Determination of silicate liquid thermal expansivity using dilatometry and calorimetry

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Abstract : A method for the determination of relaxed silicate liquid molar volume and expansivity at temperatures just above the glass transition is discussed. The method involves the comparison of heat capacity and molar expansivity in the glass transition region. Glassy and liquid heat-capacity data are obtained using differential scanning calorimetry, and glassy thermal expansion data are obtained using scanning dilatometry. The molar expansivity of the liquid is calculated by a fictive temperature normalization of the relaxation behavior of both the heat capacity and the molar expansivity in the glass transition region, with the normalized heat capacity curve being used to extend the dilatometric data into the liquid temperature range. This comparison is based upon the assumed equivalence of the parameters describing the relaxation of volume and enthalpy.

The molar expansivity of relaxed sodium trisilicate ($Na_2Si_3O_7$) has been determined in this manner at temperatures above the glass transition temperature. This low-temperature determination of liquid molar expansivity has been tested against high-temperature liquid expansivity data obtained from high temperature Pt double bob Archimedean buoyancy measurements. The low-temperature molar expansivity ($26.43 \pm 0.83 \times 10^{-4}$ cm^3 $mole^{-1}°C^{-1}$ at 540°C) determined in this manner agrees within error with the high-temperature molar expansivity ($23.29 \pm 1.39 \times 10^{-4}$ cm^3 $mole^{-1}°C^{-1}$ at 1400°C). This dilatometric/calorimetric method of liquid molar expansivity determination greatly increases the temperature range accessible for thermal expansion measurements. A weighted linear fit to the combined low and high temperature volume data gives a molar expansivity of $23.00 \pm 0.25 \times 10^{-4}$ cm^3 $mole^{-1}°C^{-1}$. The volume-temperature relationship thus derived reproduces the measured volumes from both dilatometry and densitometry with a RMSD value of 0.033 cm^3 $mole^{-1}$ or 0.14%. This represents a substantial increase in precision, which is especially important for liquids whose high liquidus temperatures restrict the temperature range accessible to liquid volume determinations.

Key-words : expansivity, dilatometry, calorimetry, relaxation.

1. Introduction

The thermal expansivity of silicate liquids is an important parameter in the calculation of melt densities over the wide range of temperatures relevant for magmatic processes (*e.g.*, Bottinga *et al.*, 1983). Expansivity data are also required as thermodynamic input for the calculation of physical properties such as derivation of melt compressibilities from fusion curves of minerals (*e.g.*, Bottinga, 1985 ; Herzberg, 1987). Thermal expansivity data are also necessary for the reduc-

tion of adiabatic wave velocity data to isothermal conditions (*e.g.*, Rivers & Carmichael, 1987). Accurate determinations of liquid expansivities are, however, hampered by experimental drawbacks which limit the precision of the data currently available. The uncertainties associated with thermal expansion of silicate liquids have been emphasized recently by Bottinga *et al.* (1983) and Herzberg (1987).

Two sources of thermal expansivity data are liquid density determinations by the double Pt bob Archimedean method and glassy data ob-

tained directly by scanning push-rod dilatometry. The high-temperature density measurements are often limited by restricted ranges of temperature accessible using the more common techniques. This temperature restriction can result from high liquidus temperatures or high superliquidus viscosities. Either results in a large uncertainty in expansivity. An example is provided by the system Na_2O-SiO_2 where, with increasing silica content, the combination of decreasing accessible temperatures and decreasing expansivities results in errors of up to several hundred percent (*e.g.* Bockris *et al.*, 1956). Bottinga *et al.* (1983) review the thermal expansivity data available for the Na_2O-SiO_2 system and conclude that the agreement between different experimental determinations of thermal expansivities at moderate silica contents is not better than ±40%. Multicomponent modeling of liquid densities yields thermal expansivities of partial molar volumes with uncertainties up to ±100% (Lange & Carmichael, 1987).

