Temperature-dependent thermal expansivities of silicate melts: The system anorthite-diopside

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Abstract—The temperature-dependent thermal expansivities of melts along the join anorthite-diopside have been determined on glassy and liquid samples using a combination of calorimetry, dilatometry, and Pt double bob Archimedean densitometry.

Supercooled liquid volumes and molar thermal expansivities were determined using scanning calorimetric and dilatometric measurements of properties in the glass region and their behavior at the glass transition. The extraction of low-temperature liquid molar expansivities from dilatometry/calorimetry is based on an assumed equivalence of the relaxation of volume and enthalpy at the glass transition using a method developed and tested by WEBB et al. (1992). This method corrects for transient effects at the glass transition which can lead to serious overestimates of liquid thermal expansivity from "peak" values. Superliquidus volumes were determined using double Pt bob Archimedean densitometry at temperatures up to 1650°C.

The resulting data for liquid volumes near glass transition temperatures (810–920°C) and at superliquidus temperatures (1400–1650°C) are combined to yield thermal expansivities over the entire supercooled and stable liquid range. The molar expansivities are, in general, temperature dependent. The temperature-dependence of thermal expansivity increases from anorthite to diopside composition. The thermal expansivity of anorthite is essentially temperature independent, whereas that of diopside decreases by ≅50% between 800 and 1500°C, with the consequence that the thermal expansivities of the liquids in the anorthite-diopside system converge at high temperature.

INTRODUCTION

THE DENSITY OF SILICATE melts during rock-forming processes is a critical factor in the efficiency of crystal-melt fractionation, which ultimately gives rise to the diversity of igneous rocks. Accordingly, the experimental determination of melt densities has been the subject of considerable investigation in the geological sciences (see summary to 1970 by BOTTINGA and WEILL, 1970; BOTTINGA et al., 1982; MO et al., 1982; STEIN et al., 1986; LANGE and CARMICHAEL, 1987; DINGWELL et al., 1988). These investigations have invariably been conducted in the superliquidus regime where problems of crystallization do not occur and high viscosities can often be avoided. Igneous petrogenesis is, however, an overwhelmingly subliquidus subject. The processes leading to both erupted and intruded products of igneous fractionation occur at temperatures down to the solidus, and in disequilibrium cases, at subsolidus temperatures.

The glassforming ability of many silicate melts is evidence of the fact that crystallization can be avoided to subsolidus temperatures if the conditions of cooling are appropriate. These melts can 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 immiscibility. Use of these low-temperature metastable liquid property data, in combination with superliquidus liquid property data for individual melt properties, provides a wide temperature range over which the liquid behavior can be interpolated. Several studies of the viscosity and heat capacity of silicate melts have utilized this possibility to provide a much more complete description of these properties of silicate melts. The results

are both quantitative and qualitative (i.e., theoretical) improvements in our understanding of silicate melts (e.g., RICHET et al., 1986). In this study we move a step further in the analysis of glass transition behavior to derive molar thermal expansivity data for metastable liquids. In this way, our knowledge of subliquidus melt densities, extant during igneous petrogenesis, is significantly improved.

METHODS

The compositions used in this investigation lie along the join anorthite ($CaAl_2Si_2O_8$)-diopside ($CaMgSi_2O_6$), representing one of the limiting joins of the albite-anorthite-diopside system. This system is of interest as it has been historically applied as a model for basalt petrogenesis (e.g., phase equilibria: BOWEN, 1915; SCHAIRER and YODER, 1960; OSBORN and TAIT, 1952; KUSHIRO, 1973; thermochemistry: WEILL et al., 1980; NAVROTSKY et al., 1980; 1989; viscosity: SCARFE et al., 1983; SCARFE and CRONIN, 1986; TAUBER and ARNDT, 1987; ultrasonic wave velocities: RIVERS and CARMICHAEL, 1987; shock wave equation of state: RIGDEN et al., 1988, 1989).

The glassy starting materials were obtained from M. Rosenhauer, Universität Göttingen. Their method of preparation is described by TAUBER (1987). Chemical analyses of these glasses are provided in Table 1 along with the details of analytical methods. The stoichiometric compositions are also included in Table 1 for comparison. These previously prepared glasses were chosen for the present investigation because viscosity data have been obtained on this system over a wide temperature range by TAUBER and ARNDT (1987) using the micropenetration method and also because a reconnaissance differential thermal analysis of these glasses has been made by KNOCHE (1990).

The dilatometric and calorimetric investigations were performed on glass cylinders (25 mm long × 8 mm diameter) using methods identical to those described by WEBB et al. (1992). The calorimetry was performed in continuous scanning mode using a Setaram® HTC instrument. The heat flow was recorded during heating runs of 5°C/

Table 1. Chemical composition of glasses (wt %).

