusion rates of gaseous species on the composition of the gas mixtures used in the experiments. Retardation of the overall evaporation rate of SiC due to diffusion of gaseous reactants to the surface of SiC or of product gaseous species from it has only a small effect on the very short lifetimes of interstellar SiC grains exposed to the solar nebula.

INTRODUCTION. Previously [1], we demonstrated that the rate of oxidative volatilization of SiC in H$_2$-CO$_2$ and CO-CO$_2$ gas mixtures with log f_{O_2} = IW - 2.8 and IW - 6 is independent of the oxygen fugacity and other compositional parameters. Together with the presence of a uniform, ~ 1 μm-thick layer of SiO$_2$ on the surface of SiC wafers exposed to log f_{O_2} = IW - 2.8 at T = 1200 °-1500 °C, this suggested that a silica layer forms quickly, protecting SiC from the surrounding gas, and that the volatilization of SiC is controlled by the reaction:

$$SiC_{(s)} + 2\ SiO_{2(s)} = 3\ SiO_{(g)} + CO_{(g)}. \tag{1}$$
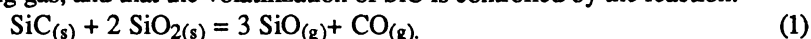
In addition to reaction (1), experimentally observed weight losses of SiC may also occur via volatilization of SiO$_2$ due to, for example,

$$SiO_{2(s)} + H_{2(g)} = SiO_{(g)} + H_2O_{(g)} \tag{2},$$

which may also be important in the H$_2$-rich solar nebula. To understand further the volatilization mechanism of SiC, we conducted two types of experiment, one on volatilization of SiO$_2$ at T = 1100°-1400°C and log f_{O_2}=IW-2.8 and IW-6; the other on the effect of dilution of H$_2$-CO$_2$ with noble gases on the evaporation rate of SiC and SiO$_2$.

EXPERIMENTAL MATERIALS AND PROCEDURE. Experimental procedures were similar to [1]. Wafers of CVD β-SiC, single crystal α-SiC and fused silica (~ 6 × 2.5 × 0.2-0.5 mm) were used in the experiments. Geometrical surface areas varied from 35 to 45 mm^2 and initial weights from 15 to 25 mg. Experiments were conducted in vertical Deltech furnaces at 1150 °-1400 °C with mixtures of H$_2$-CO$_2$ ± He, Ne or Ar at log f_{O_2} = IW - 2.8 and IW - 6, as measured with calibrated, YSZ oxygen sensors. Flow rates varied from 0.3 to 2.1 cm/s.

RESULTS. The weight loss of SiO$_2$ in H$_2$-CO$_2$, normalized to the initial geometric surface areas of the wafers, is a linear function of time, with typical reaction rates, R (±1σ), at log f_{O_2} = IW - 6 of (4.8±0.2) × 10^{-7}, (2.1±0.1) × 10^{-6}, (3.6±0.1) × 10^{-5}, and (1.1±0.1) × 10^{-4} mg/min/mm^2 at 1150°, 1200°, 1300° and 1350°C, resp. These reaction rates are about 30-40 times higher than those for SiC under the same conditions. The activation energy, E$_a$, is 548±7 kJ/mole, close to that for SiC, 579±19 kJ/mole, at the same f_{O_2}. In contrast to SiC, however, an increase in log f_{O_2} from IW - 6 to IW - 3 leads to a dramatic decline in the volatilization rate of SiO$_2$, to values typical of SiC volatilization (Fig.1). Activation energies for SiO$_2$ evaporation at log f_{O_2} = IW-3 (541±13 kJ/mole) and IW-6 are the same within error, suggesting a common mechanism for both sets of experiments.

Experiments with (He, Ne, Ar)-H$_2$-CO$_2$ (T = 1400°C, log f_{O_2} = IW-2.8) show that, while the weight loss of SiC is still a linear function of time, adding Ar or Ne to the gas mixture lowers the reaction rate (Fig.2); *e.g.*, the reaction rate is ~ 50 % lower in 50 % Ar-H$_2$-CO$_2$ and ~ 40 % lower in 50 % Ne-H$_2$-CO$_2$ than in pure H$_2$-CO$_2$. In contrast, dilution of H$_2$-CO$_2$ by He has only a very small effect on the reaction rate; the rate is only ~10 % lower in 85 % He-H$_2$-CO$_2$. Experiments at 1400°C in 50 % He-H$_2$-CO$_2$ with log f_{O_2} = IW-2.8 show that, as in the case of pure H$_2$-CO$_2$, reaction rate is independent of gas flow rate in the range 0.6 to 2.1 cm/s. Experiments conducted with SiO$_2$ at log f_{O_2} = IW-2.8 and T = 1400°C in H$_2$-CO$_2$ diluted by He and Ar showed the same effect of the noble gases on volatilization rate as in the case of SiC (Fig.2). These data, along with similar activation energies for both SiC and SiO$_2$, suggest that the same rate-limiting step is operative in the evaporation of both phases.

