

KINETICS AND VOLATILIZATION OF SiC AND SiO₂: IMPLICATIONS FOR METAMORPHISM OF UNEQUILIBRATED ORDINARY CHONDRITES; R.A. Mendybaev^{1,3}, J.R. Beckett³, L. Grossman^{1,2}, and E. Stolper³. ¹Department of the Geophysical Sciences, ²Enrico Fermi Institute, Univ. of Chicago, IL 60637; ³Division of Geological and Planetary Sciences, Caltech, Pasadena, CA 91125.

Introduction: Constraints on thermal histories and physical conditions during the formation of unequilibrated ordinary chondrites (UOCs; petrologic type 3) are largely based on inferences from more equilibrated varieties (types 4-7). In this study, we explore the possibility of a more direct indicator based on the observation [1, 2] that abundances of diamond and SiC decrease systematically in UOCs with increasing petrologic type (from 3.0 to 3.8). We use the results of volatilization experiments to lay the groundwork necessary to understand the processes by which SiC is destroyed during metamorphism of UOCs and to estimate lifetimes of presolar SiC grains in parent body environments.

Experimental: Experiments were conducted in the temperature range 750-1400°C in vertical furnaces using H₂-CO₂ (± He ± SiH₄) or CO-CO₂ gas mixtures. f_{O_2} s were in the range IW+2 to IW-3 to encompass values attributed to metamorphism in the UOC parent bodies [3, 4]. Starting materials consisted of wafers of Chemically Vapor Deposited (CVD) β -SiC, single crystal α -SiC and fused silica glass with typical sizes of 6x3x0.3 mm. Experimental details are as in [5, 6] except that Ir or Rh wire holders were used in place of Mo for experiments above IW. Individual experiments lasted from several hours to two weeks depending on experimental conditions.

Results and Discussion: A fresh SiC wafer exposed to H₂-CO₂ between IW-3 and IW+3 initially gains weight due to the formation of an iridescent layer of silica on the surface and then loses weight linearly with time. For SiO₂, weight loss is instantaneous and always linear. Figs. 1 and 2 show the temperature dependence of volatilization rates (R) for β -SiC and SiO₂ in H₂-CO₂ gas mixtures at different f_{O_2} s at a gas flow rate of 1.1 cm/s. For clarity, results at IW for 900 and 750°C, which were used in generating the plotted regression line, are not shown in Fig. 2. Results at IW-2 and IW-3 on α - and β -SiC were indistinguishable. Although R for SiO₂ is usually a little higher than that of SiC (e.g., 3.2×10^{-7} vs. 1.7×10^{-7} mg/min/mm² at 1250°C and IW-2), the activation energy, E_a , and dependence of R on f_{O_2} are similar. For a gas of constant composition, a sharp change in slope is sometimes observed at intermediate temperatures (e.g., at IW-1, $E_a \sim 220 \rightarrow 96$ at $\sim 1350^\circ\text{C}$ for SiC and $280 \rightarrow 99$ kJ/mole at $\sim 1300^\circ\text{C}$ for SiO₂), signaling a change in mechanism which remains constant over the temperature range 1300-750°C for IW. Thus, there are two regimes in H₂-CO₂ gas mixtures, one with

high E_a at high temperatures and low f_{O_2} s, and the other with low E_a at lower temperatures and more oxidizing conditions.

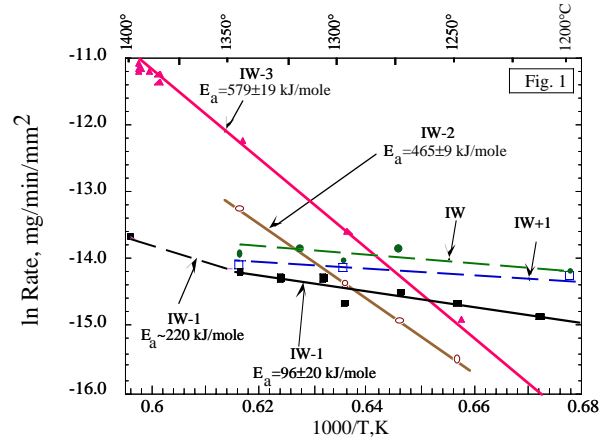


Fig.1 Dependence of SiC volatilization rate in H₂-CO₂ on temperature.

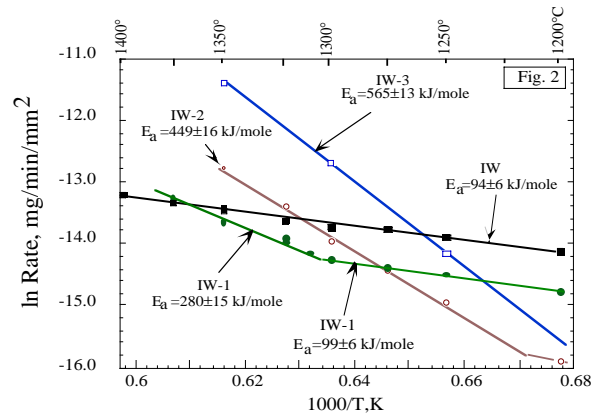


Fig. 2 Dependence of SiO₂ volatilization rate in H₂-CO₂ on temperature

The linearity of weight loss with time in both high and low E_a regimes suggests that either a surface reaction or gas-phase diffusion to or from the surface through a boundary layer is rate limiting. We concentrated on characterizing the low E_a regime because it is more relevant to the T- f_{O_2} conditions expected for UOCs [3, 4, 7]. That the reaction rate is linearly correlated with the square root of linear gas flow rate (0.1 to 2.0 cm/s) at 1250°C and IW strongly implies that gas-phase diffusion and not a surface reaction is rate limiting in this regime. There is a strong positive correlation of volatilization rates of SiC and SiO₂ (Fig. 3) with the partial pressure of H₂O in this regime, consistent with diffusive transport of