	SiO_2		Al_2O_3	Na_2O	CaO	MgO	FeO	K_2O	Σ
AN100	43.0	*	35.1	0.01	20.5	0.10	0.02	0.005	98.7
	43.2	†	36.7		20.2				
AN70DI30	46.3	*	26.5	0.14	21.3	4.77	0.09	0.05	99.2
	45.8	‡	26.8	0.17	23.0	5.08	0.10	0.05	101.0
	46.3	§	26.8		21.0	4.9			99.0
	46.3	†	27.5		21.6	4.66			
AN50DI50	47.3	*	19.9	0.12	25.0	6.88	0.08	0.02	99.3
	48.5	‡	20.8	0.13	23.1	7.27	0.10	0.03	99.9
	47.4	§	20.6		23.1	7.0			98.1
	48.6	†	20.6		22.7	8.15			
AN20DI80	52.3	*	8.70	0.08	24.3	14.1	0.09	0.06	99.6
	52.5	‡	8.50	0.08	25.1	14.7	0.11	0.06	101.1
	53.0	§	9.0		23.3	13.8			99.1
	52.5	†	8.91		24.5	14.1			
DI100	56.2	*	0.19	0.16	25.9	17.3	0.02	0.007	99.8
	56.0	‡	0.29	0.18	26.5	17.8	0.02	<0.001	100.8
	55.5	†			25.9	18.6			

* analysis by electron microprobe, Bayerisches Geoinstitut, operating conditions 15kV accelerating voltage, 15nA current on brass, 20sec count times using a 10μm defocussed beam, standards wollastonite (Ca), diopside (Mg), albite (Si, Na), orthoclase (K), Fe_2O_3 (Fe), spinel (Al).

† Stoichiometric (theoretical) compositions.

‡ instrumental analysis, Si and Al by "spectral photometer", Ca, Mg, Na and K by atomic absorption, FeO by wet chemical titration, standards granite (Si, Al, Na, Ca, Mg, Fe, K), andesite (Si, Al, Na, Mg, K), granodiorite (Si, Al, Na, Ca, Mg, K), diabase (Al, Na, Ca, Mg, K, Fe), peridotite (Al, Mg, Fe), basalt (Al, K), dunite (Al, Fe) (Mielke, 1984, 1985, 1988, personal communication).

§ X-ray fluorescence analysis (Ca, Si), electron microprobe (Mg, Al) see Tauber and Arndt (1987).

min on glasses that had been previously cooled at cooling rates of 1, 2, 5 and 10°C/min. The calorimeter is calibrated regularly against a geometrically identical cylinder of sapphire, using the heat capacity data of ROBIE et al. (1979). The heat capacity data for the 5/5 (cooling-rate/heating-rate) runs are presented in Table 2. The heat capacities are estimated to have a precision of ±2.5% at 1σ, based on the four runs performed for each sample. The measured heat capacities for the anorthite and diopside glasses are within error of those determined by STEBBINS et al. (1982), STEBBINS et al. (1983), and RICHET and BOTTINGA (1984).

The dilatometry was performed using a Netzsch® TMA 402 quartz-rod dilatometer. The samples, their thermal history, and the scanning rates were those used in the calorimetry measurements. This instrument has been calibrated against sapphire (NBS sheet 732) and the molar expansivities have an accuracy of ±3% at 1σ, calculated from the errors in the measurements of the thermal expansivity of the standard and the sample.

The high-temperature densitometry was performed using the apparatus described by DINGWELL et al. (1988) employing the double Pt bob Archimedean method. Densities obtained using this method have a precision of ±0.2% and reproduce the best value for molten NaCl within this precision (JANZ, 1980). Room-temperature densities of the glass cylinders were measured using Archimedean buoyancy in toluene and have a precision of ±0.2%.

THEORY

The theory of our procedure for obtaining relaxed liquid molar expansivity data 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. 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 (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 and experimental heating rate.

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 (TOOL and 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. For a liquid, the structure is in equilibrium and thus T_f equals T (see 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 results ultimately 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. 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, $T_f < T$; DINGWELL and WEBB, 1990).

The temperature derivative of the 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 T_f. 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 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).

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

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

where the subscripts "e" and "g" are for the liquid (equilibrium) and the glassy values of the property (MOYNIHAN et al., 1976). In the present study, the property Φ is taken to be enthalpy H, and volume V. Assuming the equivalence of volume and enthalpy relaxation behavior, Eqn. (1) can then be rewritten as

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

Thus, in the glass transition region, the behavior of any temperature-dependent property of a glass can be predicted from the known behavior of another temperature-dependent

property if the relaxation behavior of the two properties is equivalent. It has been noted by REKHSON et al. (1971) and SASABE et al. (1977) that the time scales of volume and viscosity, and refractive index and enthalpy relaxation, respectively, in silicate melts are indistinguishable. HIGGINS et al. (1972) also found that ionic and mechanical relaxation have the same activation energy and timescale in $Na_2Si_3O_7$ melt. In the above equation relating c_p and thermal expansivity dV/dT, the unknown parameter is the thermal expansivity of the relaxed liquid at temperature T' which is some 50°C above the glass transition temperature.

