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The effect of B_2O_3 on the viscosity of haplogranitic liquids

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ABSTRACT

The effect of B_2O_3 on the viscosity of a haplogranitic liquid (K_2O-Na_2O-Al_2O_3-SiO_2) has been determined at 1 atm pressure in the temperature interval of 600–1600 °C. Viscosity measurements of a haplogranite, haplogranite + 4.35 wt% B_2O_3, and haplogranite + 8.92 wt% B_2O_3 have been performed using the concentric cylinder and micropenetration methods. The viscosity of a B-enriched natural rhyolite obsidian, macusanite from Macusani, Peru, has also been determined.

The viscosity of haplogranite liquid decreases with the addition of B_2O_3 at all temperatures investigated. The viscosity decrease is nonlinear, with the strongest decrease exhibited at low B_2O_3 concentration. The temperature dependence of the viscosity of all the investigated liquids is Arrhenian, in strong contrast to the case for B_2O_3 liquid. The Arrhenian activation energy is much lower in the B_2O_3-bearing liquids than in the B_2O_3-free haplogranite, with the result that the effect of B_2O_3 on viscosity is a strong function of temperature. At temperatures corresponding to the crystallization of B-rich granitic and pegmatitic systems the addition of 1 wt% of B_2O_3 decreases the viscosity 2 orders of magnitude. The macusanite liquid exhibits a reduced viscosity compared with B-free rhyolite that is consistent with the synthetic liquid systematics. B must be considered as a fluxing agent in B-rich granitic and pegmatitic systems.

INTRODUCTION

The role of B in granitic petrogenesis has received increasing attention in recent years (Pichavant and Manning, 1984; London, 1987; Pichavant et al., 1987). Interest in the trace element geochemistry of B has also grown significantly recently because of advances in analytical methods for B_2O_3 in rocks and minerals (e.g., Troll and Saurer, 1985). More remarkable is the observation that certain granitic and pegmatitic systems can concentrate B up to 1 wt% (e.g., Pichavant and Manning, 1984). London (1987) reconstructs the content of a crystallized inclusion in spodumene to obtain 12 wt% B_2O_3 for the Tanco pegmatite. Experimental investigations of B-bearing igneous systems have probed the equilibrium phase assemblages of the *P-T-X* regime of B-rich petrogenesis (Chorlton and Martin, 1978; Pichavant, 1981, 1987; Bernard et al., 1985; London et al., 1988, 1989) but not the physical properties of such systems. The effect of B on the physical properties of glass melts is of great industrial importance, and borate and borosilicate melts have been extensively investigated (e.g., Scholze, 1988). In particular, the viscosity of borosilicate melts is much lower than that of stoichiometrically equivalent ferro-, gallio-, or aluminosilicate liquids (Dingwell and Virgo, 1988; Dingwell, 1990) and Pichavant (1987) has suggested that B_2O_3 will significantly reduce haplogranitic melt viscosity.

We have begun some studies of the effect of B on the properties of haplogranitic melts in order to constrain models for the petrogenesis of B-rich granites and pegmatites (Holtz and Dingwell, 1991; Allé et al., 1991; Knoche et al., 1991; this study). Here we report our determination of the effect of B_2O_3 on the viscosity of haplogranitic liquids.

METHODS

Starting materials for the preparation of B-bearing samples were Na_2CO_3, K_2CO_3, Al_2O_3, SiO_2, and H_3BO_3. The powders of the starting reagents were dried at 120 °C overnight prior to weighing except for the H_3BO_3, which was weighed immediately after opening the airtight seal on the original packing. Batches of powders each 100 g (decarbonated, dehydrated-equivalent) were weighed directly into plastic bottles and mixed by agitation for 5–10 min. The starting compositions were chosen to represent 5 and 10 wt% additions of B_2O_3 to a haplogranite composition (designated HPG8), near the 1-kbar (pH_2O) ternary minimum composition in the system SiO_2-$NaAlSi_3O_8$-$KAlSi_3O_8$-H_2O. The HPG8 glass is taken from Holtz et al. (1992). The macusanite starting material was a glass cobble of the same provenance and composition as samples JV1 and JV2 of Pichavant et al. (1987). The B-bearing haplogranitic compositions and macusanite

TABLE 1A. Haplogranite analyses (wt%)

Composition	Na_2O	K_2O	Al_2O_3	SiO_2	B_2O_3	Total
HPG8	4.53	4.17	11.89	77.90	—	98.48
	4.60	4.23	12.07	79.10	—	100.00
HPG8B5	4.66	3.92	11.79	75.18	4.35	99.90
	4.88	4.10	12.33	78.68		100.00
HPG8B10	4.23(3)	3.955(7)	11.6(1)	71.07(4)	8.92(9)	99.78
	4.66	4.35	12.77	78.22		100.00

