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 H₂S and CH₄ (Li et al. 2021). The resulting f_{02} estimate is significantly more reduced than that for the magnetite-wüstite (MW)-buffered experiment where H₂S and CH₄ 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_{02} 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_{02} . 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_{02} 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} m²/s, 3×10^{-14} m²/s, and 5 × 10⁻¹⁴ m²/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_{02} 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 QIFbuffered 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 H₂O 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 H₂ barrier, as shown by Truckenbrodt et al. (1997). Through our efforts to determine the f_{02} 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_{0_2} . We hereby present what we have learned during the course of this investigation in the hope that the effect of BN on f_{02} 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

INTRODUCTION

Boron nitride (BN) is an often-used pressure-transmitting material in experimental petrology; however, it has been considered to be as inert as MgO or Al₂O₃, and its redox potential has seldom been discussed. The use of BN as a capsule material or crucible for silicate systems has been previously reported (Mysen 1979; Mysen and Popp 1980) but did not gain wide popularity due to the fact that BN imposes highly reducing conditions; and furthermore that B_2O_3 , produced through oxidation of BN, acts as a fluxing agent for melting (Wendlandt et al. 1982). Based on the BN oxidation reaction:

$$2BN + \frac{3}{2}O_2 = B_2O_3 + N_2.$$
(1)

Wendlandt et al. (1982) estimated that the f_{02} imposed by BN capsules is ~3 log units below the quartz-iron-fayalite (QIF) buffer at 1027 °C and 1 bar for pure N₂ conditions; while for

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1027 °C and 3 GPa conditions, the estimated f_{O_2} is close to that of the QIF buffer. Note that such a difference arises from the different N₂ fugacity between 1 bar and 3 GPa. The reducing ability of BN was verified by Wendlandt et al. (1982) with experiments performed using BN capsules containing various starting materials. They showed that FeO and NiO were reduced to Fe and Ni metal, respectively; Fe metal was also produced in experiments with either olivines of various compositions or a garnet lherzolite as starting materials.

The redox imposing character of BN initially came to our attention after a sediment melting experiment performed in a previous study (Li et al. 2021; experiment LMD670) at 3 GPa, 1050 °C using BN as a capsule sleeve and spacer, produced a hydrous rhyolitic melt with dissolved H2S and CH4, as shown by the Raman spectra of the quenched melt (Fig. 1). Dissolution of CH₄ in silicate melt has been reported mainly in experiments performed at reduced conditions where a metal alloy phase is stable (i.e., f_{Ω_2} < IW, IW stands for iron-wüstite buffer) (Kadik et al. 2006, 2015, 2017; Mysen et al. 2009; Ardia et al. 2013; Dasgupta et al. 2013; Armstrong et al. 2015; Li et al. 2015, 2016; Dalou et al. 2019; Grewal et al. 2020). Moreover, H2S and CH4 were undetected in the melt from the magnetite-wüstite (MW)-buffered experiment in the same series with identical starting composition and P-T conditions (Fig. 1). We, therefore, interpret that the intrinsic f_{0_2} imposed by the BN capsule sleeve and spacer is lower than that of the MW buffer. In addition, graphite was a stable phase in the MW-buffered experiment, but absent in the BN experiment, also suggesting that BN imposes more reduced conditions than the MW buffer. The absence of graphite in the BN experiment (LMD670) provides an upper-bound constraint on the f_{02} of the experiment. The f_{02} limit for graphite stability can be calculated based on the reaction $C + 2H_2O = CH_4 + O_2$, with the equilibrium constant calculated according to Ohmoto and Kerrick (1977). Considering that the gas phase in equilibrium with the experimental charge should be dominated by CH_4 , we can assume f_{CH_4} as being equal to that of pure CH4 at P-T conditions of 3 GPa, 1050 °C (calculated using the CHO program). In combination with the H2O fugacity estimated based on H₂O content in melt (Li et al. 2021), the calculated f_{O_2} is ~FMQ-5.5. During the course of our previous study (Li et al.



FIGURE 1. A comparison of the Raman spectra of quenched melt from the BN experiment LMD670, the MW-buffered experiment LMD690 and the QIF-buffered experiment LMD776. (Color online.)

2021), no independent assessment was attempted to directly determine the f_{02} for the BN experiment. We thus assumed that the f_{02} imposed by BN would be similar to that of the QIF buffer, as calculated for the BN capsule at 3 GPa, 1050 °C. This appeared to be a reasonable assumption considering that the data point for the BN experiment fits the trend of variation of melt S solubility with f_{02} , and also agrees with the model prediction of Clemente et al. (2004). On a separate note, the presence of pyrrhotite, rather than Fe metal in experiment LMD670 at such reduced conditions can be attributed to its high $\log f_{S2}$, estimated to be -2.2 (Li et al. 2021), higher than the calculated $\log f_{S2}$ (-2.6 at 3 GPa, 1050 °C) for Fe metal and FeS coexistence based on the reaction Fe $+\frac{1}{2}S_2 =$ FeS.