We recover the liquid molar thermal expansivity from the dilatometric trace by normalizing both the scanning calorimetric and dilatometric data. Due to the lack of relaxed thermal expansivity data, the calorimetric and dilatometric data have been normalized by

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

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 $\alpha_v[1/V(dV/dT)]$ of the melt can also be calculated.

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. WEBB et al. (1992) have shown that the contribution to the apparent thermal expansion due to viscous deformation becomes significant (>1%) only at temperatures 5–15°C above the peak temperatures for the present heating rate.

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 thermal 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 internal consistency that permits the use of the assumption of the equivalence of the enthalpy and volume relaxation behavior.

RESULTS

A typical set of calorimetric and dilatometric data is presented in Fig. 2 for the composition AN50DI50. The effect of viscous deformation in the liquid region of the dilatometric trace is clearly visible. The normalized comparison of relaxation in the dilatometric and calorimetric traces is illustrated in Fig. 3. Expansivities of the supercooled liquids derived from the earlier mentioned normalization procedure are presented in Table 3. The thermal expansivity data of the glasses have been fitted to first-order polynomials, with the resulting molar volume equations being presented in Table 4. The room temperature and superliquidus density data are presented in Table 5.

Table 2. Measured c_p (J/g °C) data for glasses and liquids. Cooling rate 5°C/min; heating rate 5°C/min.

T (°C)	AN100	AN70DI30	AN50DI50	AN20DI80	DI100
300		1.0279	1.0117	0.9971	1.0043
310		1.0338	1.0147	1.0033	1.0105
320		1.0378	1.0180	1.0054	1.0148
330		1.0380	1.0216	1.0098	1.0208
340		1.0487	1.0273	1.0163	1.0230
350		1.0608	1.0351	1.0195	1.0251
360		1.0651	1.0383	1.0270	1.0321
370		1.0696	1.0437	1.0328	1.0374
380		1.0750	1.0515	1.0365	1.0403
390		1.0813	1.0559	1.0432	1.0402
400	1.0243	1.0862	1.0609	1.0479	1.0460
410	1.0225	1.0885	1.0658	1.0486	1.0559
420	1.0249	1.0902	1.0673	1.0487	1.0716
430	1.0293	1.0931	1.0705	1.0536	1.0800
440	1.0310	1.1012	1.0757	1.0607	1.0604
450	1.0350	1.1058	1.0830	1.0617	1.0309
460	1.0377	1.1063	1.0842	1.0674	1.0457
470	1.0445	1.1135	1.0897	1.0702	1.0745
480	1.0390	1.1178	1.0944	1.0749	1.0947
490	1.0437	1.1209	1.0928	1.0821	1.1048
500	1.0498	1.1253	1.0970	1.0878	1.1170
510	1.0633	1.1269	1.0969	1.0951	1.1263
520	1.0617	1.1274	1.1038	1.0953	1.1409
530	1.0538	1.1390	1.1111	1.0988	1.1469
540	1.0535	1.1427	1.1102	1.1055	1.1460
550	1.0662	1.1476	1.1153	1.1093	1.1601
560	1.0759	1.1512	1.1214	1.1195	1.1619
570	1.0769	1.1562	1.1241	1.1235	1.1681
580	1.0919	1.1635	1.1312	1.1290	1.1862
590	1.0901	1.1679	1.1331	1.1346	1.1857
600	1.0885	1.1740	1.1408	1.1350	1.1856
610	1.0946	1.1758	1.1471	1.1390	1.1911
620	1.1014	1.1778	1.1490	1.1467	1.2027
630	1.1101	1.1818	1.1552	1.1494	1.2023
640	1.1114	1.1874	1.1577	1.1576	1.1775
650	1.1068	1.1934	1.1610	1.1551	1.1804
660	1.1085	1.1958	1.1612	1.1553	1.1980
670	1.1208	1.2007	1.1687	1.1652	1.2341
680	1.1273	1.2029	1.1700	1.1734	1.2676
690	1.1256	1.2213	1.1909	1.1917	1.2969
700	1.1239	1.2254	1.1972	1.2295	1.3646
710	1.1386	1.2307	1.2102	1.2933	1.4856
720	1.1340	1.2328	1.2297	1.4125	1.6536
730	1.1290	1.2412	1.2679	1.5781	1.7955
740	1.1352	1.2603	1.3482	1.6653	1.7860
750	1.1308	1.2889	1.4675	1.6214	1.7402
760	1.1271	1.3473	1.6078	1.5824	1.7085
770	1.1373	1.4491	1.6494	1.5622	1.6929
780	1.1428	1.5768	1.6060	1.5550	1.6821
790	1.1441	1.6727	1.5735	1.5502	1.6749
800	1.1480	1.6637	1.5546		1.6782
810	1.1716	1.6322	1.5476		
820	1.1979	1.6058	1.5468		
830	1.2224	1.5981			
840	1.2880	1.5970			
850	1.3931	1.6022			
860	1.5135				
870	1.6108				
880	1.5905				
890	1.5457				
900	1.5235				

