A PARTIAL MOLAR VOLUME FOR B_2O_3 IN HAPLOGRANITIC MELT

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ABSTRACT

The densities and thermal expansivities of boron-bearing haplogranitic glasses and liquids have been determined using a combination of scanning calorimetry and dilatometry. B_2O_3 reduces the density of haplogranitic liquids (at 750°C) from 2.295 ± 0.006 g cm^{-3} to 2.237 ± 0.005 g cm^{-3} with the addition of 8.92 wt. % B_2O_3. These densities have been converted into molar volumes in the binary system haplogranite – B_2O_3. The partial molar volume of B_2O_3, calculated from a linear fit to the data at 750°C, is 40.30 ± 0.77 cm^3 mole^{-1} in these melts. This value compares with a molar volume of pure B_2O_3 at this temperature of 44.36 ± 0.22 cm^3 mole^{-1} (Napolitano *et al.* 1965), indicating a negative excess volume of mixing along the haplogranite – B_2O_3 join. In comparison, at 1300°C, the addition of Na_2O to B_2O_3 reduces the partial molar volume of B_2O_3 from 46.6 to 32.3 cm^3 mole^{-1} at 45 mole% Na_2O (Riebling 1966). The density results reported here, along with the viscosity-reducing effect of B_2O_3 on granitic melts (Dingwell *et al.* 1992), should both significantly accelerate processes of crystal–melt fractionation and facilitate the evolution of extremely fractionated igneous systems.

Keywords: B_2O_3, density, molar volume, haplogranite, silicate melt.

SOMMAIRE

Nous avons déterminé la densité et l'expansivité thermique de verres et liquides haplogranitiques borifères au moyen de calorimétrie à balayage et de mesures dilatométriques. L'addition de 8.92% par poids de B_2O_3 réduit la densité d'un liquide haplogranitique (à 750°C) de 2.295 ± 0.006 g cm^{-3} à 2.237 ± 0.005 g cm^{-3}. Les valeurs de densité ont été transformées en volumes molaires dans le système "binaire" haplogranite-B_2O_3. Le volume partiel molaire de B_2O_3, calculé à partir d'une dépendance linéaire des données à 750°C, est 40.30 ± 0.77 cm^3 mole^{-1} dans ces bains fondus. Cette valeur est inférieure au volume molaire du B_2O_3 pur à cette température, 44.36 ± 0.22 cm^3 mole^{-1} (Napolitano *et al.* 1965), et démontre un excès négatif de volume de mélange dans le système haplogranite-B_2O_3. Par contre, à 1300°C, l'addition de Na_2O au B_2O_3 réduit le volume partiel molaire du B_2O_3 de 46.6 à 32.3 cm^3 mole^{-1} pour une composition contenant 45% de Na_2O (Riebling 1966). Ces résultats, ainsi que la réduction de la viscosité des liquides granitiques due au bore (Dingwell *et al.* 1992), démontrent que le processus de fractionnement de cristaux du liquide devrait en être accéléré, pour ainsi faciliter l'évolution pétrogénétique dans ces systèmes fortement évolués.

(Traduit par la Rédaction)

Mots-clés: B_2O_3, densité, volume molaire, haplogranite, bain fondu silicaté.

INTRODUCTION

The role of boron in the petrogenesis of granitic rocks has received increasing attention in recent years (Pichavant *et al.* 1987, London 1987). It has been observed that some natural granitic and pegmatitic systems concentrate boron up to 1 wt.% (Černý 1982, Pichavant & Manning 1984). In some extreme cases, up to 12 wt% B_2O_3 have been observed (London 1986). A number of experimental investigations of boron-bearing igneous systems have probed chemical effects of B_2O_3 added to granitic melts. Specifically, the equilibrium phase assemblages of the P–T–*X* regime of boron-rich petrogenesis (Chorlton & Martin 1978, Pichavant 1981, Benard *et al.* 1985, London *et al.* 1988, 1989)

have been determined. In contrast, although the effect of boron on the physical properties of melts is of great industrial importance (*e.g.*, Scholze 1988), little is known about the physical properties of geologically relevant compositions. (There is a similar paucity of data for the effects of F, P, H_2O, Ta, Nb, *etc.*). This situation is particularly unfortunate for those interested in the physical evolution of granitic pegmatites at the magmatic or hydrothermal stage. We present a new method for the direct determination of highly precise data on volume and thermal expansivity of haplogranitic melts at magmatic temperatures.