A search of the literature revealed that the reducing effect of BN when used as pressure-transmitting material has been indirectly observed before. For example, Fe loss to Au capsules was reported by Ratajeski and Sisson (1999). Their experiments investigated melting of natural hornblende quartz gabbro at 8 kbar, 800–975 °C with an estimated bulk H₂O content of ~1.3 wt%. In their NaCl-graphite experimental assembly, BN powder was packed around the Au capsule to minimize oxidation of the sample. Based on the analyses of Fe content in Au capsules and FeO content in melt, they obtained an expression for the apparent equilibrium constant (*K'*) of the reaction:

FeO(melt) = Fe(Au capsule) +
$$0.5O_2$$
 (2)
lnK' = $-22.953[1000/T(K)] + 3.421 (r^2 = 0.99)$ (3)

with K' defined as

$$K' = \frac{X_{\rm Fe}^{\rm alloy} \times f_{\rm O_2}^{0.5}}{X_{\rm FeO}^{\rm molt}}$$
(4)

which is in effect representing the distribution coefficient since the activity coefficients for Fe in Au ($\gamma_{\text{Fe}}^{\text{alloy}}$) and FeO in melt ($\gamma_{\text{Fe}}^{\text{nell}}$) were not calculated. The f_{O_2} value used in the calibration was assumed to be FMQ-1, which was based on the f_{O_2} estimation for similar experiments from Patiño Douce and Beard (1994, 1995), although the latter experiments were performed without BN in their experimental assembly. When Fe content in Au capsules and FeO content in melt are known, f_{O_2} can in turn be derived from calculated K' values:

$$\log f_{O_2} = 2 \times \frac{\ln K' - \ln X_{Fe}^{\text{alloy}} + \ln X_{FeO}^{\text{melt}}}{\ln(10)}.$$
(5)

Sisson et al. (2005) performed hydrous (1.7–2.3 wt% H₂O) basalt melting experiments at 700 MPa with either BN or NaCl as capsule sleeves, and reported that sulfide was stable in experiments using BN, while titanomagnetite was stable in experiments using NaCl. The f_{O_2} for the former case was estimated to be similar to FMQ-buffered experiments, while the f_{O_2} for the latter was estimated to be between FMQ and (Re-ReO₂)-buffered conditions. Most recently, Pelleter et al. (2021) reported S contents at sulfide saturation (SCSS) in hydrous rhyolitic melts, produced by melting of Ca-poor pelite at 3 GPa, 750–1000 °C using a talc-pyrexgraphite assembly, but with either MgO or BN capsule sleeves. Higher SCSS values were obtained for experiments using MgO than those using BN as capsule sleeves. For example, the SCSS value was reported to be ~150 ppm for the experiment performed



FIGURE 2. A schematic diagram of the experimental cubic press assembly used for our experiments. (Color online.)

at 800 °C with a bulk S content of 2.1 wt% when using a BN capsule sleeve, but reached ~830 ppm for the 750 °C experiment where a MgO capsule sleeve was used. Such a difference in melt S content reflects the higher f_{O_2} conditions imposed by MgO with respect to BN. In summary, it is clear that the use of BN in these experimental studies imposed reduced conditions (\leq FMQ). However, the estimated f_{O_2} conditions were not as reduced as those we have empirically observed in our own study (<MW, likely equivalent to QIF).

To better constrain the intrinsic f_{O_2} of our experimental assembly using BN as a capsule sleeve, new experiments have been conducted and assessed in combination with further analyses of experiments from our previous work. Inspired by the work of Ratajeski and Sisson (1999), we have analyzed the post-run Fe content in Au capsules from the experimental series. We also report an additional experiment with identical starting composition and *P*-*T* conditions to those previously reported, but with a QIF buffer, which serves as a comparison to the BN experiment. An experiment employing an Fe-(Mg,Fe)O sensor as the starting material and BN as the capsule sleeve, has been performed for direct analysis of the experimental f_{02} . The application of BN in f_{02} control will also be discussed.

