EFFECT OF f_{O_2} ON SIC VOLATILIZATION RATE.

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Introduction: Our previous work on the volatilization rate of SiC in reducing gases [1, 2] was restricted to IW-2.8 and IW-6, oxygen fugacities (f_{O_2}'s) 2.8 and 6 log units below the iron-wustite (IW) buffer. These data allowed us to estimate lifetimes of interstellar SiC grains (several months at 1200°C) in a gas of solar composition (~IW-6). There is, however, evidence that f_{O_2}'s for many components in chondrites differed significantly (±4 log units) from IW-6 (e.g., [3]). In this work, we explore the possibility that nebular lifetimes of interstellar SiC grains were significantly different from those we calculated previously because of exposure to vapor at different f_{O_2}'s.

Experimental: Experimental materials (CVD β-SiC and single crystal α-SiC) and procedures were as in [1, 2]. Experiments were conducted at 1300°C in a vertical Deltech furnace using H_2-CO_2 gas mixtures. The log f_{O_2} was varied from IW-10 to IW-3 as measured by an SIRO2 oxygen sensor after taking mixed ionic-electronic conductivity of the solid electrolyte [4] into account.

Results: Fig. 1 shows the dependence of volatilization rate of single crystal α-SiC on f_{O_2} at 1300°C. We used a single SiC wafer for all experiments shown in Fig. 1 and run durations < 2hrs; the experiments also alternated between reducing and oxidizing gases. This procedure was chosen to prevent the formation of a thick silica layer at high f_{O_2}'s, and disintegration of the wafer surfaces at low f_{O_2}'s due to pit formation. The latter process led to destruction of the surface of CVD β-SiC, which caused non-reproducible results when this type of material was used in the experiments.

Weight loss was a linear function of time for all experiments with single crystal α-SiC. The figure clearly indicates that the volatilization rate of SiC is approximately constant within the range of log f_{O_2} from ~IW-6 to IW-3, in accord with our previous experiments at IW-6 and IW-2.8. Under more reducing conditions (log f_{O_2} from ~IW-6 to IW-10), the SiC volatilization rate gradually increases as the reacting gas becomes more reducing and, at log f_{O_2}~ IW-10, the volatilization rate is ~10 times higher than at IW-6.

Effect of f_{O_2} on SiC volatilization rate
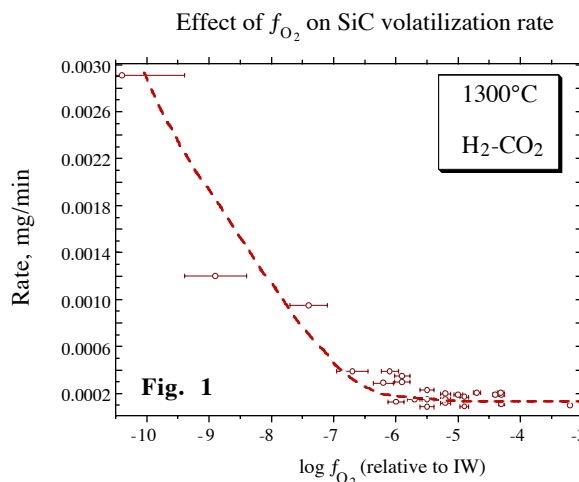
Fig. 1

Discussion: Based on our results and those of [5, 6], we can distinguish five regimes of volatilization for SiC in hydrogen-rich gas mixtures. Under very oxidizing conditions (>~IW+3 [7]), not shown in Fig. 1, a silica layer grows on the surface of SiC through a reaction such as

$$SiC_{(s)} + 3H_2O_{(g)} = SiO_{2\,(s)} + CO_{(g)} + 3H_{2\,(g)} \quad (1).$$
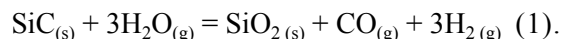
Diffusive transport of gaseous species (identity uncertain [8, 9]) through a thick silica layer is the rate-limiting step and samples gain weight (passive oxidation) as a parabolic function of time (regime 1). As the f_{O_2} is reduced from these high levels, samples lose weight with time. The weight loss is caused by formation of a relatively thick (greater than several microns) layer of silica on the SiC surface followed by its volatilization (regime 2). The mechanisms of