Dilatometric measurements of expansivity include the effects of significant viscous deformation due to gravitational body forces as the sample is heated through the glass transition (*e.g.*, Tool & Eichlin, 1931). This viscous deformation precludes the direct measurement of relaxed, liquid thermal expansivity. The use of dilatometric data on silicate melts to predict liquid expansivities requires a method for removing this deformation from the dilatometric trace. In theory the effect can be calculated but complications may arise from the non-zero load on the vertical push-rod used to measure the expansion of the glass sample. We have adopted a different approach based on the equivalence of the relaxation parameters of volume and enthalpy. The comparison of the behavior of heat capacity and molar expansivity in the glass transition region permits reconstruction of the dilatometric data to provide the needed low-temperature liquid volume and expansivity data. These low-temperature data can then be used in combination with high-temperature data to provide a more precise determination of thermal expansivity in silicate melts. The strength of this method lies in the fact that the temperature difference between the accessible temperature regions of the Archimedean buoyancy and dilatometric methods is commonly > 1000°C, a range far larger than that accessible by currently used methods of liquid density determinations.

The comparison of dilatometric and calorimetric measurements is based on the principle that the relaxation of melt properties in the glass transition region can be described by a universal set of parameters. These universal parameters can be derived from the relaxation of one property (in this case enthalpy) and then applied to predict the behavior of a second property, such as volume. We perform this analysis for a silicate melt composition, $Na_2Si_3O_7$. We measure heat capacity through the glass transition and molar expansivity up to the glass transition using differential scanning calorimetry and dilatometry, respectively. The normalized calorimeter trace is then applied to the molar expansivity curve to extend it into the liquid region. The method is tested against high-temperature expansivity data obtained from double Pt bob Archimedean buoyancy measurements. The two sets of volume data have then been combined to derive a molar-volume temperature relationship from 540-1500°C.

2. Theory

When a silicate glass is heated across the glass transition region a time-dependent (*e.g.* viscoelastic) response of its thermodynamic properties occurs. The unrelaxed, glassy values of volume and enthalpy relax to equilibrium, liquid values over a finite period of time. The relaxation behavior of melt volume, enthalpy and viscosity in the glass transition region has been intensively investigated for several compositions of interest to the glass industry (*e.g.*, Scherer, 1986). Further quantitative models of structural relaxation have been constructed (Narayanswamy, 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 P as a function of previous cooling-rate and experimental heating-rate.

The behavior of melt properties in the glass transition interval can be illustrated with the aid of Fig. 1 and 2. The 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, denoted T_f. To describe in general the relaxed (liquid) or unrelaxed (glassy) properties of a silicate melt, we need to specify the
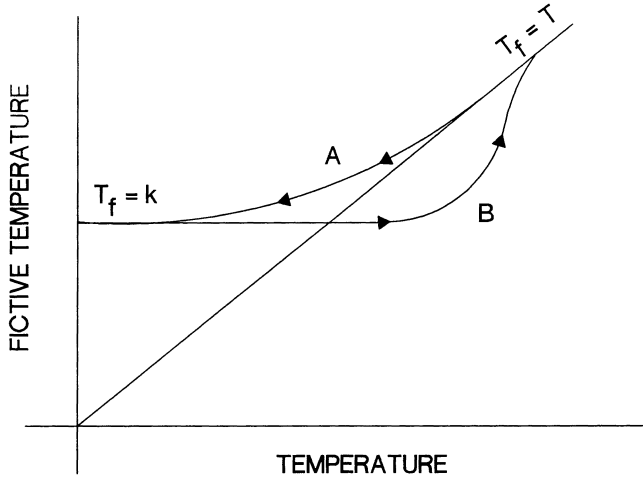
Fig. 1. The path of fictive temperature during cooling (A) and reheating (B) through the glass transition interval.

temperature and the fictive temperature of the melt. For a liquid, the structure is in equilibrium and thus T_f equals T. Upon cooling of the liquid into the glass transition region (Fig. 1, path A), the structure of the melt begins to deviate from equilibrium, *i.e.* T_f deviates from T. This deviation results ultimately in a temperature-independence of T_f at low temperatures, correspond-
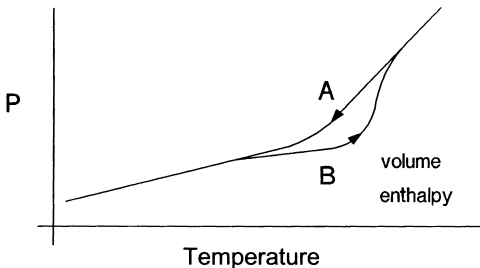

Fig. 2a. Property P during cooling and subsequent reheating across the glass transition interval in temperature space.

ing to the frozen structure of the glassy state. Upon subsequent reheating through the glass transition interval (path B), 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. Due 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).