Table 2. (Continued)

T (°C)	AN100	AN70DI30	AN50DI50	AN20DI80	DI100
910	1.5155				
920	1.5104				
930	1.5068				
940	1.5041				
950	1.5148				
peak temperature	868°C	792°C	769°C	740°C	732°C

The volume data for the supercooled liquids (derived from the dilatometry/calorimetry) and for the superliquidus liquids are presented in Table 6. The molar volumes have been combined and regressed against temperature using first- and second-order polynomials. The results of the least-squares regressions are reproduced in Table 7 (see also Fig. 4.), together with the root mean squared deviations. The value of the supercooled dV/dT obtained from the dilatometry/calorimetry comparison is used to constrain the low-temperature slope of the curve fitted to the volume data. The inclusion of a temperature derivative for the molar expansivity of diopside liquid reduces the RMSD to within the error estimates of the volume data. In contrast, the anorthite volume data are described within error by a constant value of molar expansivity. The relaxed liquid volume data from dilatometry and the superliquidus volume data for diopside and anorthite are presented in Fig. 4 along with the polynomial fits to the data. The temperature dependence of the fitted values of molar expansivity increase smoothly with increasing diopside content. For an illustration of this, the temperature-dependent thermal expansivity dV/dT and the coefficient of volume thermal expansion $\alpha_v[1/V(dV/dT)]$ resulting from the regressions of Table 6 have been plotted in the temperature range of input data (approx. 800–1600°C) in Fig. 5. (In this plot the temperature-dependent thermal expansivity for anorthite is included for consistency of the comparison.)
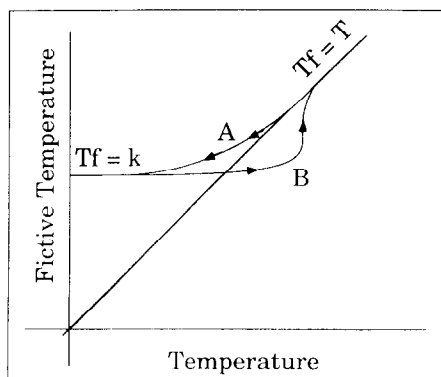

FIG. 1. The cooling (a) and reheating (b) paths of a silicate melt in temperature-fictive temperature space.

DISCUSSION

The present glass densities, 2.704 ± 0.003 g cm^{-3} for anorthite and 2.851 ± 0.003 g cm^{-3} for diopside, are within the range of those previously obtained for anorthite (2.700 g cm^{-3} by BERMAN et al., 1942; 2.64 g cm^{-3} by CUKIERMAN and UHLMANN, 1973; 2.701 g cm^{-3} by ARNDT and HÄBERLE, 1973; 2.66 g cm^{-3} by SEIFERT et al., 1982; and 2.704 g cm^{-3} by TANIGUCHI, 1989) and for diopside (2.846 g cm^{-3} by BERMAN et al., 1942; 2.870 g cm^{-3} by TANIGUCHI, 1989). The densities of glasses are dependent on thermal history, and this, combined with slight compositional variations, precludes a closer comparison of the glass data.

The superliquidus density of diopside liquid has been investigated by LICKO and DANEK (1982) using the falling sphere method and by LANGE and CARMICHAEL (1987) and TANIGUCHI (1989) using the double Pt bob method. The results of LANGE and CARMICHAEL (1987) and TANIGUCHI (1989) agree well with our diopside density data while those of LICKO and DANEK (1982) are 1% lower. The density of melts on the anorthite-diopside join has been investigated by TANIGUCHI (1989). Our results deviate from his with increasing anorthite content.

The reasons for this discrepancy for anorthite are not clear, but at 1580°C, the LANGE and CARMICHAEL (1987) calculation scheme yields a value (2.5649 g cm^{-3}) which lies between the result of this investigation (2.6007 ± 0.01214 g cm^{-3}) and the value (2.538 g cm^{-3}) of TANIGUCHI (1989). Further data are needed in the CaO-Al$_2$O$_3$-SiO$_2$ system to resolve this discrepancy.