Methods

Experimental methods

A detailed description of both the experimental design and the method for f_{0_2} estimation are presented in Li et al. (2021). Here we briefly describe the key points. All of the experiments, both new and previously reported, have been conducted using a CS-IV 6×14 MN cubic press at the High Pressure and High Temperature Laboratory, Peking University. The experimental assembly (BJC-11) has a cylindrical configuration, which comprises a BN outer sleeve, graphite heater, and a BN/MgO spacer and capsule sleeve, similar to the common assembly used in piston-cylinder experiments, the primary difference being that the cylindrical unit is further encased in a pyrophyllite cube with an edge length of 32.5 mm (Fig. 2). For experiments with buffer assemblies, a double-capsule configuration is employed with an inner capsule (2.5 mm O.D.) containing ~10 mg starting material and an outer capsule (5 mm O.D.) containing 50-60 mg of buffer material together with 4-5 mg of deionized H2O. Both inner and outer capsules are fabricated from Au tubing. Au is the preferred inert medium when the starting composition contains Fe and S, when compared to other potential capsule materials, e.g., Pb, Pd, etc. As the experimental series regarding sediment melting was intended to study sulfur solubility in sediment melt as a function of oxygen fugacity, the starting composition used (EPSM-S1) has a major element composition similar to that of the average "global subducting sediment" (GLOSS) (Plank and Langmuir 1998), but with a sulfur content of ~1.9 wt%. Due to the low H_2O activity (~0.01) in the inner capsule estimated based on H₂O content in melt, the f_{02} in the inner capsule is generally ~2 log units lower than that imposed by the buffer.

Both the QIF-buffered experiment LMD776 and the Fe-(Mg,Fe)O sensor experiment LMD783 were performed at 3 GPa, 1050 °C; identical to the *P-T* conditions of the previous experimental series (Table 1). The QIF buffer assemblage has a mixing ratio of 1:1:1 between SiO₂, Fe metal powder and fayalite. For the Fe-(Mg,Fe)O sensor experiment, the starting composition was a mix of Fe metal powder and Mg(OH)₂ to achieve H₂O-saturated conditions. The resultant Fe:MgO mixing ratio was 3:1.

Analytical methods

The measurement of Fe in Au capsules was accomplished using an electron microprobe (JEOL JXA 8230) at Peking University. By employing beam conditions of 20 kV and 50 nA and a counting time of 60 s, a detection limit of~55 ppm can be achieved. The diffusion profiles of Fe in Au capsules have also been obtained across both the inner and outer capsule walls, with a step size of 20 μ m.

The analysis of S content in melt was performed on the same electron microprobe, employing a PETH analyzing crystal, in combination with a defocused beam of 15 kV and 50 nA, and 100 s counting time. The resultant detection limit was ~20 ppm. ZnS was used as the calibration standard.

The Raman spectra of melts were recorded with a Horiba LabRam HR Evolution spectrometer at Peking University, employing a Nd:YAG laser with a wavelength of 532 nm and an emission power of 80 mW. The recording conditions are as follows: 100× objective lens, 100% laser power, 600 grating, and 500 µm pinhole. Acquisition time was 10 s for each window, accumulated over three scans.

RESULTS

Fe content in Au capsules

For experiment LMD670, the profile of Fe in the Au capsule appears as a flat line, indicating an equilibrium between the

TABLE 1. Summary of experimental conditions and run products

Experiment no.	Starting comp.	<i>P</i> (GPa)	T (°C)	Time (h)	Buffer	Estimated f_{O_2}	Phase assemblage
LMD670 ^a	EPSM-S1	3	1050	96	BN sleeve	FMQ-7.5	melt (95) ^b Po Grt ^c Coe Ap
LMD690	EPSM-S1	3	1050	46	MW	FMQ-3.8	melt (95) Po Grt Coe Ap Gr
LMD776	EPSM-S1	3	1050	48	QIF	FMQ-7.5	melt (85) Po Grt Coe Ap
LMD783 ^a	Fe+Mg(OH) ₂	3	1050	24	BN sleeve	FMQ-5.2	Fe, (Mg,Fe)O

Notes: Mineral abbreviations: Ap = apatite; Coe = Coesite; Gr = graphite; Grt = garnet; Po = pyrrhotite. Buffer abbreviations: QIF = quartz-iron-fayalite; MW = magnetite-wüstite; FMQ = fayalite-magnetite-quartz.

^a No buffers were employed in these experiments.

^b Numbers in brackets following "melt" are melt percentages in the charge, estimated by sight.

