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The redox potential of boron nitride and implications for its use as a crucible material in experimental petrology

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Abstract

The suitability of boron nitride for use as a crucible material in silicate and oxygen-bearing metal sulfide systems has been investigated. Boron nitride is unsatisfactory for use with many silicate systems because its presence in combination with a source of oxygen establishes the oxygen fugacity at values below that of the assemblage quartz + fayalite + iron, reducing transition metal ions such as Ni^{2+} and Fe^{2+} to the metallic state. B_2O_3, resulting from the oxidation of BN, acts as a flux to promote formation of melt.

Introduction

The ideal capsule material for experiments in systems of geologic interest is one that has high thermal stability, is chemically inert with respect to the experimental components, and comprises an impermeable membrane for both internally and externally originating components. Because no material satisfies all these properties, the experimentalist is left with two alternatives:

(A) To select the material that most closely approaches inertness in its relevant properties (*e.g.*, Pt capsules for the system $CaO–CO_2–H_2O$, Boettcher and Wyllie, 1968) or

(B) To select a material that will define, at appropriate values, the activities of components of the experimental system (*e.g.*, iron capsules, Kesson and Lindsley, 1976; Fe_xPt_{1-x} alloys, Huebner, 1973).

In a search for a material to contain Fe–S–O melts (Wendlandt and Huebner, 1979), we investigated the suitability of boron nitride, BN. We designed experiments to determine the range of oxygen fugacities over which BN might be stable and to ensure that the material is inert with respect to the system being investigated. Previous investigators have used crucibles of BN in studies of oxygen-absent, metal–metal sulfide systems (Usselman, 1975; Ganguly and Kennedy, 1977). Recently, the use of BN as a capsule material has been extended to experiments in silicate systems (Mysen, 1979; Mysen and Popp, 1980). We present evidence that such use of BN causes an extremely reducing environment to prevail in the charge; as a consequence, the use of BN as a capsule material for silicate systems that contain easily reduced elements may be very limited.

Thermodynamic considerations

The probable reaction for the oxidation of BN is

$$2BN + 3/2O_2 \leftrightarrows B_2O_3 + N_2. \qquad (1)$$

Below 60 kbar, hexagonal (α)B_2O_3 is the stable polymorph at melting temperatures (m.p. 450° C at 1 bar; $dP/dT \approx 110$ bars/°C) (Mackenzie and Clausen, 1961). The phase diagram of Bundy and Wentorf (1963) does not resolve whether BN will have a hexagonal or cubic (zinc blende) structure at the

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conditions of interest; as will be shown later, we observed no evidence for the presence of cubic BN and assume the hexagonal form.

Using tabulated free energies of formation for pure crystalline (hexagonal) BN and B_2O_3 melt (Stull and Prophet, 1971) the equilibrium constant, K, for the reaction at one bar can be estimated:

$$\log K_{1\text{bar}} = \log [f_{N_2}/f_{O_2}{}^{3/2}]$$

$$= 38.05\left(\frac{10^3}{T}\right) - 1.88 \qquad (2)$$

where f is fugacity and T is degrees Kelvin. Changes in pressure (relative to the standard state of 1 bar) will change the value of the equilibrium constant:

$$\left(\frac{\delta \ln K}{\delta P}\right)_T = \frac{-\Delta \bar{V}}{RT} \qquad (3)$$

and,

$$\ln K_p \approx \ln K_{1\text{ bar}} - \frac{\Delta \bar{V}\,(P - 1)}{RT}$$

where $\Delta \bar{V}$ refers to the change in molar volume of the condensed phases. Molar volume data are available for B_2O_3 melt at 500–1100°C and one bar (Mackenzie, 1956); for hexagonal BN at 0–800°C and one bar (Pease, 1952); and for hexagonal B_2O_3 at standard conditions (Berger, 1953). If such values are applicable to reaction (1),

$$\Delta \bar{V} = \bar{V}_{B_2O_3} - 2\bar{V}_{\text{hexagonal BN}}. \qquad (4)$$

For hexagonal B_2O_3 at room temperature, $\Delta \bar{V}$ = 5.43 cm^3; for B_2O_3 liquid at 520° and 800°C, $\Delta \bar{V}$ = 20.7 and 22.9 cm^3, respectively. Corrected for pressure, the corresponding values of the equilibrium constant range from

$$\log K_p = \frac{38050}{T} - 1.88 - \frac{0.028\,(\Delta P)}{T} \qquad (5)$$

to

$$\log K_p = \frac{38050}{T} - 1.88 - \frac{0.120\,(\Delta P)}{T}. \qquad (6)$$

Other variables held constant, the effect of pressure is to increase f_{N_2}/f_{O_2} or to decrease f_{O_2}. From relation (2) oxygen fugacities can be calculated for 2 extreme values of P.