TANIGUCHI (1989) has investigated the anorthite-diopside system using dilatometry. He used "peak" values of thermal expansivities (the maximum in the dV/dT curve) for the liquid at the glass transition with the result that the values obtained were consistently too high to reproduce the high-temperature volumes of his liquids. His Fig. 5 illustrates, for example, the contrast between a "peak" coefficient of thermal expansion of 240 × 10^6 °C^{-1} vs. a coefficient of thermal expansion of 125 × 10^6 °C^{-1} obtained from a polynomial fit to density at the "peak" temperature, for diopside. ARNDT and HÄBERLE (1973) investigated the thermal expansion of an anorthite glass using a procedure similar to TANIGUCHI to determine the thermal expansivity above the glass transition.
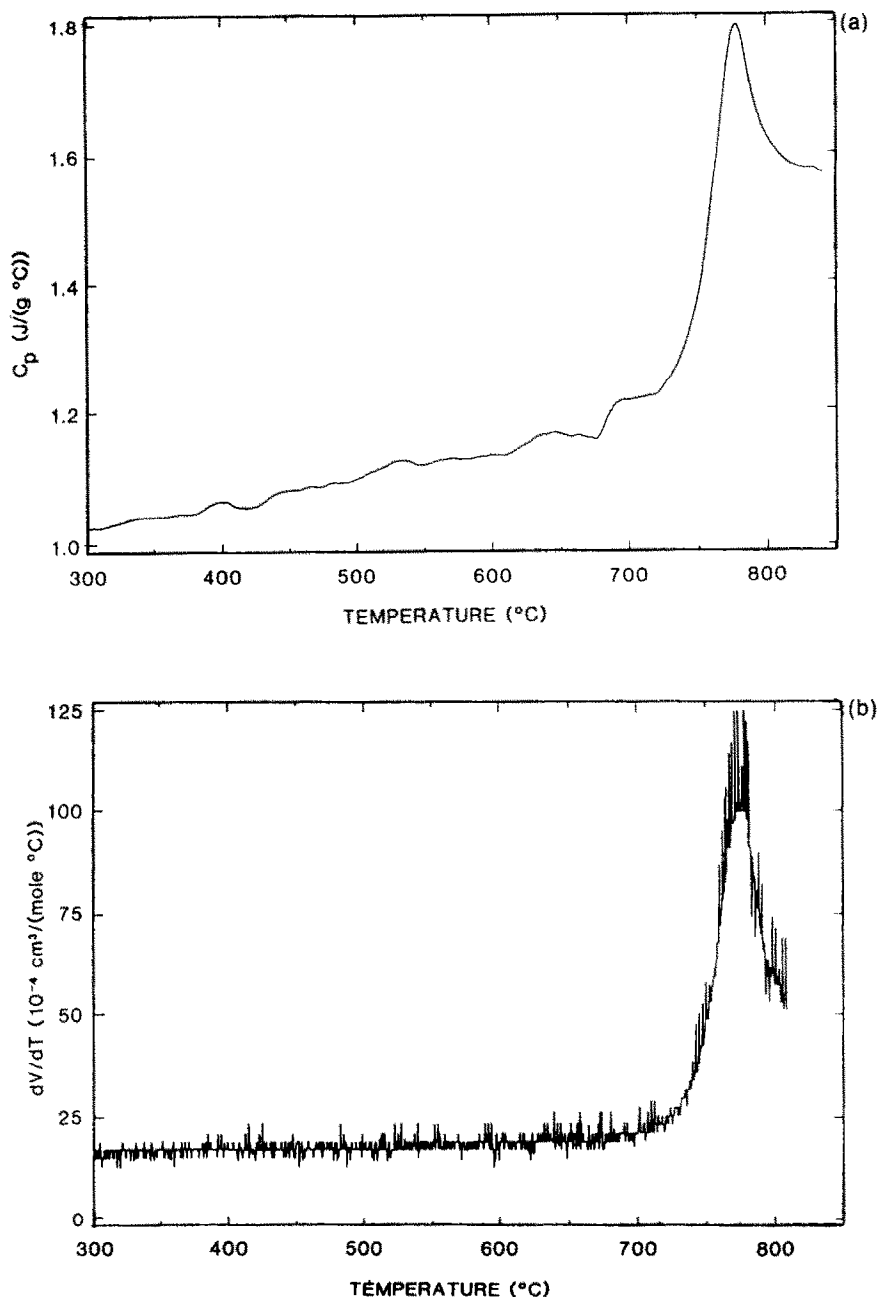
FIG. 2. Calorimetric (a) and dilatometric (b) traces for AN50DI50. The effect of viscous deformation due to body forces in the upper viscoelastic region of the dilatometric trace is visible.

In the present study our measured thermal expansivities near T_g are consistent with the values obtained from our volume fits as seen in Table 3 where our measured and fitted values of the coefficient of thermal expansion for diopside at 810°C are 125×10^{-6} °C^{-1} and 123×10^{-6} °C^{-1}, respectively.