The density of silicate melts during rock-forming processes is a critical factor in the efficiency of crystal–melt fractionation. Accordingly, the ex-

perimental determination of melt densities has been the subject of considerable investigation in the geological sciences (see summary to 1970 by Bottinga & Weill 1970; also, Mo *et al.* 1982, Lange & Carmichael 1987, Dingwell *et al.* 1988). These investigations have been conducted at low viscosities in the superliquidus regime, and thus in the absence of crystals. Processes operating during the petrogenesis of granites and pegmatites, however, occur at temperatures that are much lower than those employed in laboratory measurements of melt densities using traditional techniques. Extrapolation of experimentally determined models of the density of melts to temperatures of geological interest is complicated by the relatively large uncertainty in data on the thermal expansivity of silicate melts.

Under appropriate conditions of cooling, crystallization can be avoided, even at subsolidus temperatures, and glasses can be formed from silicate melts. The physical properties of these frozen liquids can then be investigated, just above the glass transition, as true supercooled liquids [*i.e.*, in metastable (or local) equilibrium] at temperatures and time-scales that preclude significant crystallization or liquid–liquid unmixing. Use of data on these low-temperature metastable liquids in combination with data for superliquidus melts provides a wide range in temperature over which the physical behavior of liquids can be described.

We have, therefore, begun to study the effect of boron on the physical properties of haplogranitic melts in the temperature range of geological interest, in order to construct better models for the petrogenesis of boron-rich granites and pegmatites (Holtz & Dingwell 1991, Allé *et al.* 1991, Dingwell *et al.* 1992). The present method of determining densities and thermal expansivities has several advantages over previous techniques. The molar volumes and expansivities are more precise than higher-temperature determinations using the already precise double-bob Archimedean method. The technique is applied at low temperatures and high viscosities inaccessible with other methods. These low-temperature and high-viscosity conditions preclude the loss of volatiles from the melt; therefore, we can obtain volume information that is otherwise nonexistent. The coefficient of thermal expansion is determined directly and does not incorporate errors of density determinations.

METHODS

Two boron-bearing samples were prepared from powders of Na_2CO_3, K_2CO_3, Al_2O_3, SiO_2 and H_3BO_3. The reagents were dried for 24 hrs at 120°C before being weighed into plastic bottles and mixed by agitation for 5–10 minutes. The H_3BO_3 was weighed immediately after opening the air-tight seal on the original packing. The starting compositions were chosen to represent 5 and 10 wt% additions of B_2O_3 to haplogranite HPG8 composition. The HPG8 glass is taken from Holtz *et al.* (1992); its composition is near that of the pseudoternary minimum at 1 kbar $P(H_2O)$ in the system $SiO_2 - NaAlSi_3O_8 - KAlSi_3O_8 - H_2O$. The boron-bearing haplogranitic compositions were fused directly in 100-g batches for 2 hours at 1600°C in 75-cm³ thin-walled platinum crucibles in a $MoSi_2$ box furnace. The products of these fusions had not fully reacted and were found to be bubble-rich. To 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 for ~24 hours using a $Pt_{80}Rh_{20}$ spindle. The melt was inspected periodically by removing the spindle and checking the adhered glass. The resulting crystal- and bubble-free products were cooled slowly in the viscometry furnace to 400°C and removed to cool to room temperature. Cylinders (8 mm diameter) of the glass samples were cored from the crucibles. These cylinders were prepared with parallel, polished ends and stored in a desiccator until use in the dilatometry and calorimetry experiments.

Samples of the glasses were analyzed by solution-based ICP–AES and electron-microprobe methods. The results of the analyses are presented in Table 1. The amounts of B_2O_3 in the glasses determined by analysis are within error of the intended starting compositions. The proportions of B_2O_3 determined by analysis are the basis for discussion of the results.

A combination of dilatometry and calorimetry measurements is used to determine the thermal expansivity and volume of the supercooled liquids at temperatures just above the glass transition. The

TABLE 1. GLASS COMPOSITIONS IN THE HPG8-B$_2$O$_3$ BINARY (wt%)

Composition	Na$_2$O	K$_2$O	Al$_2$O$_3$	SiO$_2$	B$_2$O$_3$	total
HPG8	4.53(5)	4.17(6)	11.89(7)	77.90(21)	-	98.48[1]
	4.60	4.23	12.07	79.10	-	100.00†
HPG8B5	4.66	3.92	11.79	75.18	4.35	99.90[2]
	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[3]
	4.66	4.35	12.77	78.22	-	100.00†

[1] Analysis is average of 10 by electron microprobe. Cameca Camebax in wavelength dispersive mode using 10μm defocussed beam and 20 s count time (15 kV, 15 nA on brass). Standards: albite (Na,Al,Si) and orthoclase (K).

[2] Analysis by ICP-AES methods described in Pichavant et al. (1987) performed at CRPG-CNRS Nancy.

[3] Analyses by ICP-AES methods described in Pichavant et al. (1987) performed at CRPG-CNRS Nancy (average of 2, with errors in parentheses).