Case a. At 1300 K and 1 bar in "pure N_2" (*i.e.*, f_{N_2} = 1 bar) the estimated oxygen fugacity of reaction (1) is

$$\log f_{O_2} = -18.3,$$

almost 3 log units below the QIF oxygen buffer (log $f_{O_2} = -15.1$) at 1300 K and 1 bar (Huebner, 1971).

Case b. If a temperature of 1300 K and a total pressure of 30 kbar prevail, and if the gas phase is predominantly N_2, generated by the decomposition of BN, f_{N_2} = 30,000 bar (assuming ideality), then the calculated value of log f_{O_2} ranges from −14.8 to −13.4, depending upon whether equation (5) or (6) is used. These values are close to that of the QIF buffer assemblage at similar conditions (−13.9), and far more reducing than that of the iron–wustite (−13.1) or Ni−NiO buffers (−8.8). If B_2O_3 liquid is present and dissolves silicate (Levin *et al.*, 1964; Fig. 2353, for example), the reduced B_2O_3 activity will cause a corresponding decrease in f_{O_2}. Thus, the f_{O_2} value of −13.4 may be a maximum value in experimental systems with silicates.

Although theoretical considerations suggest that BN will behave as a reducing agent in the presence of many oxides, including Fe, Ni, and Co, uncertainties remain. In addition to the usual uncertainties in the thermochemical data in the standard state, there are uncertainties related to the molar volume of B_2O_3 liquid, to the effects of pressure and temperature on the molar volume of reaction, to the fugacity of N_2 at pressure and temperature, and to the structural state of BN. We therefore wished to confirm the thermochemical calculations with several simple experiments.

Experimental considerations

To test the thoretical observations, samples of BN with binder (Union Carbide HBR grade) and binderless "pyrolitic" BN (PBN-Union Carbide high purity grade) were heated at a range of controlled oxygen fugacities at 1 atm and were used as capsules in experiments at 30–35 kbar. The boron nitride with binder gives sharp peaks in an X-ray powder diffraction pattern and appears, at least at low pressure, to be hexagonal. No additional reflections, which might have been attributable to the binder, were found. The pyrolitic BN showed only a single, broad X-ray reflection, centered at 26.3° 2θ (Cu$K\alpha$ radiation). Pyrolitic BN appears not well-crystallized, at least with this radiation. We found that the lack of structure persists, even when the pyrolitic BN was annealed for 1 hour at 1000° C and 30 kbar.

At 1 atm, experiments were carried out in air at 1000°C and in a gas-mixing furnace at 1100°C. The weights of samples were monitored for periods up to 28 hours by multiple weighings for the former and by a thermogravimetric balance (*in situ*) (Williams and Mullins, 1981) for the latter. BN specimens fired in air lost weight rapidly (16.5% of the total weight of approximately 25 mg in 1.5 hours for one sample) and continuously. Weight loss is a result of the release of N_2 and volatilization or dripping of B_2O_3 (m.p. 450°C; b.p. 1250°C) off the sample. After termination of the experiments at 1000°C, the charges were so oxidized that they were too fragile to handle or were frozen in quenched B_2O_3 liquid (which formed a puddle in the ceramic crucibles used for firing some samples or which coated the Pt wire used to suspend other samples). PBN sample weights, monitored by a thermogravimetric balance as a function of time and f_{O_2}, also decreased. At an oxygen fugacity 1 log unit below IW, the rate of weight loss was approximately 0.3 mg/hour (total sample weight 354 mg), whereas the rate was 0.55 mg/hr at an f_{O_2} 1 log unit above IW. After exposure to f_{O_2} below IW, the recovered charge had small beads of glass, presumed to be quenched B_2O_3 liquid, on its surface. These results are consistent with the results predicted from equation (2).

We conducted three sets of experiments at high pressure using a solid-media, piston cylinder apparatus (Boyd and England, 1960). Temperatures were measured using Pt–$Pt_{90}Rh_{10}$ thermocouples and were not corrected for the effect of pressure on the emf output of the thermocouple. In all instances the sample configuration consisted of a charge (transition metal oxide or silicate assemblage) within a BN or PBN capsule which, in turn, was enclosed within a sealed noble metal capsule. Experiments are summarized in Table 1.