Fig. 2a illustrates the behavior of property P (*e.g.*, enthalpy, molar volume) as a function of temperature. Fig. 2b illustrates the behavior of the temperature derivative of these properties (*e.g.*, heat capacity, molar expansivity). These derivative properties are used to reconstruct the temperature derivative of T_f, itself. 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 correct description of melt properties in the
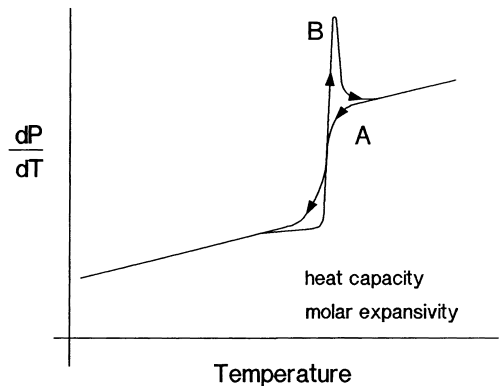

Fig. 2b. The temperature derivative of property P during cooling (A) and subsequent reheating (B) across the glass transition region.

glass transition region thus becomes the task of devising an algorithm for the temperature dependence of the fictive temperature, and this has been done for example by Moynihan et al. (1976). Despite a common origin, various melt properties can, theoretically, differ in relaxation behavior. This would imply different relaxation kinetics due to different partitioning of volume and enthalpy amongst the distribution of structures in the melt. Often, however, no such difference can be distinguished (e.g. Rekhson et al., 1971 ; Sasabe et al., 1977) and the assumption of equivalent relaxation behavior and relaxation times for different properties can be usefully employed.

The temperature derivative of the fictive temperature T_f at a temperature T' is related to the temperature dependence of the macroscopic property P by

$$\frac{dT_f}{dT}\bigg|_{T'} = \frac{\left[(\partial P/\partial T) - (\partial P/\partial T)_g\right]\big|_{T'}}{\left[(\partial P/\partial T)_e - (\partial P/\partial T)_g\right]\big|_{T_f}} \quad (1)$$

where the subscripts "e" and "g" are for the liquid (equilibrium) and the glassy values of the property (Moynihan et al., 1976). In the present study, the property P is taken to be enthalpy H, and volume V. Given the equality of the relaxation times of volume and enthalpy, Eqn. 1 can be rewritten as

$$\frac{dT_f}{dT}\bigg|_{T'} = \frac{c_p(T') - c_{pg}(T')}{c_{pe}(T_f) - c_{pg}(T_f)} =$$

$$\frac{\dfrac{dV(T)}{dT} - \dfrac{dV_g(T)}{dT}\bigg|_{T'}}{\dfrac{dV_e(T)}{dT} - \dfrac{dV_g(T)}{dT}\bigg|_{T_f}} \quad . \quad (2)$$

for heat capacity, c_p, and thermal expansivity, dV/dT. The behavior of T_f in the glass transition region can be generalized to all properties with identical relaxation times, for which sufficient glassy and liquid data exist.

3. Experiment

Synthesis

The starting materials for the preparation of the melt were Na_2CO_3 (99.5) and SiO_2 (99.95) dried at 140°C for several hours. Powders of the carbonate and oxide were weighed into a plastic bottle in quantities to yield a 100 g batch of decarbonated melt. The powders were mixed by agitation and the mixture was loaded into an 75 cm^3 Pt crucible for heating. The powder mixture was decarbonated for 12 hours at 750°C in a box furnace and then further heated to 1150°C for melting. The melt was held at 1150°C for 2 hours to ensure homogeneity. The resulting melt was allowed to cool slowly by switching off the furnace. Portions of the melt were drilled out as 8mm diameter core for the calorimetry and dilatometry and the remainder was reheated to 1250°C in a MoSi$_2$ box furnace. This remainder was removed from the furnace at 1250°C and poured onto a stainless steel plate. The fraction of melt that remained wetted to the crucible was broken out with a hammer. The glass was stored in a desiccator.