† Normalized to Na$_2$O + K$_2$O + Al$_2$O$_3$ + SiO$_2$ = 100

dilatometric and calorimetric measurements were performed on glass cylinders (8 mm diameter, 25 mm long) using methods identical to those described by Webb *et al.* (1992). The calorimetry was performed in continuous scanning mode using Setaram® HTC and DSC111 instruments. The heat flux was measured for a heating rate of 5°C min^{-1} on glasses that had been previously cooled from the relaxed state at rates of 1, 2, 5 and 10°C min^{-1}. The calorimeters were calibrated regularly against a geometrically identical cylinder of sapphire, using the heat capacity data of Robie *et al.* (1978). The heat capacities of glass and melt are estimated to have a precision of $\pm$ 2.5% at 1σ based on the four runs performed on each sample and the calibration of the calorimeters. The dilatometry was performed using a Netzsch® TMA 402 quartz-rod dilatometer. This instrument has been calibrated against sapphire (NBS sheet 732), and the molar expansivities have an accuracy of $\pm$ 3% at 1σ based on the four runs performed on each sample and the calibration of the dilatometer. The glass cylinders used in the dilatometry are those that were used in the calorimetry measurements. The scanning rates of the dilatometry measurements are identical to those of the calorimetry measurements.

The thermal histories of the glasses used in the calorimetry and dilatometry are the same, in that the glasses were cooled from the relaxed state (*i.e.*, from above the glass transition temperature) at rates of 1, 2, 5 and 10°C min^{-1}, and the measurements were performed at a heating rate of 5°C min^{-1}. The heat capacity and thermal expansion data for the 5/5 (heating-rate/cooling-rate) runs are listed in Table 2.

THEORY

The derivation of liquid expansivity and volume data from calorimetric and dilatometric measurements is based on the principles of structural relaxation in silicate melts. The more general aspects of structural relaxation in silicate melts and its influence on diffusion, viscosity, and density, have been discussed previously (Dingwell 1990, Dingwell & Webb 1989, 1990). The theory of our procedure for obtaining data on the molar expansivity of relaxed liquids from a combination of scanning calorimetry and dilatometry has been presented in full by Webb *et al.* (1992) and is reviewed here.

When a silicate glass is heated across the glass transition region, a time-dependent response of its physical properties occurs. The unrelaxed, "glassy" values of volume and enthalpy are replaced by equilibrium, "liquid" values over a finite period of time. Quantitative models of structural relaxation in melts have been constructed (Narayanaswamy 1971, Moynihan *et al.* 1976, Scherer 1984) to reproduce the details of the time-dependent response of melt properties in the glass transition interval. The models are completely general, describing the response of property Φ as a function of previous cooling-rate (from the relaxed state) and experimental heating-rate (from the unrelaxed state).

The physical properties of a silicate melt depend upon the ambient temperature T and the configuration or structure of the melt. Silicate glasses quenched from liquids preserve a configuration that can be approximated to the equilibrium structure of the liquid at some fictive temperature, T_f (Tool & Eichlin 1931). To describe, in general, the relaxed (liquid) or unrelaxed ("glassy") properties of a silicate melt, we need to specify the temperature and the fictive temperature of the melt.