We wish to stress the agreement between the expansivity data obtained from dilatometry/calorimetry and those obtained from the fits to the combined (high- and low-temperature) melt volume data (Table 3). This agreement removes the discrepancy posed by the TANIGUCHI (1989) data and improves confidence in the prediction of low-temperature melt densities.

An inspection of Fig. 4 indicates that extrapolation of diopside volume data either up or down temperature from the segments of the volume curve covered by either method, will result in serious overestimates of liquid volume. The extrapolation of high-temperature volumes and expansivity to low temperature yields a 3% error. This discrepancy lies outside the accuracy of multicomponent calculation schemes presently available (e.g., LANGE and CARMICHAEL, 1987). Clearly, a much more complete investigation of the temperature dependence of liquid expansivity is required to incorporate this correction in such schemes.

It has been demonstrated for a number of silicate melts that calorimetric or dilatometric peak temperatures represent
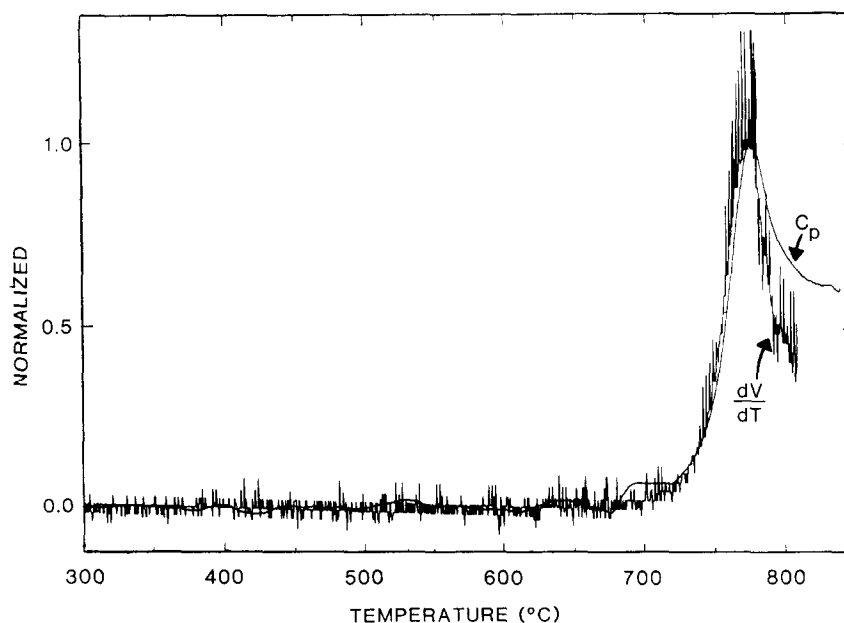
FIG. 3. The method of normalization of the dilatometric and calorimetric traces illustrated for AN50DI50.

temperatures of constant viscosity vs. composition, or "isokoms" (SCHERER, 1986). This is because the temperature-dependent processes of volume and enthalpy relaxation are strongly linked to those controlling shear flow (DINGWELL and WEBB, 1989, 1990). The time scale can be estimated from the Maxwell relation (DINGWELL and WEBB, 1989), which relates the ratio of shear viscosity and shear modulus to the shear relaxation time. Literature data for the shear

Table 3. Measured and fitted values of dV/dT and α_v [1/V(dV/dT)] for the supercooled liquids.

	$\dfrac{dV^m}{dT}$	$\dfrac{dV^f}{dT}$	α_v^m	α_v^f	Temperature
	10^{-4} cm^3 mole^{-1} °C^{-1}		10^{-6} °C^{-1}		°C
AN100	54.4±2.1	40.7±31.6	52.0±2.0	38.9±29.3	920
AN70DI30	65.0±1.7	55.6±15.4	67.4±1.8	57.7±15.6	860
AN50DI50	70.5±3.9	74.5± 3.2	78.0±4.3	82.3± 3.3	830
AN20DI80	87.8±2.3	90.0± 0.1	106.2±2.8	108.9± 0.8	810
DI100	96.9±1.9	95.3± 3.4	125.1±2.6	123.0± 4.0	810

-superscript m refers to measured expansivity from normalization procedure.

-superscript f refers to fitted expansivity at the same temperature obtained from the 2nd order polynomial fit of volumes.

Table 4. Molar volume of glasses.