The starting batch was analyzed using an electron microprobe. The analysis conditions and results are presented in Table 1.

Table 1. Glass analyses

	before	after
Na_2O	23.87(15)	23.57(11)
SiO_2	76.13(37)	76.43(16)
Al_2O_3	0.36	0.39
FeO	0.02	0.03
Total	97.99	98.42

Analyses are averages of 10 obtained using wavelength dispersive methods with a CAMECA SX-50 instrument. Operating conditions 15 kV accelerating voltage, 15 nA current on brass, a 20 μm defocussed beam and 20 s counting times. Standards were albite (Na, Si), spinel (Al) and hematite (Fe). Mg, Ca and Cr were analyzed but not found.

Calorimetry

The heat capacity of a 25mm long, 8mm diameter cylinder of the glass was determined over a 17-540°C temperature range using a Setaram HTC calorimeter operating in continous scanning mode. The heat flow was determined at heating rates of 2 and 5°C min^{-1} on glasses previously cooled at 1, 2, 5 and 10°C min^{-1}, respectively. The calorimeter was standardized using an identical cylinder of single-crystal sapphire and the heat capacity fit of Robie et al. (1979). The operation of the calorimeter has been checked against amorphous SiO_2 with satisfactory results. Heat capacities are estimated to have an accuracy of ±5%.

Dilatometry

The same glass cylinder was used in the dilatometric measurements. A Netzsch ® TMA 402 quartz-rod dilatometer was used to determine the change in length of the sample over a temperature range of 17-540°C. The same heating and cooling rates were used for the determination of the thermal expansion as for the calorimetry measurements : *i.e.*, 2 and 5°C min⁻¹ heating and 1, 2, 5 and 10°C min⁻¹ cooling rates. The length change with temperature is measured by the movement of a vertical metal and silica glass rod through the center of a linear variable displacement transducer. This rod is supported by a spring which minimizes the force exerted upon the sample.

Densitometry

The density of the liquid was measured in the temperature range of 1450°C to 1100°C using the double Pt bob method. The experimental apparatus is described by Dingwell *et al.* (1988). The present determinations were made in individual runs of descreasing temperature steps of 50°C from 1450°C to 1100°C. The bobs were tared to zero immediately prior to immersion and held after immersion for 1 hour at each temperature. The density of the liquid was computed using

$$\rho = \frac{B_1 - B_2}{V_1 - V_2} \qquad (3)$$

where ρ is the density of the liquid, B_1 and B_2, and V_1 and V_2 are the buoyancy and volumes of bobs 1 and 2, respectively. The present method yields a precision of 0.2% for melt density. A sample of melt was recovered after the density measurements and its analysis by electron microprobe is presented in Table 1. The room-temperature density of a 5 g chip of the glass was determined using the Archimedean buoyancy method in toluene and air to be 2.4418 ± 0.0041 g cm⁻³ at 28°C.

4. Results

Calorimetry

The calorimetric trace for 5°C min⁻¹/5°C min⁻¹ (cooling/heating rates) is presented in Fig. 3a. The glassy heat capacity shows a positive temperature-dependence from 1.14 J g⁻¹°C at 300°C to 1.18 J
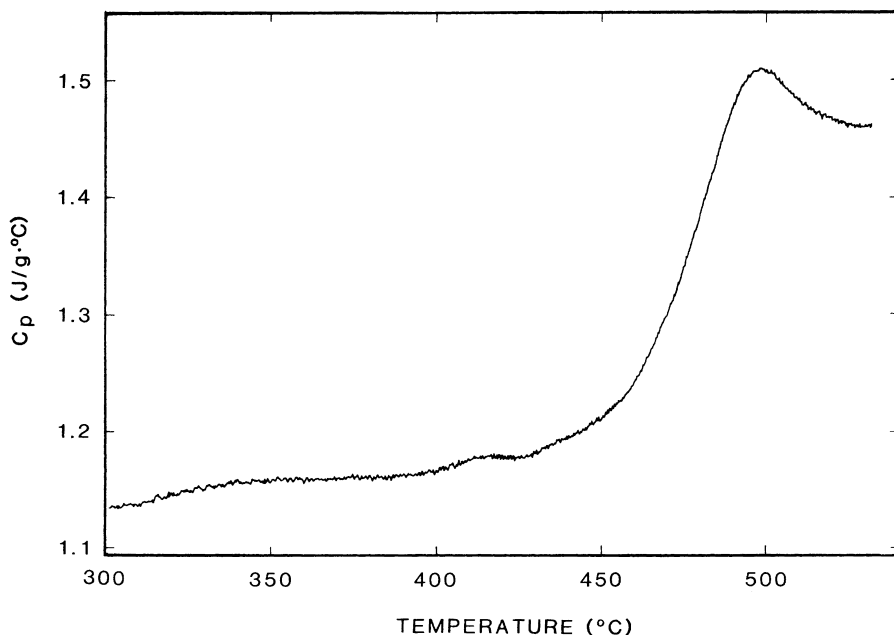