^c Mineral phases in italics appear at the colder end of the capsule only.

sample and the capsule (Fig. 3a; Online Materials¹ Table S1). The average Fe content in the Au capsule is about 0.072 ± 0.004 wt% (Online Materials¹ Table S2); while the FeO content in melt is 0.32 ± 0.05 wt%. Therefore an "apparent" Fe partition coefficient between melt and the Au capsule, calculated as the ratio between FeO in melt and Fe in Au, is ~4.4. According to the calibration of Ratajeski and Sisson (1999) (Eqs. 3 and 5), the f_{O_2} for experiment LMD670 is calculated to be ~FMQ-3.5, which is ~2 log units higher than the upper limit estimated based on graphite stability.

For the MW-buffered experiment LMD690, the profile of Fe in the Au inner capsule shows a general increasing trend from the sample-inner capsule boundary to the inner capsule-buffer boundary (Fig. 3b; Online Materials¹ Table S1), which can be attributed to the diffusion of Fe from the buffer inwards. However, on closer inspection, the profile begins with a section ($\sim 40 \ \mu m$) of decreasing Fe content, which may represent the diffusion of Fe from the sample to the Au capsule. Analyses of Fe in Au close to the sample returned an average of 0.083 ± 0.007 wt% (Online Materials¹ Table S2). With an FeO content of 0.86 ± 0.07 wt% in melt, the "apparent" Fe partition coefficient between melt and the Au capsule is ~10.4, suggesting the f_{02} is ~0.8 log units higher than that for experiment LMD670. Such a variance in f_{02} is far smaller than what would have been anticipated. This may be due to the fact that Fe partitioning between the sample and the Au capsule had yet to reach equilibrium. If we take the lowest point of the profile (Fig. 3b), 0.021 wt%, which is the apparent

FIGURE 3. The Fe content profiles in both inner and outer Au capsules for the BN experiment LMD670 (a), the MW-buffered experiment LMD690 (b and c), and the QIF-buffered experiment LMD776 (d and e). Note that scales for the y-axis vary between graphs for different experiments. The variation in profile length reflects the variability of capsule width, both regionally within each capsule and between capsules from individual experiments, caused by the compression encountered during experimental runs. The two profiles for experiment LMD670 represent data obtained from first a position closer to the center of the capsule (red line) and second a distal position (blue line). The temperature gradient may explain the smoother profile for the hotter position (red line). (Color online.)

meeting point of the two diffusion sections, the calculated difference in f_{02} is ~2 log units.

The QIF-buffered experiment

For the QIF-buffered experiment LMD776, the profile of Fe in the inner Au capsule also shows a general increasing trend from the sample toward the buffer (Fig. 3d; Online Materials¹ Table S1), reflecting the diffusion of Fe from the buffer inwards. The wavy pattern observed in the Fe concentration profiles for both inner and outer Au capsules may indicate a progressive approach toward equilibrium (Figs. 3d and 3e). The capsule Fe content is generally higher than that observed for the MW-buffered experiment LMD690, which may arise from either the lower f_{02} or the faster diffusion rate of metallic Fe due to a higher concentration gradient or a combination of both. The Fe content in the region of the Au capsule close to the sample has an average of 0.30 \pm 0.04 wt% (Online Materials1 Table S2), while the FeO content in melt is 1.36 ± 0.04 wt%, resulting in an apparent partition coefficient of ~4.5, similar to that for experiment LMD670. The fact that the beginning of the profile shows a minimal slope (Fig. 3d) may suggest equilibrium has been attained between the sample and the Au capsule. If this is indeed the case, the f_{02} imposed by the BN capsule sleeve would appear to be similar to that of the OIF buffer.

The post-run buffer assembly has an interesting morphology, which is worth documenting (Online Materials¹ Fig. S1 and Table



S3). Note that we are observing only one longitudinal cross section of the capsule, and as such the possibility of heterogeneous distribution of buffer materials latitudinally cannot be ruled out. Large olivine and ferrosilite crystals form a shell surrounding the inner capsule. The formation of ferrosilite may be due to the reaction of fayalite and SiO₂, or alternatively to the reduction of olivine, which produces ferrosilite and metallic Fe. At one end of the capsule, we observe the intergrowth of skeletal olivine and coesite between the olivine-ferrosilite layer and the outer capsule. While the ferrosilite-fayalite-Fe assemblage imposes slightly lower f_{02} than QIF (Woodland and O'Neill 1997), it can be considered similar within the accepted degree of experimental uncertainty. We found no presence of Fe metal in the outer capsule, which may imply complete loss of Fe to the Au capsule, and consequently lower Fe activity. Woodland and O'Neill (1997) observed lowered H2O activity in the QIF assemblage at 1.7 GPa, 700-1000 °C due to increased solubility of silicates in H₂O at high pressure and high temperature. If the skeletal olivine and coesite represent quench crystal formation, i.e., high solubility of coesite and olivine at 3 GPa, 1050 °C, then H₂O activity will also be significantly lowered. The final $f_{\rm H_2}$ in the outer capsule depends on the counterbalance of these two effects. The leveling off of the Fe profile in the outer capsule of experiment LMD776 (Fig. 3e) suggests that the buffer assemblage may have reached, or be close to reaching, equilibrium with the $f_{\rm H2}$ imposed by the assembly.