TABLE 2. MEASURED HEAT CAPACITY AND THERMAL EXPANSIVITY

| Temperature	c_p			$\dfrac{dV}{dT}$		
(°C)	J g^{-1} °C^{-1}			10^{-4} cm^3 °C^{-1}		
	HPG8	HPG8B5	HPG8B10	HPG8	HPG8B5	HPG8B10
300		1.07	1.07	19.20	16.50	19.90
310		1.07	1.07'	18.90	18.90	19.78
320		1.08	1.08	19.00	18.92	18.91
330		1.08	1.09	19.20	18.88	19.87
340		1.09	1.09	19.60	18.78	18.79
350		1.09	1.10	18.40	18.35	19.70
360		1.10	1.10	18.20	17.99	16.52
370		1.10	1.11	18.40	18.74	18.44
380		1.11	1.12	18.60	19.00	18.97
390		1.12	1.12	18.30	18.46	19.41
400	1.11	1.12	1.13	18.80	18.61	18.63
410	1.11	1.12	1.13	18.30	18.90	19.62
420	1.12	1.12	1.13	18.70	18.07	22.06
430	1.12	1.13	1.14	17.80	18.21	19.43
440	1.12	1.13	1.14	18.30	18.05	17.28
450	1.13	1.13	1.14	18.30	18.25	18.99
460	1.12	1.14	1.15	17.90	18.10	18.78
470	1.12	1.14	1.15	17.40	18.35	22.57
480	1.12	1.15	1.15	17.90	19.07	14.14
490	1.13	1.15	1.16	17.05	18.12	18.29
500	1.13	1.15	1.16	16.80	18.05	17.75
510	1.13	1.16	1.16	17.50	18.58	17.80
520	1.13	1.16	1.17	16.06	18.99	16.58
530	1.13	1.17	1.17	17.80	18.93	19.79
540	1.13	1.17	1.17	16.54	18.69	16.59
550	1.13	1.18	1.18	16.74	18.31	20.28
560	1.13	1.18	1.19	17.09	18.04	20.79
570	1.14	1.18	1.20	16.80	17.77	23.09
580	1.15	1.19	1.22	17.31	18.32	26.04
590	1.15	1.19	1.23	17.06	17.74	28.83
600	1.15	1.19	1.25	17.04	18.42	36.20
610	1.15	1.20	1.27	16.27	19.77	47.01
620	1.15	1.20	1.29	16.35	21.11	54.59
630	1.15	1.21	1.31	16.00	25.29	63.34
640	1.15	1.22	1.33	14.06	31.75	80.07
650	1.15	1.24	1.34	17.56	38.69	73.86
660	1.15	1.26	1.33	15.92	46.90	65.42
670	1.15	1.29	1.32	16.57	57.66	50.79
680	1.16	1.31	1.32	16.42	64.62	51.29
690	1.15	1.33	1.31	16.81	64.04	46.51
700	1.16	1.33	1.31	16.43	61.27	41.41
710	1.16	1.33	1.31	14.83	56.21	40.50
720	1.16	1.32	1.31	16.22	52.95	34.31
730	1.17	1.31	1.30	15.46	48.73	34.53
740	1.17	1.31	1.30	16.26	46.97	31.28
750	1.16	1.31		17.29	42.57	23.88
760	1.15	1.31		14.24	41.45	20.22
770	1.16	1.32		19.07	40.22	16.60
780	1.16	1.32		17.88		
790	1.17			20.06		
800	1.19			23.06		
810	1.19			26.78		
820	1.21			31.24		
830	1.24			37.12		
840	1.25			40.46		
850	1.27			41.68		
860	1.27			40.97		
870	1.27			36.75		
880	1.26			34.29		
890	1.26			29.12		
900	1.27			26.18		
910	1.26			12.76		
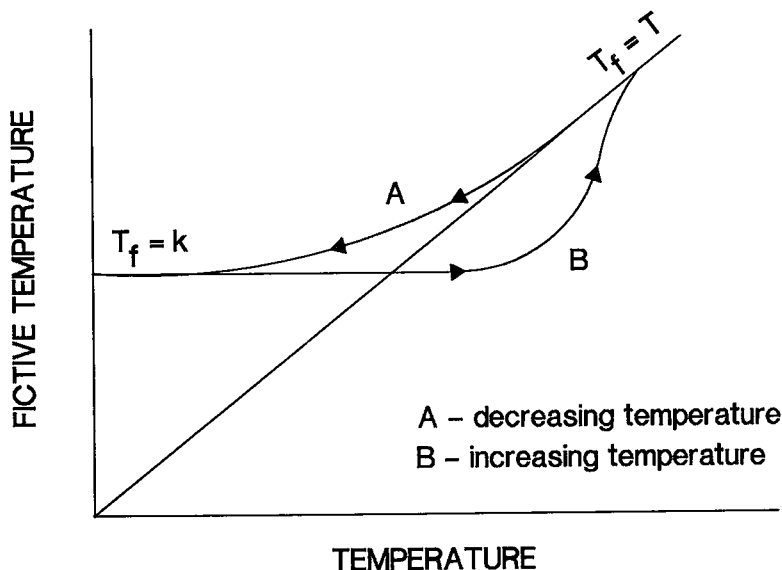
Fig. 1. The cooling (A) and heating (B) paths of a silicate melt in temperature-fictive temperature space.

For a liquid, the structure is in equilibrium, and thus T_f equals T (Fig. 1). Upon cooling of the liquid into the glass transition region, the structure of the melt begins to deviate from equilibrium, i.e., T_f deviates from T. This deviation ultimately results in a temperature independence of T_f at low temperatures corresponding to the frozen structure of the glassy state. Upon subsequent reheating through the glass transition interval, the value of T_f once again assumes that of T, and liquid values of melt properties are observed. The path of the value of the property taken during reheating is, however, different from that observed during cooling. Owing to the finite rate of equilibration available for relaxation at the onset of the glass transition region, there is an overshoot in the transient value of the melt property [i.e., the fictive temperature of the structure is lower than the temperature, $T_f < T$ (Dingwell & Webb 1990)].