Fig. 3a. Scanning calorimetric determination of the heat capacity of $Na_2Si_3O_7$ across the glass transformation interval.
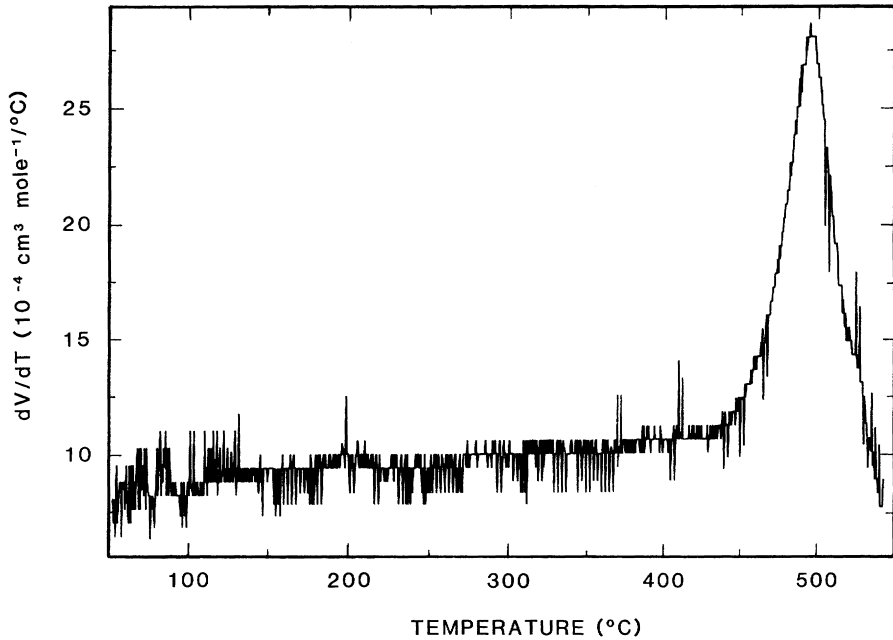
Fig. 3b.Scanning dilatometric determination of the molar expansivity of $Na_2Si_3O_7$ across the glass transition interval. The onset of viscous deformation occurs in the glass transformation interval.

$g^{-1}°C^{-1}$ at 420°C, just before the onset of relaxation. The liquid heat capacity is 1.46 J $g^{-1}°C^{-1}$. The temperature range of the liquid data is too small to yield a temperature derivative of the heat capacity. The heat capacity increases by 23% across the glass transition. These values of heat

Table 2. Liquid densities of $Na_2Si_3O_7$

Temperature (°C)	Density (g cm^{-3})	Molar volume (cm^3 mole^{-1})
1500	2.2051	27.463
1450	2.2107	27.393
1400	2.2187	27.294
1350	2.2284	27.175
1300	2.2337	27.111
1250	2.2452	26.972
1200	2.2555	26.849
1150	2.2732	26.640
1100	2.2802	26.558
540		25.313(0.015)

capacity were checked against a powdered sample of the same glass run in a Setaram DSC 111 instrument with good agreement.

Dilatometry

The molar expansivity of $Na_2Si_3O_7$ (for cooling/heating rate 5°C min^{-1}/5°C min^{-1}) is presented as a function of temperature in Fig. 3b. Above the glass transition temperature, the effect of viscous flow acts to decrease the measured molar expansivity. The molar expansivity of the glass at 420°C is $11.1\pm0.4\times10^{-4}$ cm^3 mole$^{-1}°C^{-1}$. This value rises in the transition region to a maximum value of $\sim30\times10^{-4}$ cm^3 mole$^{-1}°C^{-1}$. The measured value drops steeply to erroneously low values beyond the maximum due in part to viscous deformation of the sample.

