

The effect of B₂O₃ on the viscosity of haplogranitic liquids

D. B. DINGWELL, R. KNOCHE, S. L. WEBB

Bayerisches Geoinstitut, Universität Bayreuth, Postfach 10 12 51, W8580 Bayreuth, Germany

M. PICHAVANT

Centre National de la Recherche Scientifique, Centre de Recherche sur la Synthèse et Chimie des Minéraux,
1a, rue de la Férollerie, 45071 Orléans Cedex 2, France

ABSTRACT

The effect of B₂O₃ on the viscosity of a haplogranitic liquid (K₂O-Na₂O-Al₂O₃-SiO₂) has been determined at 1 atm pressure in the temperature interval of 600–1600 °C. Viscosity measurements of a haplogranite, haplogranite + 4.35 wt% B₂O₃, and haplogranite + 8.92 wt% B₂O₃ 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 B₂O₃ at all temperatures investigated. The viscosity decrease is nonlinear, with the strongest decrease exhibited at low B₂O₃ concentration. The temperature dependence of the viscosity of all the investigated liquids is Arrhenian, in strong contrast to the case for B₂O₃ liquid. The Arrhenian activation energy is much lower in the B₂O₃-bearing liquids than in the B₂O₃-free haplogranite, with the result that the effect of B₂O₃ 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 B₂O₃ 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 B₂O₃ 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% B₂O₃ 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 B₂O₃ 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 B₂O₃ on the viscosity of haplogranitic liquids.

METHODS

Starting materials for the preparation of B-bearing samples were Na₂CO₃, K₂CO₃, Al₂O₃, SiO₂, and H₃BO₃. The powders of the starting reagents were dried at 120 °C overnight prior to weighing except for the H₃BO₃, 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 B₂O₃ to a haplogranite composition (designated HPG8), near the 1-kbar (pH₂O) ternary minimum composition in the system SiO₂-NaAlSi₃O₈-KAlSi₃O₈-H₂O. 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 ₂ O	K ₂ O	Al ₂ O ₃	SiO ₂	B ₂ O 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 cm³ thin-walled Pt crucibles using a MoSi₂ 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 MoSi₂ 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 Pt₈₀Rh₂₀ 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 B₂O₃ during these fusions but remained close to the binary system, haplogranite-B₂O₃. The analyzed B₂O₃ contents are the basis for discussion of the results.

Low-temperature viscosities were determined using a

TABLE 1B. Macusanite analyses (wt%)

	After	Before
SiO ₂	72.54(15)	72.70(32)
TiO ₂	0.03(4)	0.09(17)
Al ₂ O 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 ₂ O	4.08(12)	4.07(6)
K ₂ O	3.56(14)	3.62(7)
Cr ₂ O ₃	0.01(2)	0.01(4)
B ₂ O ₃	0.44	0.53
Li ₂ O	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). Li₂O, B₂O₃, and F by methods reported in Pichavant et al. (1987).

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 SiO₂, 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

$$\eta = \frac{0.1875Pt}{r^{0.5}\alpha^{1.5}} \quad (1)$$

(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 α = 0 upon application of the force).

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 μ m, 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 log₁₀ Pa s, and the measured viscosities have an accuracy of ± 0.1 log₁₀ Pa s. With sample sizes 3 mm thick, together with an indentation distance less than 100 μ m 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	—

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 $\pm 5\%$ at 1σ . 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

$$\log_{10}\eta = a + b/T \quad (2)$$

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 temper-

TABLE 2B. Fit parameters

Composition	a	$b \times 10^4$	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

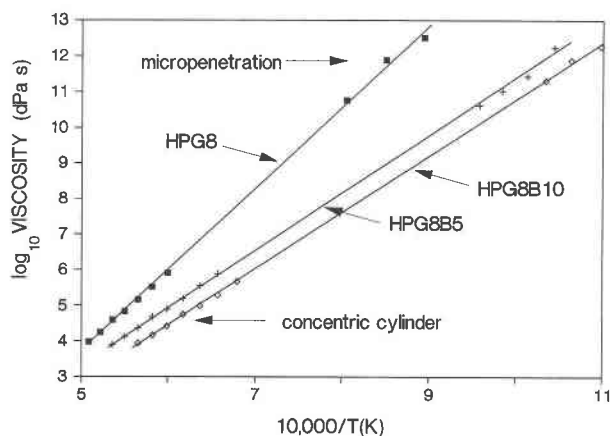


Fig. 1. The viscosity of haplogranite melts with added B_2O_3 determined using concentric cylinder and micropenetration methods.

ature dependence of viscosity yields an activation energy, E in the Arrhenius equation

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

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 HPG8 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).