The temperature derivative of the physical properties of a glass and a liquid [e.g., molar heat capacity (dH/dT) and molar thermal expansivity (dV/dT)] can be used to describe the temperature derivative of the fictive temperature. To do this, the temperature derivative of any property in the glass transition interval (e.g., enthalpy, volume) is normalized with respect to the temperature derivative of the liquid and "glassy" properties. This normalized temperature derivative, which is equal to dT_f/dT, must equal zero for the glass (T_f is constant) and 1 for the liquid (T_f equals T). The temperature derivative of the fictive temperature T_f at a temperature T' is related to the temperature dependence of a macroscopic property Φ by;

$$\frac{dT_f}{dT}\bigg|_{T'} = \frac{[(\delta\Phi/\delta T) - (\delta\Phi/\delta T)_g]|_{T'}}{[(\delta\Phi/\delta T)_e - (\delta\Phi/\delta T)_g]|_{T_f}} \quad (1)$$

where the subscripts e and g are for the liquid (equilibrium) and the "glassy" values of the property (Moynihan et al. 1976). It is thus necessary to devise an algorithm to describe the temperature dependence of the fictive temperature in order to describe the physical properties of a melt in the region of the glass transition.

In the present study, enthalpy H and volume V take the place of the general property Φ in Eqn. 1. Assuming the equivalence in behavior of volume and enthalpy relaxation for melts with identical thermal histories (Webb 1992), Eqn. 1 can then be rewritten as (Webb et al. 1992, Knoche et al. 1992):

$$\frac{dT_f}{dT}\bigg|_{T'} = \frac{c_p(T') - c_{pg}(T')}{c_{pe}(T_f) - c_{pg}(T_f)} = \frac{\dfrac{dV(T)}{dT} - \dfrac{dV_g(T)}{dT}\bigg|_{T'}}{\dfrac{dV_e(T)}{dT} - \dfrac{dV_g(T)}{dT}\bigg|_{T_f}} \quad (2)$$