The FeO content in the melt of experiment LMD776 (Online Materials¹ Table S3) is far higher than would be predicted for such low f_{O_2} conditions, as shown by the decreasing trend of FeO content in melt with decreasing f_{O_2} for our experimental series (Li et al. 2021). As depicted by the FeS saturation reaction:

FeS(sulfide solid/melt) + $\frac{1}{2}O_2 = FeO(silicate melt) + \frac{1}{2}S_2$ (6)

at sulfide saturation, lower f_{02} leads to lower f_{82} , or lower FeO content in melt, or both. We have observed decreasing trends for both f_{S_2} and FeO content in melt for our experimental series with fixed bulk S content (Li et al. 2021). The higher FeO content in the melt of experiment LMD776 may result from Fe contaminating the starting composition due to Fe diffusion from the buffer. The melt S content falls within the trend observed in our previous study, that is, the lnS (ppm) in melt has a negative linear correlation with $\ln X_{FeO}$ in melt with a slope close to -1 (Fig. 4). Such a correlation for low FeO (<~5 wt%) melts is predicted by the thermodynamic framework for modeling sulfur content in melt at sulfide saturation (SCSS) as a function of the standard state Gibbs free energy of the FeS saturation reaction (Eq. 6), sulfide capacity $(C_{\rm S}^{2-})$, the activity of FeO in melt $(a_{\rm FeO}^{\rm melt})$ and the activity of FeS in sulfide melt $(a_{\text{FeS}}^{\text{sulfide}})$ (O'Neill and Mavrogenes 2002; O'Neill 2021); and in the case of hydrous rhyolitic melt with the relation (Li and Zhang 2022):

$$\ln[\text{HS}]_{\text{SCSS}} = -\Delta G_{\text{FeS-FeO}}^{\circ}/RT + \ln C_{\text{HS}} - \ln a_{\text{FeO}}^{\text{melt}} + \ln a_{\text{FeS}}^{\text{sulfide}}$$
(7)

where C_{HS} represents the hydrosulfide capacity, defined for the dissolution of H₂S in hydrous melt. Interested readers may find further details in the above references. The main point is that such an observation (Fig. 4) provides indirect evidence that the

sample and the near side of the inner capsule may be at or close to an equilibrium state.

Further evidence supporting similar f_{0_2} conditions for experiments LMD670 and LMD776 comes from the Raman spectra of their respective melts (Fig. 1). First, their spectra show similar patterns in terms of silicate peaks. As shown in our previous study, such patterns are notably different between reduced (FMQ-3.8 and below) and oxidized (FMQ-2.2 and above) experiments (see Fig. 4 of Li et al. 2021). Second, they present H₂O and CH₄ peaks with similar intensity, suggesting similar H₂O and CH₄ fugacity and, consequently, similar H₂ and O₂ fugacity.

The Fe-(Mg,Fe)O sensor experiment

Fe diffusion into the Au capsule is observed clearly as a gray band under a stereomicroscope for the Fe-(Mg,Fe)O sensor experiment LMD783 (Fig. 5a), demonstrating reduced redox conditions. The achievement of equilibrium in the sample is demonstrated by the even distribution of Fe metal and (Mg,Fe) O in the sample (Fig. 5b) and by homogeneous (Mg,Fe)O compositions (Online Materials¹ Table S4). The band of (Mg,Fe)O near the edge of the sample is interpreted to be a result of the loss of Fe metal to the capsule (Fig. 5a). This band of (Mg,Fe) O may have acted as a physical barrier preventing further Fe loss from the sample, and consequently enabling the attainment of equilibrium.

The f_{O_2} of the experiment can be calculated based on the reaction Fe + $\frac{1}{2}O_2$ = FeO according to the calibration of O'Neill et al. (2003), with the composition of (Mg,Fe)O reflecting deviation from the IW buffer. The molar ratio of Mg/Fe in (Mg,Fe)O (~1) results in a calculated f_{O_2} of IW-0.6, i.e., QIF+0.2, at 3 GPa, 1050 °C. Considering analytical and experimental uncertainties, this demonstrates that the assumption that BN imposed f_{O_2} conditions similar to that of the QIF buffer is valid for our experimental assembly.



