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The use of boron nitride to impose reduced redox conditions in experimental petrology

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Abstract

Boron nitride (BN) is a commonly used pressure-transmitting material in experimental petrology. It is often considered to be as inert as MgO or Al_2O_3, and its redox potential is seldomly discussed. It is generally implied that, when used as a capsule sleeve, BN may impose relatively reduced conditions, similar to the effect of the fayalite-magnetite-quartz (FMQ) buffer. However, sediment melting experiments performed at 1050 °C and 3 GPa with BN as the capsule sleeve, produced a hydrous rhyolitic melt with dissolved H_2S and CH_4 (Li et al. 2021). The resulting f_{O_2} estimate is significantly more reduced than that for the magnetite-wüstite (MW)-buffered experiment where H_2S and CH_4 were undetected (Li et al. 2021), possibly to the extent of the quartz-iron-fayalite (QIF) buffered conditions produced when BN is used as a capsule or crucible (Wendlandt et al. 1982). To establish an explanation for such a discrepancy, we have conducted further investigation to better constrain the f_{O_2} imposed by BN, when used as a capsule sleeve. Here we report results on analyses of Fe content in Au capsules, a comparative experiment using a QIF buffer and an experiment with an Fe-(Mg,Fe)O sensor for direct analysis of f_{O_2}. The calibration of the equilibrium between FeO in melt and Fe in the Au capsule, from Ratajeski and Sisson (1999) appears to be inadequate in constraining f_{O_2} for our experiments. However, we were able to obtain Fe diffusion coefficients in Au from the Fe diffusion profiles observed in the capsule of the Fe-(Mg,Fe)O sensor experiment, and both the inner and outer capsules of the MW-buffered experiment, with resulting values of 1×10^{-13} m^2/s, 3×10^{-14} m^2/s, and 5×10^{-14} m^2/s, respectively. The QIF-buffered and Fe-(Mg,Fe)O sensor experiments provide several lines of evidence supporting the observation that BN imposes QIF-like redox conditions. First, the Fe-(Mg,Fe)O sensor returned an f_{O_2} value of QIF. Second, the "apparent" partition coefficients between FeO content in melt and Fe in the Au capsules are similar between the BN experiment and the QIF-buffered experiment. Third, we observe CH_4 and H_2O peaks with similar intensities in the Raman spectra of melts from these two experiments, suggesting similar H_2 and thus O_2 fugacity. As our experiments were performed on a cubic press with the experimental assembly encased in a pyrophyllite cube, we interpret that the significantly reduced conditions imposed by BN are likely due to high H_2O activity maintained by dehydration of pyrophyllite, which can be explained using the reaction $2BN + 3H_2O = B_2O_3 + N_2 + 3H_2$. Lower H_2O activity will reduce or inhibit the oxidation of BN and its f_{O_2} buffering ability. If heat-treated, BN acts as a highly efficient H_2 barrier, as shown by Truckenbrodt et al. (1997). Through our efforts to determine the f_{O_2} imposed by using BN as a capsule sleeve in our experimental assembly, we are able to demonstrate the reducing ability of BN as an assembly component and, furthermore, shed light on the process by which BN imposes such reduced f_{O_2}. We hereby present what we have learned during the course of this investigation in the hope that the effect of BN on f_{O_2} control is both recognized and further exploited in future experimental studies.

Keywords: BN, oxygen fugacity control, Fe in Au calibration, Fe-(Mg,Fe)O sensor, experimental petrology