In the above equation, which relates c_p and thermal expansivity dV/dT, the only unknown parameter
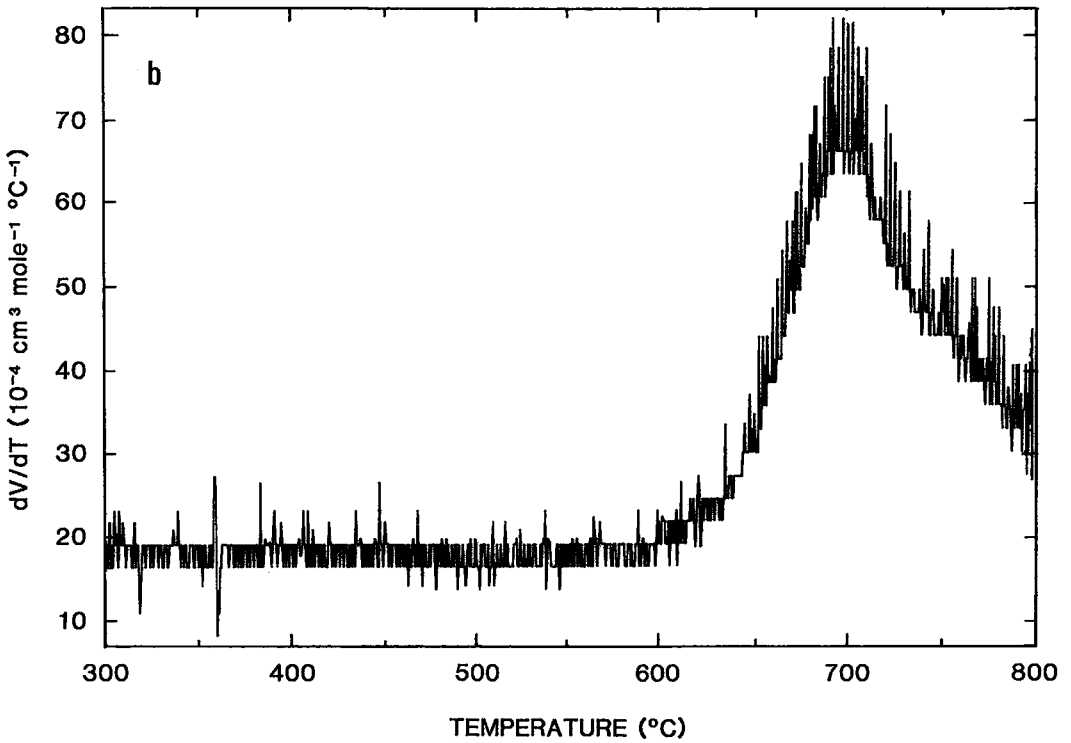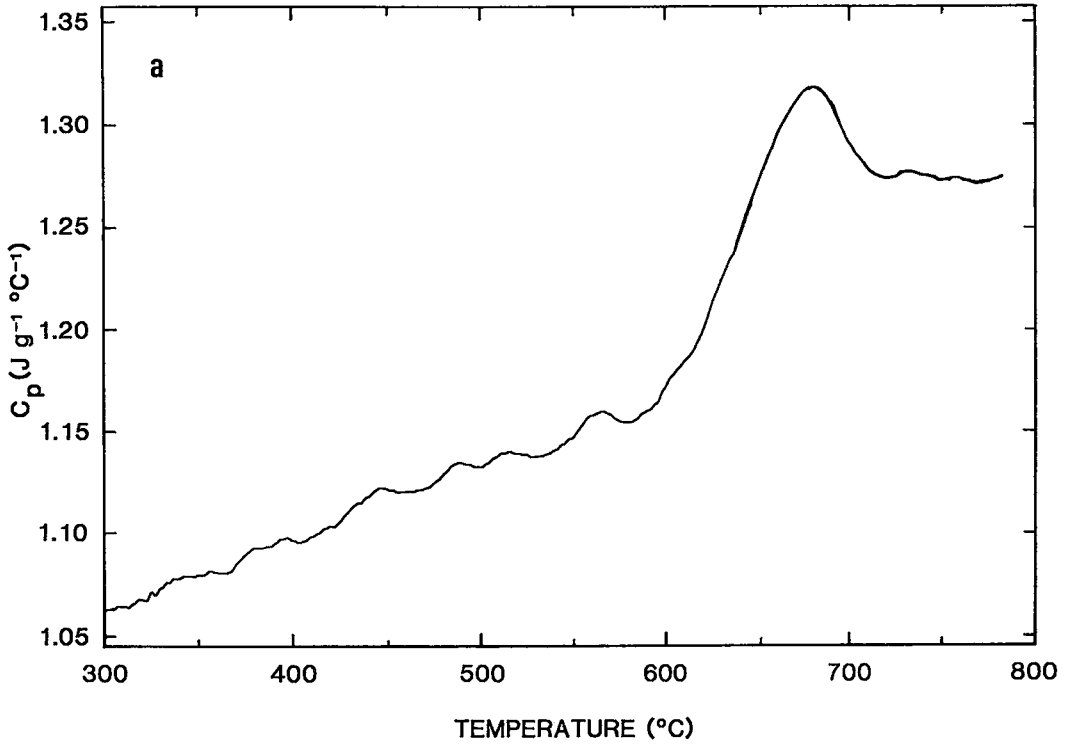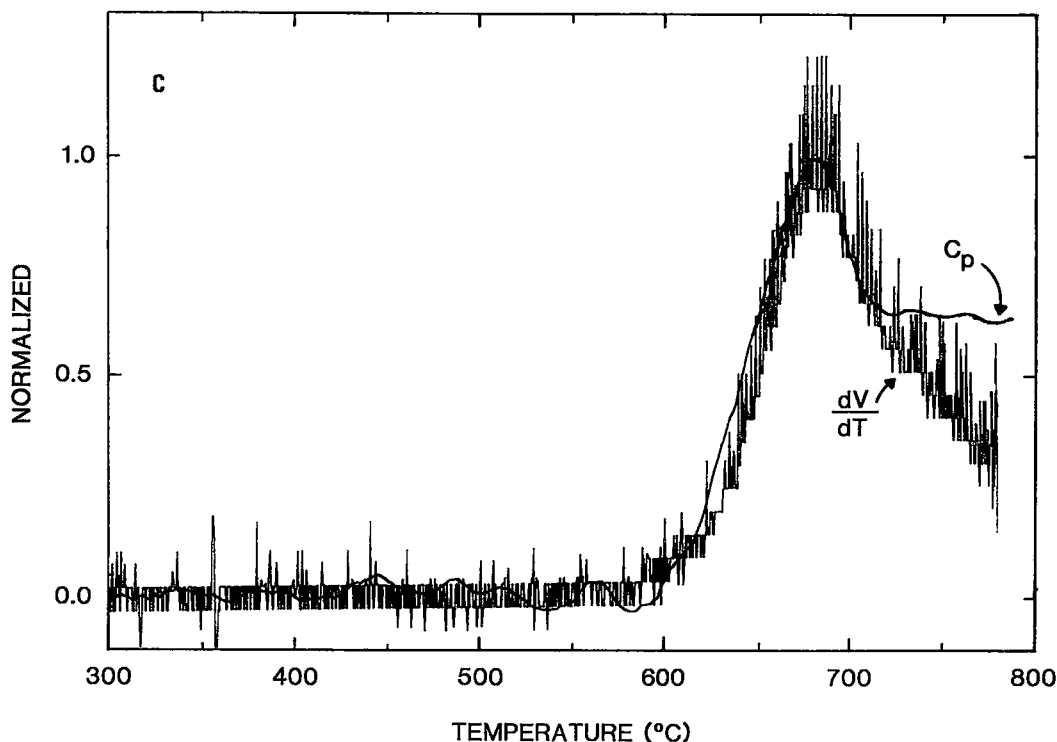
Fig. 2. a. A calorimetric trace of heat capacity for HPG8B5 for a heating rate of 5 K min^{-1}. The glass was quenched from the liquid at a rate of 2 K min^{-1}. b. A dilatometric trace of expansivity for HPG8B5 for a heating rate of 5 K min^{-1}. The glass was quenched from the liquid at a rate of 2 K min^{-1}. c. The normalized comparison of the dilatometric and calorimetric traces through the glass transition region.