Densitometry

The density data of Table 2 are plotted against temperature in Fig. 4. These density data are in excellent agreement with those of Bockris *et al.* (1956). The 1400°C value from this study is 2.2187 ± 0.0044 g cm^{-3} and that for the equivalent

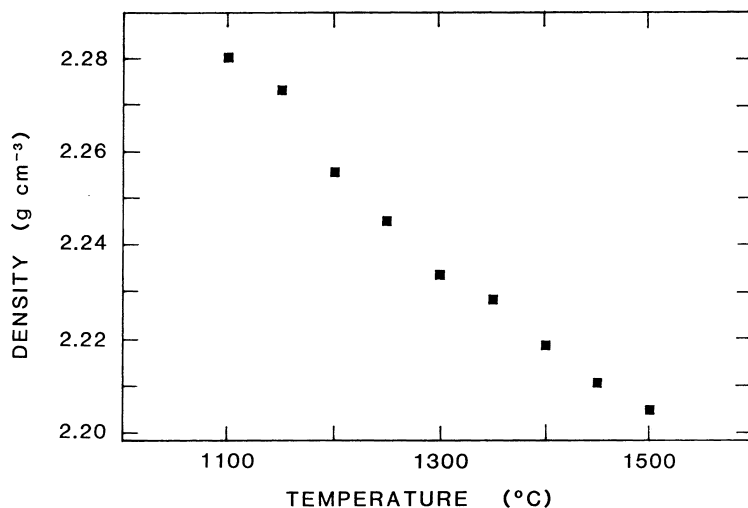Fig. 4. The density of $Na_2Si_3O_7$ in the temperature range of 1100˚C to 1500˚C determined by the double Pt bob Archimedean method.

composition from Table 2 of Bockris *et al.* (1956) is 2.218± 0.004 g cm⁻³.

A linear least squares fit to the density data of Table 2 yields a temperature dependent molar volume described by

$$V \text{ (cm}^3 \text{ mole}^{-1}) = 24.023(182) + 2.33(14) \times 10^{-3} \, T \quad (4)$$

(for T in ˚C), where a 0.2% error is assumed for all density values. This molar expansivity is in

disagreement with the value of Bockris *et al.* (1956) obtained over the same temperature range using the double bob Archimedean method.

5. Discussion

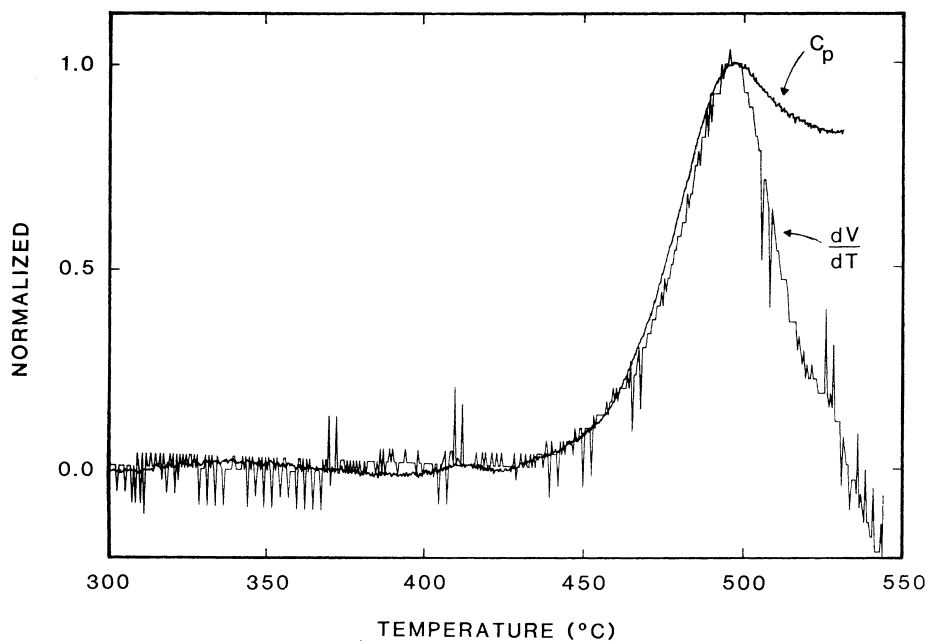We recover the liquid molar expansivity from the dilatometric trace by normalizing both the

Fig. 5. Comparison of calorimetric and dilatometric traces normalized to the peak temperature.