FIGURE 4. InS (ppm) vs. $\ln X_{FeO}$ in melt for 3 GPa, 1050 °C experiments reported previously in Li et al. (2021) and experiment LMD776 from this study. Note that the fitting of the trendline is based on previous experiments.



FIGURE 5. Stereoscopic photos of experiment LMD783 showing (a) the diffusion of Fe into the Au capsule and (b) the intergrowth of Fe metal and (Mg,Fe)O. The Fe diffusion profile is plotted in c. The fitting of the Fe diffusion profile to Equation 8 is shown in d. (Color online.)

The diffusion coefficient of Fe in Au

We are able to obtain the diffusion coefficient for Fe in Au by fitting the Fe concentration profile in the Au capsule of experiment LMD783 (Fig. 5c) to the following equation from Zhang (2010):

$$\ln C = \ln C_0 - x^2 / 4Dt \tag{8}$$

where *x* is the distance, *t* is time and *D* is the diffusion coefficient. This equation describes thin-source diffusion into a semi-infinite medium. By plotting ln*C* vs. x^2 , the coefficient of this linear trend can be used to derive the diffusion coefficient, with a resulting value of 1×10^{-13} m²/s (Fig. 5d). Through fitting with the same equation, the Fe concentration profiles in both the inner and outer capsules of experiment LMD690 return slightly lower diffusion coefficients, 3×10^{-14} m²/s and 5×10^{-14} m²/s, respectively (Fig. 6). These values compare favorably with published diffusion coefficients at 1028 °C: 1×10^{-12} m²/s at 0.1 MPa in He (Duhl et al. 1963), 1×10^{-13} m²/s at 5 GPa in H₂, and 3×10^{-14} m²/s at 5 GPa without H₂ (Yamazaki et al. 2004). Considering that the diffusion coefficient at 5 GPa in H₂ is three times higher than that in the absence of H₂, the lower values obtained for experiment LMD690 may be due to its

more oxidized conditions compared to those for experiment LMD783. The possibility that the profile for the inner capsule of experiment LMD690 may have been affected by reverse diffusion of Fe from the sample and that Fe diffusion in the capsule of experiment LMD783 may have reached its outer boundary represent other possible factors contributing to the variation in obtained diffusion coefficients.

DISCUSSION

Determining f_{0_2} based on Fe content in Au capsules

Calculating f_{02} based on the calibration from Ratajeski and Sisson (1999) has the advantage of avoiding the uncertainties associated with calculating the FeO activity in hydrous rhyolitic melt and the Fe activity in Au. However, the resultant f_{02} values are too high to be considered reasonable. One possible cause is that the assumed f_{02} of FMQ-1 for the experiments of Ratajeski and Sisson (1999) is overestimated. This possibility also agrees with the fact that similar experiments from Patiño Douce and Beard (1994, 1995), performed without BN, have an estimated f_{02} range of FMQ-2~FMQ. The calibration of Ratajeski and Sisson (1999) is similar to the calibration for Fe partitioning between Pt metal and silicate melt obtained by Grove (1982). However, the calibrations from Ratajeski and Sisson (1999) and Grove (1982) are not necessarily equivalent, considering the difference in $\gamma_{\text{FeO}}^{\text{mell}}$ between rhyolitic melt and basaltic melt and the difference in $\gamma_{\text{Fe}}^{\text{alloy}}$ between Fe-Au and Fe-Pt systems. Considering that Fe diffuses more readily into Pt than Au at similar f_{O_2} conditions, the apparent equilibrium constant K'should have a higher value for the Fe-Pt system than that for the Fe-Au system. Similar K' values obtained by Ratajeski and Sisson (1999) for the Fe-Au system can therefore be attributed to overestimated f_{O_2} (Eq. 4).

The f_{O2} conditions for the equilibrium between FeO in melt and Fe in Au can be assessed in comparison to the calibration for the IW buffer by O'Neill (1988). Apart from the melt and alloy compositions, other parameters required include the equilibrium constant for the exchange reaction between the FeO melt component and the FeO solid phase (wüstite), and activity coefficients γ_{FeO}^{melt} and γ_{Fe}^{metal} , as demonstrated by the equation below:

$$\Delta IW = 2 \log \left[(X_{\text{reo}}^{\text{red}}) / (X_{\text{reo}}^{\text{alloy}}) \right] + 2 \log \gamma_{\text{reo}}^{\text{reo}} - 2 \log \gamma_{\text{reo}}^{\text{reo}} - 2 \log K (\text{FeO}^{\text{red}} - \text{FeO}^{\text{s}})$$
(9)