is the thermal expansivity of the relaxed liquid at temperature T' in the glass transition interval.

Owing to the lack of data on relaxed thermal expansivity, we recover the molar thermal expansivity of the liquid from the dilatometric trace by normalizing both the scanning calorimetric and dilatometric data:

$$\Phi'(T) = \frac{\Phi(T) - \Phi_g(T)}{\Phi_p - \Phi_g(T)} \qquad (3)$$

where the subscripts p and g refer to peak and "glassy" values. The relaxed value of thermal expansivity can now be generated from the peak and extrapolated "glassy" values of thermal expansivity; the volume and coefficient of volume thermal expansion α_v [1/V(dV/dT)] of the melt can also be calculated.

We wish to stress that the above method can only be applied to calorimetric and dilatometric data obtained on the same sample using identical thermal histories and heating rates. It is only this internal consistency that permits the use of the assumption of the equivalence in behavior of the enthalpy and volume relaxation. Small changes in composition or fictive temperature of the melt can strongly influence relaxation behavior.

RESULTS AND DISCUSSION

Examples of the heat capacity and expansivity data are illustrated in Figures 2a and 2b. The density and data on the coefficient of volume thermal expansion for the HPG8, HPG8B5 and HPG8B10 melts are tabulated in Table 3. The data on room-temperature density were determined by immersion in toluene. B_2O_3 reduces the room-temperature (28°C) density of haplogranitic glasses, quenched from the melt at 5°C min^{-1}, from 2.316 ± 0.005 g cm^{-3} to 2.269 ± 0.005 g cm^{-3} with the addition of 8.92 wt.% B_2O_3, or approximately 0.2% per wt.% of B_2O_3. These densities have been converted into molar volumes based on the

TABLE 3. VOLUME AND COEFFICIENT (α_v) OF VOLUME THERMAL EXPANSION DATA FOR BORON-BEARING HAPLOGRANITIC MELTS

	HPG8	HPG8B5	HPG8B10
wt% B_2O_3	-	4.35	8.92
molar wt. haplogranite	64.35	64.61	65.00
mol. fraction B_2O_3	-	0.0404	0.0835
density (g cm^{-3}) (28°C)	2.316±0.005	2.299±0.005	2.269±0.005
density (g cm^{-3}) (750°C)	2.295±0.006	2.269±0.005	2.237±0.005
mol. volume (cm^3) (750°C)	28.039±0.076	28.476±0.055	29.057±0.059
α_v = dV/(VdT) (×10^{-6} °C^{-1})			
of glass	14.6±1.0 (730°C)	15.9±1.0 (580°C)	16.3±1.0 (530°C)
of liquid	29.9±3.0 (920°C)	47.0±3.0 (740°C)	49.1±3.0 (710°C)

errors are standard deviations propagated through the calculations

haplogranite and B_2O_3 components. The coefficient of volume thermal expansion of the glasses measured up to the glass transition increases with the addition of B_2O_3 from 14.6 ± 1.0 × 10^{-6}°C^{-1} to 16.3 ± 1.0 × 10^{-6}°C^{-1}. The liquid expansivities for the HPG8B5 and HPG8B10 have been derived using the normalization procedure outlined above. The expansivity of liquid HPG8 was difficult to determine from the dilatometry–calorimetry comparison owing to the small peak due to the glass transition. The expansivity of liquid HPG8 was

therefore estimated based on our results obtained across the glass transition for rhyolite, albite and other similar · compositions. The coefficient of volume thermal expansion of the liquids increases from 29.9 ± 3.0 × 10^{-6}°C^{-1} to 49.1 ± 3.0 × 10^{-6}°C^{-1} with the addition of 8.92 wt.% B_2O_3.