DISCUSSION. The same volatilization rate of SiC at log f_{O_2} = IW - 2.8 and IW - 6 indicates that the surface of the SiC wafers has a protective SiO$_2$ layer and the rate of volatilization of SiC is controlled by reaction (1). Experimental data on volatilization of SiC and SiO$_2$ in H$_2$-CO$_2$ with log f_{O_2} = IW - 6 show, however, that reaction (2) is much faster than (1). If reaction (2) is responsible for SiC weight losses, then the similar SiC volatilization rates at log f_{O_2} = IW-2.8 and IW-6 may reflect incomplete coverage of SiC surfaces by SiO$_2$ at IW-6.

Evaporation of a reactive solid in flowing gas includes the following steps: transport of a gaseous reactant to the surface of the solid phase, chemical reaction on the surface, and transport of gaseous products away from the

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surface via diffusion. The rate of mass transport of a reactant, *e.g.* $H_2O_{(g)}$ or $H_{2(g)}$, to the surface of SiC or SiO$_2$, or of a gaseous product, *e.g.* $SiO_{(g)}$ or $H_2O_{(g)}$, from the surface can be estimated by the expression for mass transport to or from a flat plate [2-3]:

$$J_i = 0.664(L\upsilon\rho/\eta)^{1/2}(\eta/\rho D_i)^{1/3}D_i\Delta P_i/LR_oT \qquad (3),$$

where J_i is the mass flux of species i ; L is the length of the sample wafer parallel to the flow direction (~ 0.3 cm); υ, ρ and η are the gas flow rate, density and viscosity; D_i is the diffusion coefficient of species i in the flowing gas which varies as $T^{3/2}$; ΔP_i is the difference in partial pressure of species i between the flowing gas and the surface of the solid phase and R_o is the gas constant. From equation (3), mass flux is a very weak function of ρ, so that, for fixed sample geometry and composition of the flowing gas, J_i depends on $T^{1/2}$, $\upsilon^{1/2}$ and ΔP_i. The lack of dependence of the weight loss rate on the flow rates of the gas mixtures (from 0.6 to 2.1 cm/s) , and the exponential dependence of the reaction rates on temperature observed in our H$_2$-CO$_2$ experiments strongly suggest that the rate-limiting step in the evaporation processes, in the absence of noble gases, is a chemical reaction at the surface, rather than mass transport to or from the surface. Our experiments with Ar and Ne show, however, that the delivery or removal of gaseous species must also be important to the overall kinetics. Calculations of diffusion coefficients of different gaseous species (H$_2$O, SiO, CO, O$_2$) in H$_2$-CO$_2$, He-H$_2$-CO$_2$, Ne-H$_2$-CO$_2$ and Ar-H$_2$-CO$_2$ at different temperatures show that D_i for all likely gaseous species decrease with increasing concentration of noble gas in the gas mixture, and that the heavier the noble gas, the greater its effect on D_i. For example, in 50 % He-H$_2$-CO$_2$, D_i is only ~ 5 % smaller than in pure H$_2$-CO$_2$, while in 50 % Ne and 50 % Ar, D_i is lower by ~ 40-45 % and ~ 55-60 %, respectively. Dependence of D_i and, as a result, of J_i on the composition of the gas mixture is in good agreement with the experimentally measured effects of the noble gases on the reaction rates (Fig. 2).

As mentioned above, the volatilization rate of SiC in (He)-H$_2$-CO$_2$ with log f_{O_2} = IW - 2.8 is independent of gas flow rate in the range 0.6-2.1 cm/s. Reaction rates are lower, however, at lower flow rates, which may indicate that, under such conditions, mass transport of the gaseous species becomes rate-limiting. Taking into account this observation, the fact that the velocities of dust particles relative to the gas in the solar nebula might be as low as 0.01 cm/s [4], and the dependence of D_i, ΔP_i and ρ on the total pressure in the system, we calculated volatilization rates of SiC in the solar nebula using equation (3). For a 10 μm SiC grain with υ = 0.01 cm/s and P_{tot} = 10^{-3} atm, the mass flux J_i will be about 20 times lower than the flux calculated at the same T for H$_2$-CO$_2$ and log f_{O_2} = IW - 6 for samples with L = 0.3 cm, as in our experiments. If P_{tot} = 10^{-4} atm and υ = 0.01 cm/s, the calculated flux will be ~ 60 times lower than in our experiments. Increasing υ from 0.01 cm/s to 1 cm/s increases J_i by a factor of 10, as does decreasing the grain size from 10 μm to 0.1 μm. Based on these calculations, it can be concluded that, if the mechanism of volatilization of SiC is the same in the solar nebula as in our experiments, then lifetimes of SiC grains will increase by factors of 6 - 60, compared to the values reported in [1]. At P_{tot} = 10^{-4} atm, the lifetimes of 10 μm grains will be up to ~ 2 months at 1400 °C and ~ 50 years at 1200 °C, which are still very small compared to the solar nebular cooling time.

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Temperature Dependence of SiC and SiO$_2$ Volatilization Rate

E$_a$=579±19 kJ/mole
E$_a$=563±9 kJ/mole
E$_a$=548±7 kJ/mole
E$_a$=541±13 kJ/mole

Fig. 1

Effect of dilution by noble gases on the volatilization rates of SiC and SiO$_2$
(T=1400°C; log f(O$_2$)=IW-2.8; flow rate=1.0 cm/s)

Fig. 2