H₂O, a reactant for oxidation, being rate limiting. In contrast, a simultaneous positive correlation of P(CO) with volatilization rate is inconsistent with this species being rate limiting because CO is a product of oxidation, and, therefore, a negative correlation would have been expected. P(O₂) or P(CO₂) are not rate limiting in the low E_a regime because the volatilization rate does not vary monotonically with them. In addition, it is unlikely that transport of an Si-bearing species away from the SiO₂-gas interface is rate limiting because preliminary experiments with H₂-CO₂-He-SiH₄ at 1250°C and IW reveal no correlation with the concentration of SiH₄. We conclude that, in H₂-CO₂ gas mixtures, transport of H₂O(g) is rate limiting in the low E_a regime.

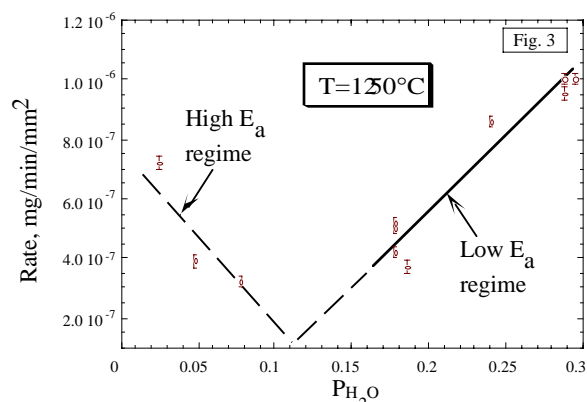


Fig. 3 Dependence of SiO₂ volatilization rate on P_{H₂O}

In UOCs, the vapor composition is not restricted to the H₂-CO₂ binary. We have, therefore, begun experiments in CO-CO₂ gas mixtures as a forerunner to performing experiments in CO-H₂-CO₂. For CO-CO₂, there is a high E_a regime (e.g., for IW-3, volatilization rates are the same as for H₂-CO₂ [6]). At 1250°C for IW and IW+2, however, SiC wafers in CO-CO₂ gain weight (1 day runs) and follow parabolic ($R \propto \text{time}^{1/2}$) kinetics. The weight gain reflects the formation of a protective silica layer, which slows further oxidation of SiC. For run times exceeding an hour, oxidation of SiC in this regime of parabolic kinetics is much slower than for the linear kinetics in H₂-CO₂ gas mixtures at the same f_{O_2} . We have not yet studied the temperature dependence for volatilization rates in CO-CO₂ gas mixtures at IW or IW+2 but, based on literature data for oxidation of SiC in the parabolic regime [8], it is likely that the mechanism will remain the same to low temperatures. There will be a limiting boundary in gas composition between the linear and parabolic kinetic regimes, and it may be possible to take advantage of this to constrain P(H₂O) and other partial pressures of vapor species in the UOC parent body.

Applications: Given that small quantities of SiC persist even in type 3.7-3.8 UOCs [2], that T_{max} for these chondrites was ~450°C [7] or even higher [9], and

that cooling rates were typically in the range 2-20°/Myr [10, 11], actual lifetimes of SiC in type 3.8 UOCs would have been on the order of 10⁷-10⁸ yr, assuming a 300°C closure temperature. If the initial grain size distribution for SiC in UOCs was the same as for Murchison, ~90% of the mass was in grains with diameters of 0.4-2.0 μm [12]. Fig. 4 shows lifetimes for spherical 0.4-2.0 μm SiC grains calculated by extrapolating the linear kinetics of our experimental data on the volatilization of SiO₂ in H₂-CO₂ gas mixtures with a gas flow rate of 1.1 cm/s to lower temperatures. Calculated survival times for 0.4-2 μm grains are ~10⁴-10⁵ yr depending on temperature. Taking into account that gas flow in chondritic parent bodies was probably close to zero [13] increases calculated lifetimes by ~4x, in no way sufficient to account for a 3-4 order of magnitude discrepancy. We conclude that SiC in UOCs oxidized via parabolic kinetics and, therefore, that the vapor was water-poor relative to H₂-CO₂ at the same f_{O_2} . This implies that P(H₂O) was less than 0.03 (for IW-3 [3]) - 0.35 (for IW-1 [4]) atm for total pressures ≤ 1 atm. Since the actual boundary between linear and parabolic kinetics is probably much closer to CO-CO₂ than to H₂-CO₂ under reducing conditions, it is likely that results of future experiments will severely limit possible values of P(H₂O) in the vapor during the metamorphism of UOCs.

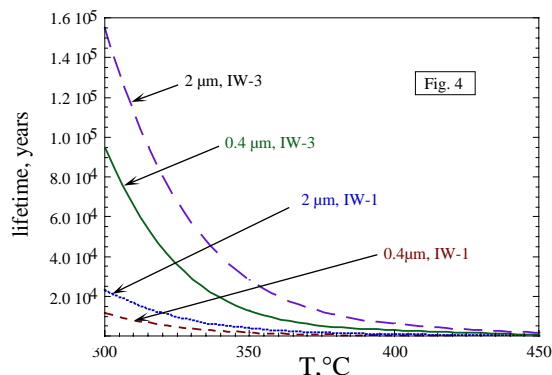


Fig. 4: Calculated lifetimes of presolar SiC grains in UOC parent bodies

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