The estimated value is ~0.18 for $\log \gamma_{\text{Fe0}}^{\text{mel}}$ based on the expression from O'Neill (2021), while the $\log K$ term for the FeO melt component and wüstite exchange reaction is calculated to be ~0.37 for the 3 GPa, 1050 °C conditions of experiment LMD670, based on the thermodynamic database of Holland and Powell (2011). Although a positive deviation from ideal mixing has been observed for Fe-Au alloys at ambient pressures (Seigle 1956), the activity of Fe in the Au capsule is unknown for the very low Fe end of the Au-Fe solid solution. The low f_{O_2} for experiment LMD670 suggests that $\log \gamma_{\text{Fe0}}^{\text{HeV}}$ has a positive value (~2).

When referring to redox sensors employing Fe alloys, Woodland and O'Neill (1997) state that "the method loses accuracy as the activity of Fe decreases, leading to unacceptably large errors when $a_{\text{Fe}}^{\text{iloy}}$ is less than about 0.1." This could also be the case for our experiments.

An explanation for the QIF-like intrinsic f_{02} conditions for our BN experiment

Both the comparability with the QIF-buffered experiment and direct f_{O_2} measurement using the Fe-(Mg,Fe)O sensor suggest that BN in our experimental assembly imposed f_{O_2} conditions similar to that of the QIF buffer and thus far more reduced than the estimated FMQ-like conditions assumed in previous studies. Such experimental studies used natural samples as their starting materials, which would have imposed higher f_{O_2} when compared to the reduced starting material used in our experimental series. However, as the difference in estimated f_{O_2} is so large, we suspect that this likely results from the difference in the intrinsic f_{H_2} of the experimental setup.

Truckenbrodt et al. (1997) investigated the redox conditions in piston-cylinder experiments employing fired BN or unfired pyrophyllite as packing materials surrounding the capsule in NaCl-graphite assemblies. They reported that C-O-H fluids from experiments using fired BN as a packing material maintained the initial $f_{\rm H_2}$ of the starting organic compounds (C₄H₄O₄, C₉H₁₀O₂, and C14H22O), while experiments with unfired pyrophyllite resulted in equivalent $f_{\rm H2}$ for all three starting compositions, similar to cobaltcobalt oxide (CoCoO)-buffered conditions, and representative of the intrinsic $f_{\rm H_2}$ of the NaCl-graphite assembly. This interesting result demonstrates that fired BN does not impose reduced f_{O_2} on the sample charge. This is likely due to the fact that heat treatment of BN increases its crystallinity and purity and consequently reduces its ability to react with oxygen (Udayakumar et al. 2011). Moreover, their experimental results demonstrate that the dehydration of pyrophyllite is key for transmitting the intrinsic $f_{\rm H_2}$. Matjuschkin et al. (2015) state that "As pointed out by Luth (1989), the availability of H_2 to "transmit" any intrinsic f_0 , to the sample might depend on how well the larger parts of the assembly are dried or on the dehydration of talc if used as an assembly component." Under such a consideration, we may derive the following reaction describing the oxidation of BN involving H₂O:

$$2BN + 3H_2O = B_2O_3 + N_2 + 3H_2$$
(10)



FIGURE 6. The fitting of Fe diffusion profiles in both the inner (**a**) and outer (**b**) capsules from experiment LMD690 to Equation 8. Note that *x* represents the distance measured from the buffer for both profiles. The profile from the inner capsule of experiment LMD690 is shown in blue in Figure 3b with the first 40 μ m section excluded for the purpose of fitting. (Color online.)

through the addition of the BN oxidation reaction (Eq. 1) and the H₂O dissociation reaction:

$$H_2 O = H_2 + \frac{1}{2}O_2.$$
(11)

The f_{H_2} imposed by the BN sleeve is, therefore, a function of the H₂O activity, i.e., higher H₂O activity, higher f_{H_2} . Previously reported experiments by Li et al. (2021) were performed using a cubic press. The experimental assembly used has a cylindrical configuration, similar to piston-cylinder assemblies, but further encased in a pyrophyllite cube (Fig. 2). The more reduced conditions observed in our BN experiment may be explained by a higher H₂O activity, which may arise from dehydration of pyrophyllite in our experimental assembly.

