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 Pyrolytic 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$_2$ in purity and physical properties of the samples. Numbers next to experimental results indicate a sequence of experiments in H$_2$-CO$_2$ gas mixtures. Numbers next to experimental results indicate 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 observed at temperatures at least as low as 700°C. In the investigated CO-CO$_2$ gas mixtures, 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$_2$O, CO and/or O$_2$:

\begin{align}
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_2(g). \quad (4)
\end{align}

Walker et al. [8] found that the relative rates of reactions (1) : (2) : (3) : (4) with spectroscopic graphite at 800°C and P$_1$=0.1 atm are 3x10$^{-3}$ : 3 : 1 : 1x10$^2$. 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 significantly 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’
Experiments conducted with different forms of graphite at T<1050°C and low (<10^-2 atm) partial pressures of H2O and CO2 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 H2, at least for H2 : H2O ratios from 0 to 10; CO has a similar effect [7-10]. Equilibrium partial pressures of H2, H2O, CO and CO2 in a solar gas at Ptot=10^3 atm and T=800°-1000°C are equal to 8.3x10^-4, 6x10^-7, 6x10^-7 and <7x10^-10 atm. In the experimental H2-CO2 mixture with log fO2 ~ IW-5, for example, they are ~1, 1x10^-2, 1x10^-3 and 3x10^-6 atm. Taking into account that reaction rates of (2) and (3) are comparable at the same concentrations of H2O and CO2, 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.

**References:**