V (cm^3 $mole^{-1}$) = a + $b \times 10^{-4}$ T + $c \times 10^{-7}$ T^2 with T = temperature in °C.

	a	b	c	Temperature (°C)
AN100	102.87	15.00	2.94	20-780
AN70DI30	94.94	14.72	4.50	20-710
AN50DI50	88.83	16.53	3.57	20-680
AN20DI80	81.01	15.54	5.07	20-660
DI100	75.93	14.25	8.75	20-660

cooling/heating rate: 5/5 (°C/min)

Table 5. Molar weight (g) and glass and liquid densities (g cm^{-3}).

	densities						molar weight
Temperature (°C)	20.5	1422	1447	1522	1572	1622	
AN100	2.704	–	–	–	2.6033	2.5954	278.211
AN70DI30	2.735	–	2.6197	2.6107	–	–	259.714
AN50DI50	2.784	2.6293	–	2.6168	–	–	247.382
AN20DI80	2.824	2.6324	–	2.6202	–	–	228.885
DI100	2.851	2.6340	–	2.6178	–	2.6010	216.553

Table 6. Observed molar liquid volumes (cm^3 $mole^{-1}$).

Temperature (°C)		1422	1447	1522	1572	1622
AN100	104.466 (920°C)	–	–	–	106.869	107.194
AN70DI30	96.445 (860°C)	–	99.139	99.480	–	–
AN50DI50	90.439 (830°C)	94.087	–	94.536	–	–
AN20DI80	82.632 (810°C)	86.949	–	87.354	–	–
DI100	77.504 (810°C)	82.215	–	82.723	–	83.258

All volumes are ±0.2% at 1σ.

Table 7. Molar liquid volumes.

$V \ (cm^3 \ mole^{-1}) = a + b \times 10^{-3} \ T + c \times 10^{-6} \ T^2$ with T = temperature in °C.

	a	b	c	$\sum (residual)^2$
AN100	100.36(1.52)	4.93(2.56)	-0.47(1.01)	0.0172
	101.07(0.05)	3.74(0.05)		0.0176
AN70DI30	90.50(0.70)	8.32(1.27)	-1.61(0.53)	0.0057
	92.61(0.04)	4.52(0.04)		0.0108
AN50DI50	82.75(0.14)	11.05(0.26)	-2.17(0.11)	0.0004
	85.50(0.04)	5.98(0.05)		0.0143
AN20DI80	73.17(0.03)	14.37(0.06)	-3.32(0.03)	0.0001
	77.26(0.07)	6.70(0.07)		0.0345
DI100	67.79(0.15)	14.47(0.28)	-3.05(0.121)	0.0016
	71.72(0.09)	7.23(0.09)		0.0988

moduli of diopside and anorthite glasses (BANSAL and DOREMUS, 1986) allow us to confirm this approximation for the anorthite-diopside system as illustrated in Fig. 6. The viscosity-temperature relationships of melts on the anorthite-diopside join are reproduced from TAUBER and ARNDT (1987). The calorimetric/dilatometric peak temperature for each composition has been plotted on the corresponding viscosity-temperature relationship. The resulting array of points describes an isokom. The similar values of shear modulus for diopside and anorthite melts (BANSAL and DOREMUS, 1986) and the isokom obtained in Fig. 6 lead to the conclusion

that enthalpy, volume, and shear relaxation vary sympathetically across the anorthite-diopside join and confirm the approximation of the Maxwell relation as a source of shear relaxation times. The glass transition, consistently measured
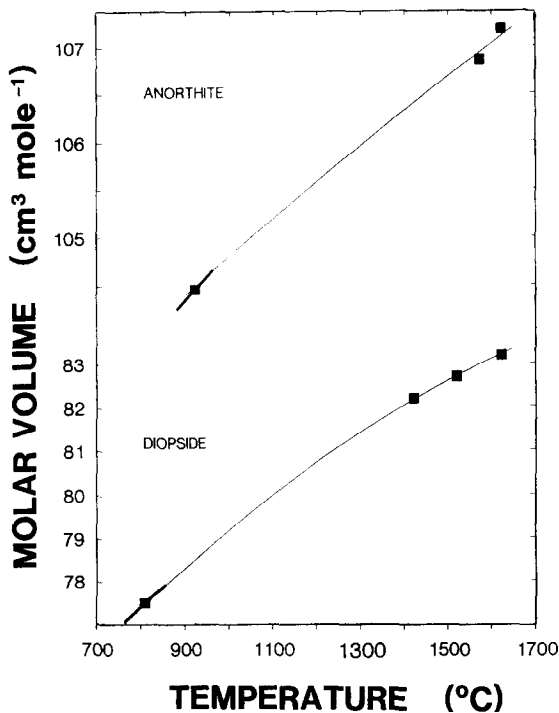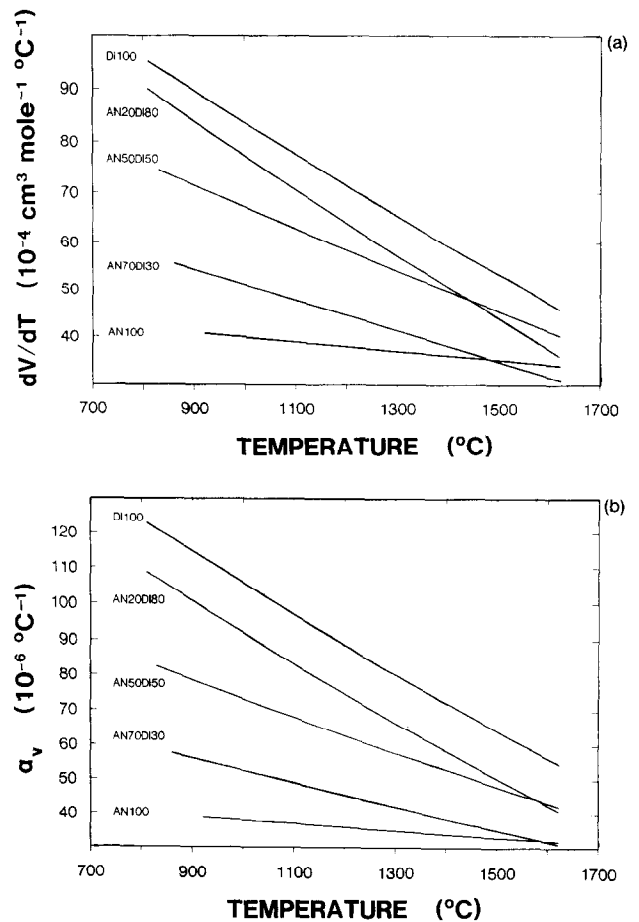