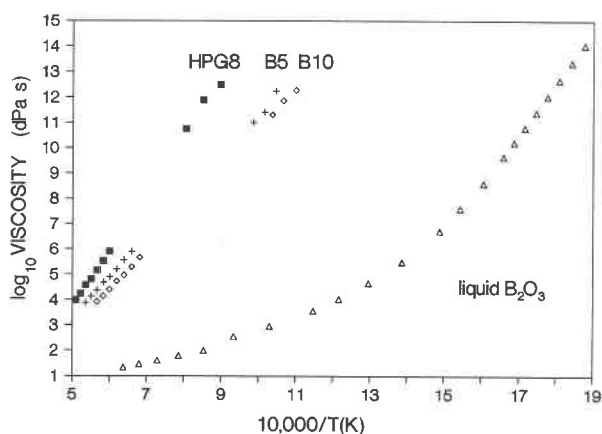


Fig. 2. Comparison of the viscosity-temperature relationship of haplogranite + B_2O_3 with that of B_2O_3 liquid.

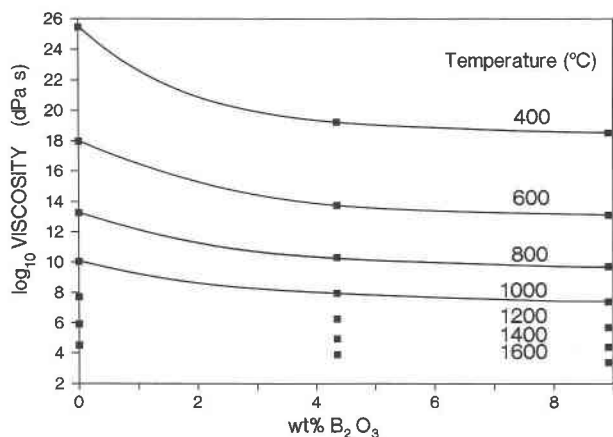


Fig. 3. The effect of B_2O_3 addition on the viscosity of haplogranite melts. Isotherms drawn at 200 °C intervals.

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.

ACKNOWLEDGMENTS

Francois Holtz is thanked for supplying some of the chemical analyses. Dave London and Frank Spera are thanked for helpful reviews.

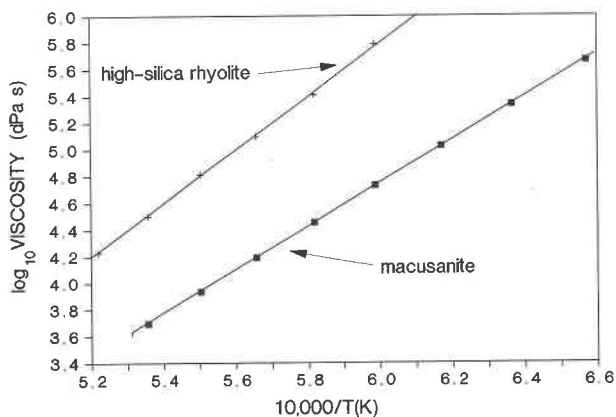


Fig. 4. Comparison of the viscosities of LGM rhyolite and macusanite melts.

