KINETICS AND VOLATILIZATION OF SiC AND SiO_2: IMPLICATIONS FOR METAMORPHISM OF UNEQUILIBRATED ORDINARY CHONDRITES; R.A. Mendybaev 1,3, J.R. Beckett 3, L. Grossman 1,2, and E. Stolper 3. 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 H_2-CO_2 (± He ± SiH_4) or CO-CO_2 gas mixtures. fO_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 H_2-CO_2 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 SiO_2, weight loss is instantaneous and always linear. Figs. 1 and 2 show the temperature dependence of volatilization rates (R) for β-SiC and SiO_2 in H_2-CO_2 gas mixtures at different fO_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 SiO_2 is usually a little higher than that of SiC (e.g., 3.2x10^-7 vs. 1.7x10^-7 mg/min/mm^2 at 1250°C and IW-2), the activation energy, E_a, and dependence of R on fO_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 ~220 → 96 at ~1350°C for SiC and 280 → 99kJ/mole at ~1300°C for SiO_2), signaling a change in mechanism which remains constant over the temperature range 1300-750°C for IW. Thus, there are two regimes in H_2-CO_2 gas mixtures, one with high E_a at high temperatures and low fO_2's, and the other with low E_a at lower temperatures and more oxidizing conditions.

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- fO_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 SiO_2 (Fig. 3) with the partial pressure of H_2O 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 ∝ 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 fO2. 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 10^7-10^8 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 0.4-2.0µm [12]. Fig. 4 shows lifetimes for spherical 0.4-2.0µm 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 lifetimes for 0.4-2µm grains are ~10^1-10^5 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 fO2. 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