The intrinsic H₂O activity of such assemblies remains unknown. At the commencement of each run, gaskets form along the edges of the pyrophyllite cube during compression. If we can consider the experimental assembly as a closed system after gasket formation, then H₂O activity of the experimental assembly depends on the dehydration of pyrophyllite and also the consumption of H2O due to BN oxidation. The BN oxidation reaction, according to reaction 10, produces both N2 and H2. The H₂ fugacity can be calculated by assuming similar conditions to those imposed by the QIF buffer (O'Neill 1987) plus pure H₂O and, subsequently, the H₂ activity can be estimated to be ~ 0.6 . Based on the stoichiometry of reaction 10, and an assumption of ideal mixing between gas species and similar fugacity coefficients, N2 activity can be estimated to be ~0.2. The H2O activity is also ~ 0.2 if the gas phase is dominated by H₂, N₂, and H₂O. The reduced N₂ activity implies that the f_{O_2} value would be ~1.4 log units lower than that of the QIF buffer (Eq. 1), however, the similarly reduced H₂O activity means that f_{H_2} remains the same as that of the QIF buffer (Eq. 10). There may be other gas species present, but not considered, for example, CH₄, from the reaction of H₂O with graphite. Although much simplified, such an inverse modeling approach suggests that BN in our experimental assembly can maintain $f_{\rm H_2}$ similar to that of the QIF buffer plus H₂O, especially in the limiting case when a gas phase is present due to the dehydration of pyrophyllite.

The application of BN as an f_{02} control in solid media assemblies

The intrinsic f_{02} of our experimental assembly, using BN as a capsule sleeve and spacer, appears significantly more reduced than that reported by previous studies using common pistoncylinder assemblies containing BN. The primary difference lies in the usage of the pyrophyllite cube in our experimental setup. This represents a simple way to impose a reduced redox state relevant for investigating lunar conditions or reduced end-members of the martian environment, although the resultant chemical system will be H₂O-bearing. According to reaction 10, lowering H₂O activity will reduce or inhibit the BN oxidation reaction and its f_{02} buffering ability. Piston-cylinder experiments normally employ NaCl, talc, or BaCO₃ tube as the pressure transmitting material encasing the graphite furnace and MgO, Al₂O₃, pyrophyllite, BN, or pyrex as assembly components within the graphite furnace. An available source of H₂O is required to impose the intrinsic f_{O_2} of the experimental assembly onto the sample charge. This could be either moisture absorbed by the pressure-transmitting material or H₂O from dehydration of talc and pyrophyllite.

The material immediately surrounding the capsule exerts the dominant control on the f_{O_2} of the sample. It is evident from previous studies that BN can impose more reduced conditions than MgO, which is useful when the variation of f_{O_2} is a factor of research interest, although the exact value of f_{O_2} needs to be determined independently. The starting material can also have a buffering effect on f_{O_2} due to the exchange of H₂ between the sample and the assembly (Holloway et al. 1992). Whether it is the intrinsic f_{O_2} of the assembly or that of the sample which is desired, the redox potential between the sample and assembly can result in either gain or loss of H₂O and Fe from the charge. Therefore, BN provides a suitable choice of pressure-transmitting material for reduced experimental redox conditions as it minimizes possible modification of the starting composition.

A cautionary note on using BN as a pressure-transmitting material: the experimental charge may be contaminated with boron. As investigated and reported by Matjuschkin et al. (2015), when BN powder was packed around a Pt capsule, 2000–3000 ppm boron was detected in glasses produced from experiments run at 1200–1265 °C for 24–26 h. It appears that the magnitude of boron contamination is similar to that of carbon infiltration (Matjuschkin et al. 2015). It is worth keeping this issue in mind, especially for high-temperature experiments.

An alternative approach to f_{O_2} control is to use the packing material surrounding the capsule as a barrier between the capsule and assembly to either maintain the redox state of the sample or prolong the life of the oxygen buffer assemblage. Matjuschkin et al. (2015) investigated the H₂ permeability of different pressuretransmitting materials and demonstrated that pyrex functions better than MgO or Al₂O₃ at limiting the diffusion of H₂, therefore maintaining the intended f_{H_2} within the capsule. The experimental results of Truckenbrodt et al. (1997) suggest that fired BN also acts as an excellent H₂ barrier.

IMPLICATIONS

Controlling f_{0_2} in solid media assemblies is a challenging task. More often than not, the f_{02} of such experimental runs is not directly measured or controlled but reflects the intrinsic f_{0_2} of either the assembly or the sample or somewhere in-between. The double-capsule configuration employing a buffer assemblage is currently the most effective approach for achieving f_0 , control but requires a large capsule volume and is more difficult and time-consuming to prepare. Therefore, imposing approximate f_{02} by selecting the appropriate capsule or pressure-transmitting material for the assembly is still the first choice for the majority of experimental studies. Through our efforts to determine the f_{02} imposed by our chosen experimental assembly using BN as a capsule sleeve, 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_{02} control is both recognized and further exploited in future experimental studies.

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