Table 3a. Expansivity of $Na_2Si_3O_7$

cooling/heating rate		$\dfrac{dV}{dT}$			
$°C\ min^{-1}/°C\ min^{-1}$		$10^{-4}\ cm^3\ mole^{-1}°C^{-1}$			
		420°C	peak	540°C	1400°C
2	2	11.18(0.79)	32.57	27.39(1.92)	–
1	5	11.11(0.77)	32.92	27.16(1.89)	–
2	5	10.91(0.84)	32.94	28.02(2.14)	–
5	5	11.37(0.77)	29.32	27.04(1.83)	–
10	5	11.13(0.78)	25.13	23.87(1.62)	–
average		11.10(0.35)		26.43(0.83)	
					23.29(1.39)
fit to all volumes				23.00(0.25)	

Table 3b. Coefficient of volume thermal expansion of $Na_2Si_3O_7$

cooling/heating rate		α_v			
$°C\ min^{-1}/°C\ min^{-1}$		$10^{-6}\ °C^{-1}$			
		420°C	peak	540°C	1400°C
2	2	44.43(3.14)	128.80	108.30(7.65)	–
1	5	44.13(3.07)	130.06	107.31(7.48)	–
2	5	43.34(3.39)	130.09	110.62(8.65)	–
5	5	45.16(3.05)	115.84	106.74(7.21)	–
10	5	44.21(3.14)	99.34	94.32(6.70)	–
average		44.33(1.41)		104.65(3.34)	91.10(6.68)*
				92.30(5.39)*	85.36(4.52)
fit to all volumes				90.90(0.94)	84.31(0.81)

* – extrapolated

scanning calorimetric and dilatometric data (DeBolt et al., 1976). Due to the lack of relaxed molar expansivity data, the calorimetric and dilatometric data have been normalized by

$$P'(T) = \frac{P(T) - P_g(T)}{P_p - P_g(T)} \qquad (5)$$

where the subscripts "p" and "g" refer to peak and glassy values of the property P. The comparison of the two normalized curves is illustrated in Fig. 5. The similar peak positions and peak widths observed for heat capacity and thermal expansivity are consistent with the assumption of

equivalent relaxation behavior for volume and enthalpy. The relaxed value of the molar expansivity can now be calculated from Eqn. 2.

Setting the peak values from the calorimetric and dilatometric data to be equal requires the assumption that insignificant viscous deformation is recorded by the dilatometer at temperatures up to the peak temperature. The assumption that the peak in molar expansivity calculated from the dilatometry measurements is not significantly affected by the viscous deformation of the sample was based on the following calculation. The rate of linear deformation of a cylinder of shear viscosity
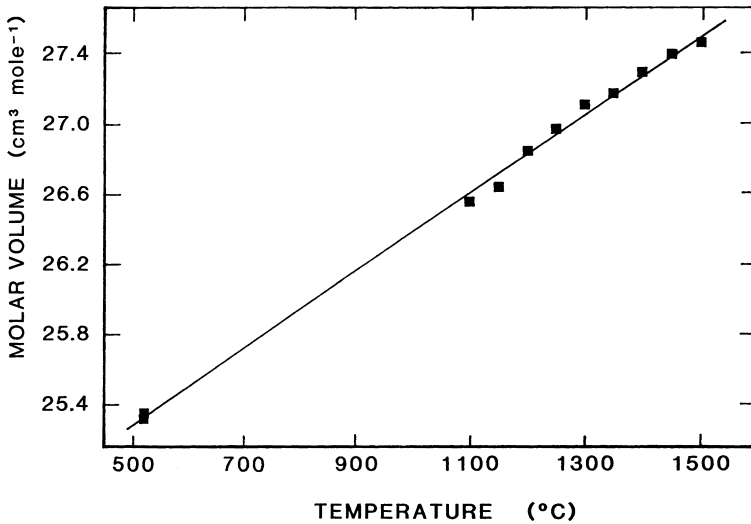
Fig. 6. Linear fit to the liquid volume data obtained from density (high temperature) and dilatometry/calorimetry (low temperature) measurements. The thermal expansivity obtained from the combination of dilatometry and calorimetry constrain the slope of the fitted line at low temperatures.