Note: Analyses by methods described in Pichavant et al. (1987) performed at CRPG-CNRS Nancy.

were fused directly for several hours at 1600 °C in 75 cm^3 thin-walled Pt crucibles using a $MoSi_2$ box furnace. The products of these fusions were bubble-rich. To eliminate the bubbles and promote full reaction and homogenization of the samples, the crucibles were transferred to a second $MoSi_2$ box furnace equipped with a concentric cylinder viscometer. The samples were heated to 1600 °C and stirred at 20, 50, or 100 rpm using a $Pt_{80}Rh_{20}$ spindle. The sample was inspected periodically by removing the spindle and checking the adhered melt. The bubble-free products of this process (determined by subsequent optical microscopic inspection) were cooled slowly in the viscometry furnace to less than 400 °C and removed to cool to room temperature. Cylinders (8-mm diameter) of the glasses were cored from the thin-walled crucibles. Some of these cylinders were sawed into disks 3–4 mm long and polished on both ends. The polished disks were stored in a desiccator until used in the micropenetration experiments. The remainder of the samples were broken from the crucibles with a hammer and stored until used in concentric cylinder experiments.

Samples of the glasses were analyzed by solution-based ICP-AES and electron microprobe methods. The results of the analyses are presented in Tables 1a and 1b. The samples lost approximately 10% of the added B_2O_3 during these fusions but remained close to the binary system, haplogranite-B_2O_3. The analyzed B_2O_3 contents are the basis for discussion of the results.

Low-temperature viscosities were determined using a micropenetration technique. This involves determining the rate at which a sphere under a fixed load moves into the melt surface. These measurements were performed in a Netzsch TMA 402 vertical silica-glass pushrod dilatometer. The sample is placed at the bottom of the sample holder with the indent sphere being held in place by a rod of SiO_2, which is attached to a weight pan. The metal connection between the silica glass rod and the weight pan acts as the core of a calibrated LVDT. The movement of this metal core as the sphere is pushed into the melt is converted into the displacement. The present system uses precision spheres of alumina with diameters of 3 mm (Frialit-Degussit), and a force of 1 N. The absolute shear viscosity is determined from

$$\eta = \frac{0.1875Pt}{r^{0.5}\alpha^{1.5}} \tag{1}$$

(Pocklington, 1940; Tobolsky and Taylor, 1963) for the radius of the sphere r, the applied force P, indent distance α, and time t ($t = 0$ and $\alpha = 0$ upon application of the force).

TABLE 1B. Macusanite analyses (wt%)

	After	Before
SiO_2	72.54(15)	72.70(32)
TiO_2	0.03(4)	0.09(17)
Al_2O_3	15.89(8)	16.00(18)
FeO	0.49(4)	0.53(7)
NiO	0.04(5)	0.06(14)
MgO	0.03(1)	0.03(2)
MnO	0.01(2)	0.08(6)
CaO	0.19(2)	0.21(4)
Na_2O	4.08(12)	4.07(6)
K_2O	3.56(14)	3.62(7)
Cr_2O_3	0.01(2)	0.01(4)
B_2O_3	0.44	0.53
Li_2O	0.72	0.74
F	1.05	1.34
Total	99.08	100.01

Note: Numbers in brackets are the standard errors on averages of microprobe analyses (number of analyses, after, $n = 5$; before, $n = 9$). Li_2O, B_2O_3, and F by methods reported in Pichavant et al. (1987).

The glass samples used are cylinders with diameters of 8 mm that are at least 3 mm thick. The measurements are performed over indentation distances of less than 100 μm, as Equation 1 is derived on the assumption that the indentation distance is much less than the radius of the indent sphere ($\alpha \ll r$). The technique has been calibrated against the viscosity of NBS711 lead silica glass over a viscosity range of 9–11 $\log_{10}$ Pa s, and the measured viscosities have an accuracy of ± 0.1 $\log_{10}$ Pa s. With sample sizes 3 mm thick, together with an indentation distance less than 100 μm and an indenter radius of 3 mm, no edge effects and no end effects were observed in this range of viscosities.

The concentric cylinder experiments were performed on the remainder of the batch melts that had been remelted into cylindrical viscometry crucibles and stirred to a bubble-free state. The shear viscosities of the liquids were determined using the concentric cylinder method at 1 atm in equilibrium with air.

