VOLATILIZATION OF GRAPHITE IN REDUCING GASES: PRELIMINARY RESULTS.

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Introduction: Previously [1, 2], we presented experimental data on evaporation rates of silicon carbide in various gas mixtures over wide temperature intervals and different f_{O_2}'s. These data allowed us to calculate lifetimes of interstellar silicon carbide grains under solar nebular conditions. Large isotopic anomalies are also present in some meteoritic graphite, indicating a presolar origin [3, 4]. Graphite, like SiC, is thermodynamically unstable under solar nebular conditions and should have undergone volatilization while immersed in the solar nebula and inside meteorite parent bodies. Survival of presolar graphite in combination with an understanding of its kinetics of volatilization may give us information on the physical conditions and duration of exposure of presolar grains in various environments. In this paper, we present data on volatilization in reducing gas mixtures of highly ordered graphite grains, which are close in crystal structure to the outer rinds of the "onion-like" interstellar graphite particles [4].

Experimental Procedure: We used essentially the same experimental configuration employed in experiments with silicon carbide. A piece of HOPG (Highly Oriented Pyrolitic Graphite) from Advanced Ceramics Corp. was cut into wafers about 5x7x0.5 mm and a fresh surface of the sample was exposed by peeling off the top layers of the graphite with Scotch tape. Wafers were ultrasonically cleaned successively in acetone, isopropanol and ethanol, dried in vacuum at 120°C and kept in a desiccator prior to use. Experiments were conducted in vertical Deltech and Astro furnaces with flowing (~0.8 cm/s) mixtures of H_2-CO_2 (log f_{O_2} ~ IW-4 and IW-5) and CO-CO_2 (log f_{O_2} ~ IW+1) in the temperature interval 750°-1000°C. Oxygen fugacities were measured by SIRO2 yttria-stabilized zirconia oxygen sensors.

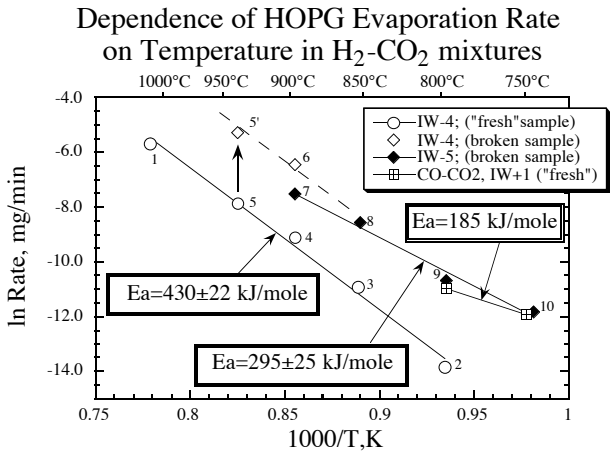
To solve the known problems (*e.g.*, [5, 6]) with equilibration of flowing H_2-CO_2 gas mixtures at low (<1200°C) temperatures, we developed an experimental technique [7] in which the entire gas stream is forced to pass through an ~2.5 cm-thick bed of Pt catalyst (3.2 mm alumina pellets coated with Pt) placed ~1 cm below the hot spot. This technique allows equilibrium gas speciation to be reached in flowing H_2-CO_2 gas mixtures (log f_{O_2} varied from QFM to IW-3) at temperatures at least as low as 700°C. In the investigated CO-CO_2 gas mixtures (IW+1 to IW-3), deviations between expected and measured f_{O_2}'s were only observed at temperatures near the graphite stability field, regardless of whether or not a catalyst was present. The accuracy of our f_{O_2} measurements in both H_2-CO_2 and CO-CO_2 gas mixtures is <±0.1 log units, comparable to that obtained at T>1200°C.

Kinetics of graphite volatilization: Volatilization of graphite in H_2-CO_2 and CO-CO_2 mixtures occurs mostly by reaction with H_2, H_2O, CO_2 and/or O_2:

$$C_{(s)} + 2H_{2\,(g)} = CH_{4\,(g)}, \quad (1)$$
$$C_{(s)} + H_2O_{(g)} = CO_{(g)} + H_{2\,(g)}, \quad (2)$$
$$C_{(s)} + CO_{2\,(g)} = 2CO_{(g)}, \quad (3)$$
$$2C_{(s)} + O_{2\,(g)} = 2CO_{(g)}. \quad (4)$$

Walker et al. [8] found that the relative rates of reactions (1) : (2) : (3) : (4) with spectroscopic graphite at 800°C and P_i =0.1 atm are $3x10^{-3}$: 3 : 1 : $1x10^5$. Given the reducing nature of our gas mixtures (*e.g.*, P_{H_2} : P_{H_2O} : P_{CO_2} : P_{O_2} ~1 : 10^{-2}: 10^{-4}: 10^{-22} at 800°C in H_2-CO_2 with log f_{O_2} ~ IW-4), reaction (4) is insignificant in our experiments. Reactions (2) and (3) are very similar in terms of reaction mechanisms, effects of temperature and concentration of oxidizing agent on overall reaction rate, retardation of the reaction by reaction products, *etc*. [8-11]. It is well established that the rates of (2) and (3) are controlled by chemical reaction in the temperature range 400° - 1200°C and by diffusion processes (*e.g.*, transport of reacting gases to the surface of or inside the sample) at higher temperatures. The experimentally determined apparent activation energy, E_a, for reaction (2) varies from 170 to 350 kJ/mole at low temperatures and that for reaction (3) from 230 to 400 kJ/mole [8, 11]. Such wide ranges in E_a likely reflect variations in purity and physical properties of the samples.

