Reduction in piston-cylinder experiments: The detection of carbon infiltration into platinum capsules

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ABSTRACT

Problems associated with intermittent and variable degrees of sample blackening are often reported for studies involving the preparation of CO2-bearing silicate glasses in piston-cylinder apparatus. This phenomenon is generally attributed to H infiltration, which leads to the reduction of CO2 and the precipitation of graphite with the concomitant formation of water. In this study we demonstrate that carbon diffusion into platinum capsules may be a common cause of blackened glasses and this process may be detected using fourier transform infrared spectroscopy (FTIR) to identify the presence of CO without elevated H2O contents. The simulated infiltration of 12C from a graphite furnace into a 13C-bearing sample is illustrated using secondary ion mass spectroscopy (SIMS) and micro-FTIR analysis.

Careful FTIR monitoring of variable sample reduction has helped to identify the precautions required to reduce C (and H) infiltration in solid media assemblies and it appears that physical barriers can be more important than the chemical buffers traditionally employed.

INTRODUCTION

Examples of blackened samples prepared in piston-cylinder apparatus can be found throughout the experimental literature and many petrologists will acknowledge that similar problems are often observed but not reported. For experiments where oxidized carbon species are included in the bulk composition, the blackening is generally attributed to the reduction of these species to produce graphite. It is commonly suggested that infiltration of H2 causes graphite to precipitate by the following types of reaction:

\[ \text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \text{(to some CO/CO}_2 \text{ ratio)} \] (1)

then

\[ \text{CO}_2 + 2\text{H}_2 \rightarrow \text{C} + 2\text{H}_2\text{O}. \] (2)

In many experiments, the diffusion of H2 into capsules is actually utilized to impose a controlled fO2 (more correctly fH2O; see Luth 1989) during the experiment with the sample-bearing capsule being enclosed in a second sealed capsule containing the required buffer assemblage and H2O (e.g., Eugster 1957). Reduction and the perceived entry of H2 into single capsules that are not intentionally buffered has led to the concept of an “intrinsic fO2” in which the pressure vessel and/or solid media assembly are thought to act as both the source and buffer of fH2O.

Mysen and co-workers at the Geophysical Lab (Hol-

loway et al. 1976; Mysen 1976; Mysen et al. 1976) have prepared many CO2-bearing glass samples using a talc piston-cylinder assembly without blackening of samples. This has been attributed to a high overall intrinsic fO2 near the hematite-magnetite buffer for this assembly (Eggler et al. 1974). This intrinsic fO2 is considerably higher than values measured in other laboratories (nickel-nickel oxide for Allen et al. 1972; below nickel-nickel oxide for Merrill and Wyllie 1974; slightly below nickel-nickel oxide for Brey and Green 1976; near wustite-magnetite for Watson et al. 1982; just below quartz-fayalite-magnetite for Watson 1987). Eggler et al. (1974) attributed the high fO2 environment in their assembly to the presence of boron nitride, which may act as a sink for H2 (see Wendlandt et al. 1982). This conclusion was apparently supported by the blackening of CO2-bearing glasses when the boron nitride was removed from the talc assembly. However, Brey and Green (1976) suggested that Pyrex could be used successfully in place of boron nitride to reduce migration of H2 from an outer talc sleeve to the capsule.

More recent studies of CO2 solubility in silicate melts have favored a combination of NaCl and Pyrex in 12.7 mm assemblies. With the elimination of the talc as a source of H2O, it might be expected that the bulk amount of H2 available for infiltration would be reduced to an insignificant level. However, blackening still occurs in these assemblies and several workers have pursued a double capsule technique to maintain a high fO2 (or low fH2O) and avoid graphite formation (e.g., Boettcher 1984; Brey 1976; Brey and Green 1976; Fine and Stolper 1985; Stol-

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