due to the application of a stress σ is $\dot{\varepsilon} = \sigma/3\eta$. The contribution of viscous deformation to the calculated coefficient of volume thermal expansion is then

$$\alpha'_v = \frac{dV}{VdT} = 3\dot{\varepsilon}\frac{\Delta time}{\Delta T} = \frac{\sigma}{\eta \ heating-rate}. \quad (6)$$

The stress can be calculated from the diameter of the sample together with the applied mass. The mass resting upon the sample is made of half its own mass plus ~1 g due to the glass measuring rod for a total of ~2.5 g. The viscosity of $Na_2Si_3O_7$ (Taylor & Rindone, 1970) is $\eta(Pa \ s) = 10^{-21.337+24461/T(K)}$. Therefore α'_v becomes significant (greater than 1×10^{-6} °C⁻¹) at temperatures greater than 503°C and 513°C for heating rates of 2°C and 5°C per minute, respectively. The matching of the dilatometric and calorimetric peaks occurs at temperatures 5-15°C lower than these.

The glassy and liquid molar expansivity of $Na_2Si_3O_7$ derived from the dilatometric data are presented in Table 3. The dilatometric-derived value of liquid molar expansivity is $26.43\pm0.83\times10^{-4}$ cm³ mole⁻¹°C⁻¹ in good agreement with the high temperature densitometry-derived expansivity $23.29\pm1.39\times10^{-4}$ cm³ mole⁻¹°C⁻¹. A weighted linear fit to the high-temperature molar volume data and 5 estimates of the molar volume at 540°C results in the molar volume of $Na_2Si_3O_7$ being described by

$$V \ (cm^3 \ mole^{-1}) = 24.061(27) + 2.300(25)\times10^{-3} \ T \quad (7)$$
(for T in °C).

The RMSD is 0.033 cm³ and the standard error in the molar expansivity is ±1%. This represents a significant improvement over the molar expansivity estimated from the high-temperature data alone (±6%) or the corrected dilatometric data (±3%) and a substantial improvement over typically larger errors associated with individual molar expansivities of silicate liquids in previous studies.

Critical to the success of our assumptions in treating the calorimetric and dilatometric data has been the use of a single sample and the same set of experimental conditions to obtain heat capacity and expansivity data. Small changes in composition or fictive temperature of a silicate melt can strongly influence relaxation behavior. 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. It is only this equivalence that permits our assumption of the equivalence of the enthalpy and volume relaxation behavior.

It is clear from Fig. 3b that the selection of any uncorrected value of molar expansivity as a liquid value, from a dilatometric trace, cannot, except fortuitously, yield a correct value. The practice of choosing some characteristic part of the uncorrected curve to yield liquid expansivity is

to be discouraged. The result, for example, of choosing the peak value of expansivity will be a significant overestimation of liquid expansivity which will compare poorly with that obtained from high-temperature densitometry.

A final note to the utility of expansivity determinations using the normalization procedure presented here is that the volume data obtained from the corrected dilatometric curves fill in a range otherwise inaccessible to experiments. The high viscosities encountered at the glass transition temperatures obtained with these cooling/heating rates preclude the use of immersion techniques. A significant number of geological processes occur nevertheless in liquids with such extremely high viscosities. Water-rich and poor felsic magmas host the operation of petrogenetic processes such as crystal growth and dissolution, magma degassing and even eruption at temperatures which lie just above the glass transition. The extraction of low-temperature volume data from dilatometry will be pursued further in future.

6. Conclusion

The reduction of the behavior of melt properties in the glass transition region to a universal set of parameters that describe the evolution of fictive temperature during reheating allows the extension of dilatometric molar expansivity data into the liquid state using corresponding scanning calorimetric heat capacity data. This method yields excellent agreement with molar expansivity obtained by high-temperature densitometry. The combination of the methods allows the error associated with molar expansivity to be reduced to ±1%.

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