Experimental results: Observed volatilization rates of two wafers of HOPG in H_2-CO_2 and CO-CO_2 gas mixtures are substantially higher than those for silicon carbide under the same conditions. A linear dependence of weight loss with time was observed in all our experiments in different gas mixtures at different temperatures independent of run duration (from 1.5 hrs at 1000°C up to 2 weeks at 750°C). This strongly suggests that the active surface area of the sample during the experiments did not change signficantly during loss of up to 5% of the sample's original weight. Fig. 1 shows the dependence of graphite oxidation rate on temperature in H_2-CO_2 and CO-CO_2 gas mixtures. Numbers next to experimental points reflect a sequence of experiments in H_2-CO_2 gas mixtures. After run #5, the sample broke into two pieces (~47.7 mg and ~2.8 mg). The larger piece was used in succeeding runs (#5´ - #10). The apparent activation energy for graphite oxidation in the H_2-CO_2 mixture with log f_{O_2} ~ IW-4 (#1 - #5) is equal to 430±22 kJ/mole. Exposing a fresh surface of the sample to the flowing gas at the same conditions (#5´



and #6) leads to a higher weight loss rate, probably due to an increase in the active surface area of the sample. In the H_2-CO_2 mixture with log f_{O2} ~ IW-5, the dependence of the reaction rate with temperature is distinctly different and E_a =295±25 kJ/mole.

The volatilization rate at 800°C in a CO-CO_2 mixture with log f_{O2} ~ IW+1 was the same whether or not the catalyst was present. The observed reaction rate was similar to that in H_2-CO_2 with log f_{O2} ~ IW-5 despite dramatic differences in the partial pressures of CO and CO_2: 0.6 and 0.4 atm in CO-CO_2 at T>625°C, and 10^{-3} and $10^{-5.5}$ atm in H_2-CO_2 with log f_{O2} ~ IW-5 at 800°C. The activation energy for CO-CO_2 based on measurements at 800° and 750°C is 185 kJ/mole. The lower activation energy *vs.* H_2-CO_2 probably reflects differences in mechanism.

Discussion: The differences in E_a of the graphite volatilization as well as in the reaction rate obtained with the same sample at the same temperature in H_2-CO_2 with log f_{O2} ~ IW-4 (*e.g.*, #6) and IW-5 (*e.g.*, #7) are probably caused by differences in speciation of the gas phase. Calculations show that equilibrium partial pressures of H_2 and H_2O at IW-4 and IW-5 are the same independent of temperature. P_{CO} and P_{CO2} gradually increase with temperature in the range of 700°- 900°C and remain almost constant at T>900°C, while P_{CH4} is constant at T<700°C and gradually decreases at higher temperatures. Partial pressures of CO and CO_2 at IW-4 are much higher (*e.g.*, 5 and 20 times at 900°C) than at IW-5. Although more experimental data are needed to understand fully the graphite volatilization mechanism in reducing H_2-CO_2 mixtures, we can use our experimental data together with literature data to estimate lifetimes of graphite grains under solar nebular conditions.

Experiments conducted with different forms of graphite at T<1050°C and low (<10^{-2} atm) partial pressures of H_2O and CO_2 show that the apparent order of reaction with respect to partial pressures of reactants ranges from 0.5 to 1 for different types of graphite [9, 10]. It has also been established that reaction rates are almost inversely proportional to the partial pressure of H_2, at least for H_2 : H_2O ratios from 0 to 10; CO has a similar effect [7-10]. Equilibrium partial pressures of H_2, H_2O, CO and CO_2 in a solar gas at P^{tot}= 10^{-3} atm and T= 800° - 1000°C are equal to 8.3×10^{-4}, 6×10^{-7}, 6×10^{-7} and <7×10^{-10} atm. In the experimental H_2-CO_2 mixture with log f_{O2} ~ IW-5, for example, they are ~1, 1×10^{-2}, 1×10^{-3} and 3×10^{-6} atm. Taking into account that reaction rates of (2) and (3) are comparable at the same concentrations of H_2O and CO_2, and that P_{CO2} is much lower than P_{H2O} in the solar nebula, reaction (3) is probably not very important in a solar gas at these conditions. Assuming that the rate of (2) is proportional to P_{H2O} and inversely proportional to P_{H2}, we calculate a graphite volatilization rate in a solar gas to be ~10 times slower than in our experiments. Using experimentally obtained reaction rates at IW-4 with a fresh wafer, we estimate lifetimes of well-graphitized carbon mantles (maximum thickness ~1 µm [4]) around "onion-like" interstellar graphite particles in the solar nebula to be ~7 hrs at 1000°C and ~200 years at 700°C, which are >10^4 times shorter than lifetimes of ~1 µm-sized SiC grains under the same conditions. These extremely short lifetimes imply that presolar graphite grains would not survive long, high-temperature events in the solar nebula, unless they were coated with phases resistant to volatilization.

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