The high-temperature viscosities were measured with a Brookfield HBTD head (full-scale torque = 5.75×10^{-1} N m) and rotation speeds of 0.5–50 rpm. This study used the crucible and low-viscosity spindle design of Dingwell and Virgo (1988). The furnace, viscometer assembly, and computer interface, as well as the operating method and calibration, are described by Dingwell (1989a, 1989b,

TABLE 2A. Shear viscosities ($\log_{10}$ dPa·s)

T (°C)	HPG8	HPG8B5	HPG8B10	Macu
1692	3.98	—	—	—
1643	4.24	—	—	—
1594	4.58	3.88	—	3.70
1544	4.81	4.13	—	3.94
1495	5.15	4.37	3.92	4.19
1446	5.53	4.68	4.14	4.45
1397	5.90	4.89	4.40	4.73
1348	—	5.19	4.72	5.03
1298	—	5.55	4.96	5.34
1249	—	5.89	5.29	5.67
1200	—	—	5.66	—
969.2	10.77	—	—	—
903.3	11.90	—	—	—
844.2	12.50	—	—	—
743.2	—	11.02	—	—
714.3	—	11.42	—	—
685.2	—	12.25	—	—
694.2	—	—	11.32	—
667.3	—	—	11.87	—
638.2	—	—	12.27	—

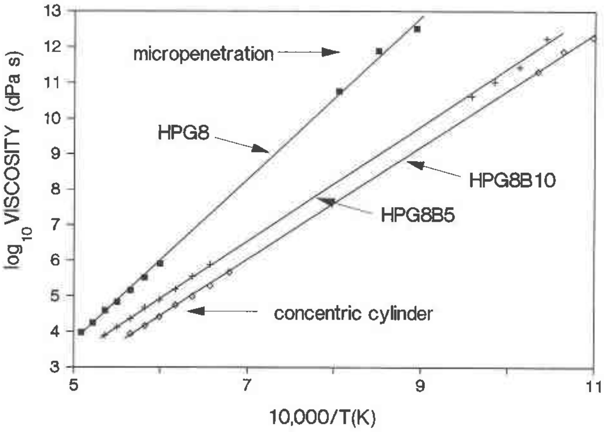

Fig. 1. The viscosity of haplogranite melts with added B_2O_3 determined using concentric cylinder and micropenetration methods.

1990). The viscosities measured are relative. The instrument has been calibrated most recently by standard glass DGG-1 available from the Deutsche Glastechnische Gesellschaft. The viscosity data are accurate to ±5% at 1 σ. Newtonian rheology was observed over the limited dynamic range of these measurements (approximately 0.3 $\log_{10}$ units). This result is consistent with the fact that the calculated relaxation times for shear in these liquids using the Maxwell approximation (Dingwell and Webb, 1989, 1990) and the Newtonian viscosity data from this study are several $\log_{10}$ units lower than the inverse of our experimental strain rates. We appear to be observing relaxed viscosities of a liquid.

After the viscometry was completed, each sample was removed from the furnace, cooled to room temperature, and drilled out of the crucible with diamond coring bits. The crucible was cleaned in HF and used for the next sample.

RESULTS AND DISCUSSION

The viscosity data for HPG8, HPG8B5, and HPG8B10 are presented in Table 2a. The temperature-dependent viscosities were regressed using an equation of the form

$$\log_{10}\eta = a + b/T \tag{2}$$

and the *a* and *b* parameters are included in Table 2b. The viscosity data from both micropenetration and concentric cylinder measurements can be described within error using Equation 2, as illustrated in Figure 1. The temperature dependence of viscosity yields an activation energy, *E* in the Arrhenius equation

$$\log_{10}\eta = \log_{10}\eta_0 + E/2.303\ RT. \tag{3}$$

The values of *E* derived from the regressions using Equation 3 range from 436 kJ/mol to 304 kJ/mol. The macusanite liquid viscosity data are included in Table 2a.

The viscosity-temperature data of the HPGB series are compared with liquid B_2O_3 data of Macedo and Napolitano (1968) in Figure 2. The curves differ qualitatively from one another. The B_2O_3 liquid exhibits a complex, strongly non-Arrhenian temperature dependence of viscosity. Macedo and Napolitano (1968) have used a Vogel-Fulcher-Tamann (VFT) form of equation to describe the temperature dependence of B_2O_3 viscosity but point out the existence of a high-temperature Arrhenian segment of the total viscosity-temperature curve. Part of the complexity involved in the B_2O_3 liquid structure may involve the presence of more than one coordination number for B (e.g., Johnson et al., 1982).