volatilization of SiC covered with such a layer and that of pure SiO_2 are the same [7] and include either a reaction with $H_2O_{(g)}$ (log $f_{O_2} >$ IW-2 at 1250°C [7]) or with $H_{2(g)}$ at lower f_{O_2}'s. A third regime for SiC volatilization occurs in the range ~IW-3 to ~IW-6 for our data (Fig. 1), within which weight loss is a linear function of time and the reaction rate is essentially independent of the f_{O_2}. The entire wafer surface is covered by a layer of silica, but TEM and RBS studies of wafers exposed to IW-2.8 [1, 10] show that the layer is very thin (<1 μm) so that transport through the layer is not rate-limiting. SiC volatilization probably occurs via:

$$SiC_{(s)} + 2SiO_{2\,(s)} = 3SiO_{(g)} + CO_{(g)} \qquad (2),$$
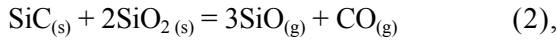
which is expected to be essentially independent of gas composition, leading to a constant reaction rate within the f_{O_2} range from ~IW-6 to ~IW-3 (Fig. 1). Under more reducing conditions (< IW-6), there are at least two major competing reactions involved in the volatilization of SiC:

$$SiO_{2\,(s)} + H_{2\,(g)} = SiO_{(g)} + H_2O_{(g)} \qquad (3),$$

which leads to higher volatilization rates of *silica* as the f_{O_2} is reduced [2, 11], and

$$SiC_{(s)} + 2H_2O_{(g)} = SiO_{(g)} + CO_{(g)} + 2H_{2\,(g)} \quad (4),$$

which describes the direct vaporization of SiC without a silica intermediary. The rate of SiC oxidation via reaction (4) decreases with decreasing f_{O_2} [9, 12], but is only operative where there are bare SiC surfaces (i.e. no silica). Our TEM study of an SiC wafer exposed to IW-6 showed [10] that, although most of the surface of the wafer is silica-free, some oxygen-bearing phase is present. We speculate that for f_{O_2}'s in the range between IW-6 and some value more reducing than IW-10, silica, which completely covers the surface under more oxidizing conditions (regimes 1-3), becomes restricted to grain boundaries and/or pits (regime 4). If the weight loss of the wafer via reaction (3) is much greater than that via (4), and if the rate of (3) increases more rapidly with decreasing f_{O_2} than the effective surface area of SiO_2 decreases, then the overall rate of SiC volatilization increases with decreasing H_2O/H_2 ratio or f_{O_2} as observed in Fig. 1. When the f_{O_2} is reduced even further (regime 5; not shown in Fig. 1), silica is completely absent and direct vapori-

zation of SiC occurs by a reaction such as (4) so that the reaction rate decreases with further decreases in f_{O_2}.

Our data are restricted to regimes 2-4 but oxidation of SiC was observed in regime 5 by [5] and [6] in H_2-H_2O gases. At 1400°C, for example, the rate first increases by a factor of ~3 with increasing P_{H_2O} from $2x10^{-5}$ atm (IW-9.4) to $8x10^{-5}$ atm (IW-8.2), then decreases by about the same amount as P_{H_2O} is increased to ~$2x10^{-4}$ atm (IW-7.4), and remains nearly constant for further increases of P_{H_2O} up to $5x10^{-3}$ atm (IW-4.6).

The lifetime of interstellar SiC grains in the solar nebula based on SiC volatilization experiments at log f_{O_2}= IW-6 (e.g., 3 months for 1 μm diameter grains to 8 months for 10 μm grains at 1200°C [1]) will remain the same even under oxidizing conditions (up to log f_{O_2}= IW-3). For a vapor more reducing than a solar gas, the volatilization rate is higher and, therefore, the lifetimes of presolar SiC grains will be shorter than calculated from experiments at IW-6. Our results suggest that presolar SiC grains were never exposed to hot (>1000°C) solar nebular gas for an extended period of time (~10^2-10^3 yrs). They were either isolated from the gas phase through inclusion in stable refractory minerals, and/or they were added to the solar nebula at a late stage, when the temperature was so low that their volatilization rates were prohibitively long.

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