REFERENCES CITED

- Allé, P., Chaussidon, M., Chakraborty, S., and Dingwell, D.B. (1991) Experimental determination of chemical diffusivity in haplogranitic melts. *Eos*, 72, 533.
- Bernard, F., Moutou, P., and Pichavant, M. (1985) Phase relations of tourmaline leucogranites and the significance of tourmaline in silicic magmas. *Journal of Geology*, 93, 271–291.
- Chorlton, L., and Martin, R.F. (1978) The effect of boron on the granite solidus. *Canadian Mineralogist*, 16, 239–244.
- Dingwell, D.B. (1987) Melt viscosities in the system $NaAlSi_3O_8-H_2O-F_2O_{-1}$. *Geochemical Society Special Publication*, 1, 423–433.
- (1989a) The effect of fluorine on the viscosity of diopside melt. *American Mineralogist*, 74, 333–338.
- (1989b) Shear viscosities of ferrosilicate liquids. *American Mineralogist*, 74, 1038–1044.
- (1990) Shear viscosities of galliosilicate liquids. *American Mineralogist*, 75, 1231–1237.
- Dingwell, D.B., and Virgo, D. (1988) Melt viscosities in the $Na_2O-FeO-Fe_2O_3-SiO_2$ system and factors controlling the relative viscosities of fully polymerized silicate melts. *Geochimica et Cosmochimica Acta*, 52, 395–403.
- Dingwell, D.B., and Webb, S.L. (1989) Structural relaxation in silicate melts and the onset of non-Newtonian melt rheology in geologic processes. *Physics and Chemistry of Minerals*, 16, 508–516.
- (1990) Relaxation in silicate melts. *European Journal of Mineralogy*, 2, 427–449.
- Holtz, F., and Dingwell, D.B. (1991) Water solubility in boron-rich silicate melts. *Eos*, 72, 533.
- Holtz, F., Behrens, H., Dingwell, D.B., and Taylor, R.P. (1992) Water solubility in aluminosilicate melts of haplogranitic compositions at 2 kbar. *Chemical Geology*, in press.
- Hunold, V.K., and Brückner, R. (1979) Physikalische Eigenschaften und struktureller Feinbau von Natrium-Aluminosilikatgläsern und -Schmelzen. *Glastechnische Berichte*, 53, 149–161.
- Johnson, P.A.V., Wright, A.C., and Sinclair, R.N. (1982) A neutron diffraction investigation of the structure of vitreous boron trioxide. *Journal of Non-Crystalline Solids*, 50, 281–311.
- Knoche, R., Webb, S.L., and Dingwell, D.B. (1991) A partial molar volume for B_2O_3 in haplogranitic melts. *Eos*, 72, 533.
- London, D.L. (1987) Internal differentiation of rare-element pegmatites: Effects of boron, phosphorus and fluorine. *Geochimica et Cosmochimica Acta*, 51, 403–420.
- London, D.L., Hervig, R.L., and Morgan, G.B., VI (1988) Melt-vapor solubilities and elemental partitioning in peraluminous granite-pegmatite systems: Experimental results with Macusani glass at 200 MPa. *Contributions to Mineralogy and Petrology*, 99, 360–373.
- London, D.L., Morgan, G.B., VI, and Hervig, R.L. (1989) Vapor-undersaturated experiments with Macusani glass + H_2O at 200 MPa, and

- the internal differentiation of granitic pegmatites. *Contributions to Mineralogy and Petrology*, 102, 1–17.
- Macedo, P.B., and Napolitano, A. (1968) Inadequacies of viscosity theories for B_2O_3 . *Journal of Chemical Physics*, 49, 1887–1895.
- Neuville, D., Courtial, P., Dingwell, D.B., and Richet, P. (1991) Viscosity and thermodynamic properties of rhyolite and andesite melts. *Terra Abstracts*, 3, 417.
- Pichavant, M. (1981) An experimental study of the effect of boron on a water saturated haplogranite at 1 kbar vapour pressure. *Contributions to Mineralogy and Petrology*, 76, 430–439.
- (1987) Effects of B and H_2O on liquidus phase relations in the haplogranite system at 1 kbar. *American Mineralogist*, 72, 1056–1070.
- Pichavant, M., and Manning, D.A.C. (1984) Petrogenesis of tourmaline granites and topaz granites; the contribution of experimental data. *Physics of the Earth and Planetary Interiors*, 35, 31–50.
- Pichavant, M., Valencia Herrera, J., Boulmier, S., Briquieu, L., Joron, J.-L., Juteau, M., Marin, L., Michard, A., Sheppard, S.M.F., Treuil, M., and Vernet, M. (1987) The Macusani glasses, SE Peru: Evidence of chemical fractionation in peraluminous magmas. *Geochemical Society Special Publication*, 1, 359–373.
- Pocklington, H.C. (1940) Rough measurement of high viscosities. *Proceedings of the Cambridge Philosophical Society*, 36, 507–508.
- Riebling, E.F. (1966) Structure of sodium aluminosilicate melts containing at least 50 mole% SiO_2 at 1500 °C. *Journal of Chemical Physics*, 44, 2857–2865.
- Scholze, H. (1988) *Glas: Struktur und Eigenschaften*, 407 p. Springer, New York.
- Tobolsky, A.V., and Taylor, R.B. (1963) Viscoelastic properties of a simple organic glass. *Journal of Physical Chemistry*, 67, 2439–2442.
- Troll, G., and Saurer, A. (1985) Determination of trace amounts of boron in geological samples with carminic acid after extraction with 2-ethylhexane-1,3-diol. *Analyst*, 110, 283–286.

MANUSCRIPT RECEIVED SEPTEMBER 27, 1991

MANUSCRIPT ACCEPTED JANUARY 9, 1992