TABLE 2B. Fit parameters

Composition	*a*	*b* × 10⁴	*E* (kJ/mol)
HPG8	−7.69(12)	2.28(3)	436
HPG8B5	−4.70(8)	1.61(1)	308
HPG8B10	−5.11(5)	1.589(7)	304
Macu	−4.995(5)	1.624(4)	311

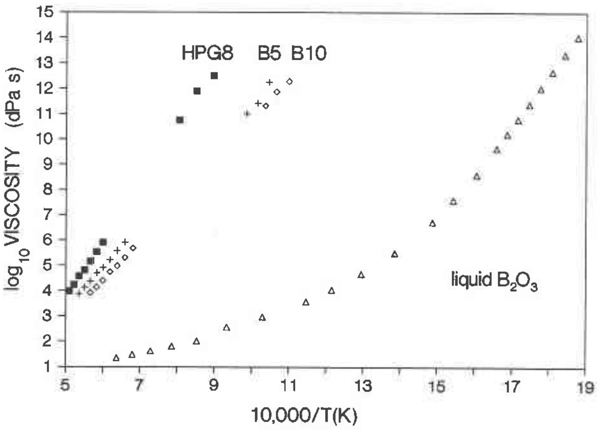

Fig. 2. Comparison of the viscosity-temperature relationship of haplogranite + B_2O_3 with that of B_2O_3 liquid.

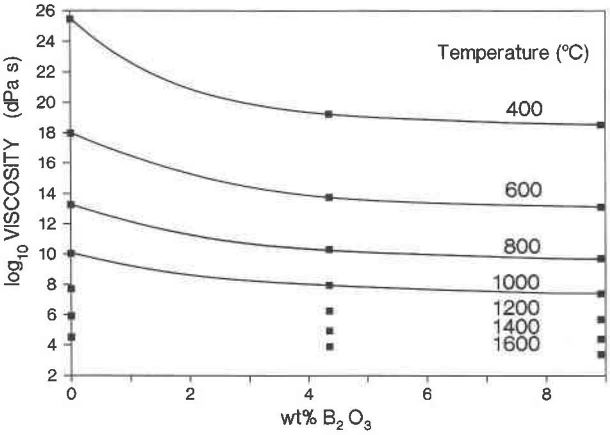

Fig. 3. The effect of B_2O_3 addition on the viscosity of haplogranite melts. Isotherms drawn at 200 °C intervals.

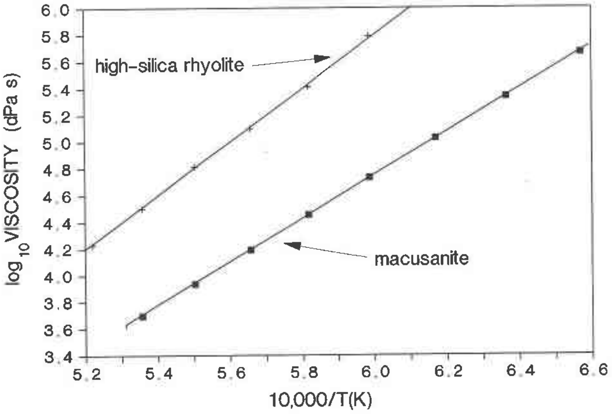

Fig. 4. Comparison of the viscosities of LGM rhyolite and macusanite melts.

The effect of B_2O_3 on the viscosity of haplogranite melt is represented as a series of isotherms in Figure 3. The effect of B_2O_3 on viscosity increases strongly with decreasing temperature. At 600 °C the addition of 1 wt% of B_2O_3 to haplogranite reduces viscosity by 2 orders of magnitude. The reduction in viscosity accompanying the addition of B_2O_3 to haplogranite can be compared with the measured viscosity decreases resulting from the addition of Li_2O, Na_2O, K_2O, and F_2O_{-1} to albite melt (Dingwell, 1987; and unpublished data). The effect of B_2O_3 on the viscosity of haplogranite at 1200 °C is much less than the viscosity reduction caused by these other, depolymerizing components. The effect of excess Al_2O_3 on albite and jadeite melt viscosity has been measured by Riebling (1966) and Hunold and Brückner (1979). Comparison of their data indicates that the viscosity reduction accompanying the exchange of Al_2O_3 for Na_2O at jadeite composition is less than observed here for B_2O_3.

The viscosity-temperature relationship of the macusanite is compared in Figure 4 with that of a high silica rhyolite (Neuville et al., 1991). The macusanite exhibits a reduced viscosity that probably results from a combination of several compositional effects, including high Li_2O, F, and B_2O_3 contents, as well as lower SiO_2 content. These data indicate that the macusanite will have a strongly reduced viscosity at the lower temperatures relevant to its petrogenesis.

CONCLUSION

The viscosity-reducing effect of B_2O_3 will be significant in granitic and pegmatitic melts containing 0.5–1.0 wt% B_2O_3. Further, the effect of B_2O_3 in increasing the solubility of H_2O in haplogranitic and pegmatitic melts (London et al., 1988; Holtz and Dingwell, 1991) will indirectly reduce the viscosity of H_2O-saturated melts.

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