In the first series of experiments, the charges consisted of NiO or FeO. For all sample capsule configurations, the sample in contact with the BN was reduced to the metallic state, consistent with the results predicted from equation (5) or (6). In the second set of experiments, olivines of varying composition were run at 1050°, 1125°, and 1250°C. All run products contained Fe-metal, concentrated in the proximity of the surrounding BN capsule. Evidently, equations (5) and (6) give maximum values of f_{O_2} at 30 kbars. Last, a melting experiment on a garnet lherzolite nodule (PHN 1611, described by Nixon and Boyd, 1973) resulted in unequivocal evidence of the reducing nature of BN (see Fig. 1): Metallic iron concentrated near the boundary with BN.

The experiments show that BN establishes f_{O_2} values below those of QIF at 30 kbar. If the

Table 1. Experiments at high pressures

Sample	Inner Capsule	Outer Capsule	P, kbar	T, °C	Duration, hrs.	Results
I.						
NiO	BN	$Pt_{95}Au_5$	30	1000	1	Ni^o, NiO
NiO	PBN	Au	30	1000	0.75	Ni^o, NiO
FeO	PBN	Pt	30	1000	1	Fe^o, FeO
II.						
Fo_{68}	PBN	Pt	30	1200	23	Fe^o, Ol, Px
Fo_{68}	PBN	Pt	30	1125	24	Fe^o, Ol, Px
Fo_{68}	BN	Pt	30	1050	24	Fe^o, Ol, Px
Fo_{81}	BN	Pt	30	1200	24	Fe^o, Ol, Px
Fo_{81}	BN	Pt	30	1050	24	Fe^o, Ol, Px
III.						
PHN 1611	BN	Pt	35	1625	0.87	Fe^o Blebs in charge

Abbreviations: BN, boron nitride; PBN, pyrolitic boron nitride; Ni^o, Fe^o, metallic nickel and iron, respectively; Ol, olivine; Px, orthopyroxene; $Fo_{\%}$, mole percent forsterite in olivine.

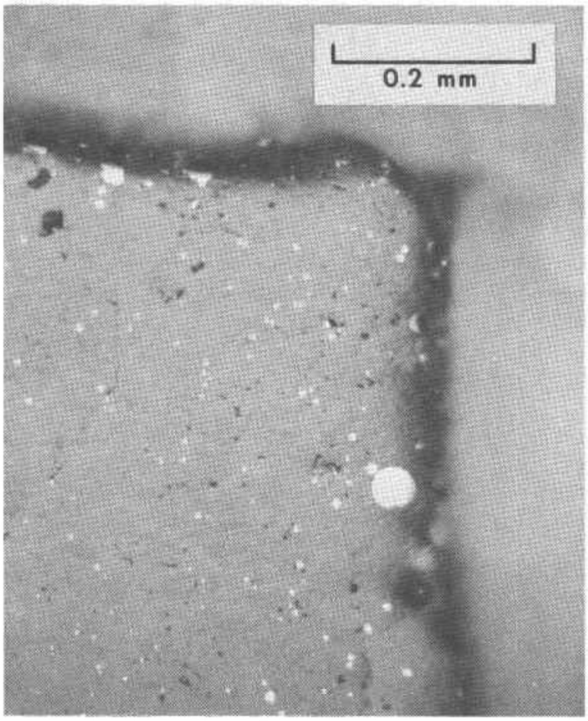

Fig. 1. Photomicrograph of the experimental charge containing sample PHN 1611 (run at 35 kbar and 1625°C for 0.87 hour) seen in reflected light. The BN inner capsule is the fuzzy gray material; the Pt outer capsule is *not shown*. The silicate portion of the charge, olivine + orthopyroxene + clinopyroxene + melt, contains spherules of Fe metal (identified by SEM with non-dispersive X-ray analysis) which increase in abundance and size toward the BN-silicate charge interface.

observations at 1 bar are correctly interpreted, BN is also an effective reducing agent at low pressures.

Conclusions

The use of boron nitride as a crucible material for experiments in all but the most reduced systems (metals, sulfides) is ill-advised because of its reducing effect on many silicate and oxide assemblages, including the system Fe–S–O. Furthermore, B_2O_3, occurring as an impurity or formed by reduction of components in the sample, is an efficaceous flux, reducing the melting point of silicates and oxides hundreds of degres (Levin *et al.*, 1964); for example, the 1 atm melting point of SiO_2 is lowered almost 1300°, to approximately 440°C, by the presence of B_2O_3. The results of this study indicate that discretion should be exercised in the use of BN as a crucible material.

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