Our technique of normalization yields a completed dilatometric trace across the glass transition (Fig. 2c). We can use such a trace to integrate the volume change of the sample up to a temperature just above the glass transition. The integrated data on expansivity and the room-temperature data on molar volume yield the high-temperature molar volumes of the relaxed liquids at temperatures just above the glass transition for each composition. The comparison of these high-temperature molar volumes at a single temperature requires a correction using the liquid expansivities. This has been calculated for a temperature of 750°C. The calculated molar volumes and densities of the three melts at 750°C are presented in Table 3.

The molar volumes at 750°C are plotted in Figure 3 as a function of the mole fraction of B_2O_3. The data on molar volume have been regressed to the mole fractions of the haplogranite and B_2O_3 components (Table 4). Included in Figure 3 is the linear regression to the volume data and a line illustrating the volumes that would result from a partial molar volume of B_2O_3 equal to the molar volume of the pure liquid (44.36 cm^3 mole^{-1}: Napolitano et al. 1965). The standard error of the linear fit is comparable to our estimated experimen-
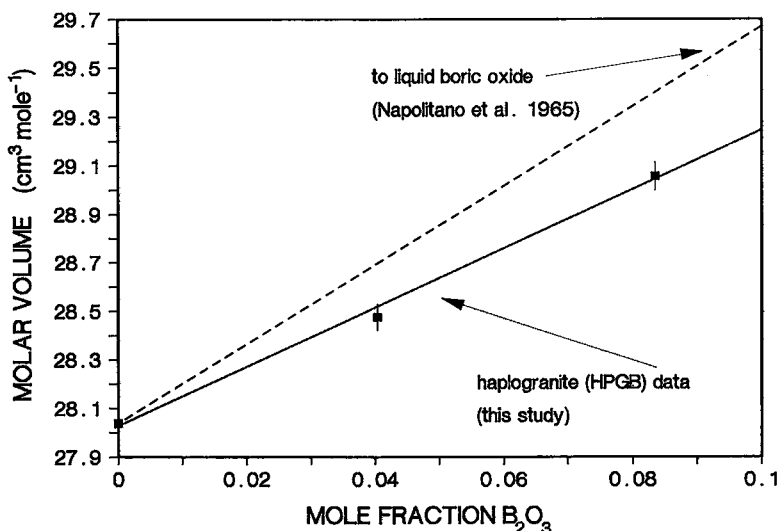

Fig. 3. Volume – composition relationship along the haplogranite – B_2O_3 join.

TABLE 4. FIT PARAMETERS FOR MOLAR VOLUMES OF HAPLOGRANITE AND B_2O_3 MELT AT 750°C

$V_{haplogranite}$	$V_{B_2O_3}$	V_{excess}	note
cm^3 mole^{-1}			
28.019±0.043	40.30 ±0.77	-	1
28.023±0.037	44.358±0.041	-4.44±0.73	2

1 fit to volumes of this study using a linear relation of volume
2 fit to data of this study and B_2O_3 data of Napolitano et al. (1965)
the standard errors in the fit are shown

tal uncertainties in molar volume. A partial molar volume of 44.36 cm^3 mole^{-1} for B_2O_3 is inconsistent with the quoted uncertainties of the measured volumes. For this reason, a second fit was performed on the volume data, including the volume of B_2O_3 liquid and a binary excess term. The results of this fit also are included in Table 4.

Riebling (1966) has determined that at a much higher temperature (1300°C), the partial molar volume of B_2O_3 undergoes a decrease from 46.6 to 32.3 cm^3 mole^{-1} with the addition of 45 mole% Na_2O. The data of this study are in qualitative agreement with that observation, i.e., a negative excess volume of mixing exists in both cases.

GEOLOGICAL IMPLICATIONS

A reduction in melt density will increase the density contrast between leucogranitic and pegmatite-forming melts and their equilibrium crystalline products. The decrease in melt density due to the addition of B_2O_3 will accelerate crystal–melt fractionation processes that rely on density contrast. The effect of B_2O_3 on liquid density is complemented by the strong reduction in viscosity associated with incorporation of B_2O_3. In the haplogranitic samples studied here, the relative decrease in viscosity due to the addition of B_2O_3 is found to increase with decreasing temperature (Dingwell et al. 1992). A third aspect of the effect of B_2O_3 on melt properties is the enhancement of water solubility in B_2O_3-bearing melts. London et al. (1988) have reported solubility of water for a macusanite composition, and Holtz & Dingwell (1991) have reported an increase in water solubility for the present series of haplogranitic melts with added B_2O_3. The increased solubility of water means that crystallizing pegmatitic systems that are driving toward water saturation will evolve much further in composition before water saturation is achieved or until a boron-bearing phase is stabilized. All three of these effects, decreased density,

decreased viscosity and increased solubility of water, should combine to extend the igneous stage of boron-rich granitic and pegmatitic systems to lower temperatures and more extreme chemical compositions.

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