FIG. 5. Temperature dependence of (a) dV/dT derived from the fits to high- and low-temperature volumes and (b) $\alpha_v [1/V(dV/dT)]$ derived from the fits to high- and low-temperature volumes.

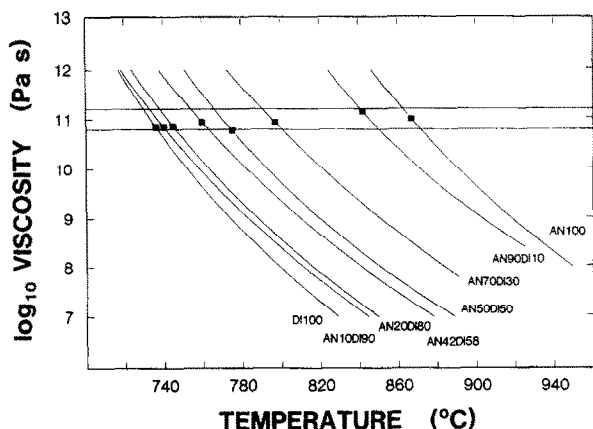FIG. 4. Relaxed liquid volume data from dilatometry and densitometry for anorthite and diopside.

FIG. 6. Comparison of peak temperature and viscosity along the diopside-anorthite join. The glass transition temperature T_g approximates an isokom.

and described in silicate melts, approximates an isokom (e.g., RICHET, 1984).

The viscosity of diopside and anorthite melts exhibit very similar curvatures when plotted vs. temperature (Fig. 6). RICHET (1984) has interpreted this non-Arrhenian nature according to the configurational entropy theory of viscous relaxation (ADAM and GIBBS, 1965). In this theory it is the temperature dependence of the configurational entropy which parameterizes the non-Arrhenian nature of the temperature dependence of viscosity. The extant data on the configurational entropy of silicate melts, obtained by thermodynamic paths through the crystal and melting (RICHET, 1984) and by low-temperature adiabatic data for the configurational entropy of the frozen structure of the glass at the glass transition temperature (RICHET et al., 1986), confirm the applicability of the configurational entropy model where sufficient data exist for a rigorous test.

An alternative model is based on the concept of unoccupied or "free" volume in the liquid structure (e.g., COHEN and GREST, 1979). Although it is difficult to visualize the manner in which "free" volume could increase with pressure, necessary to explain the negative pressure dependence of liquid viscosity (e.g., SCARFE et al., 1987), this model has been advocated for the present system (TANIGUCHI, 1989). Here we wish to point out that the apparent contrast between similar (subparallel) viscosity-temperature relationships for diopside and anorthite (RICHET, 1984) and very dissimilar temperature dependencies of thermal expansion for these liquids (this study) appear to point to a detachment of the temperature dependence of volume from the temperature dependence of the liquid viscosities.

What is the structural origin of the temperature dependence of expansivity? The difference in stoichiometry between diopside and anorthite offers several possibilities. Quenched diopside melts illustrate that there is a nonrandom distribution of nonbridging oxygens (MYSEN et al., 1982). Furthermore, this dispersion is modifying-cation (Ca or Mg) specific. Thus, any change in the distribution of Ca vs. Mg in the melt should result in a change in the distribution of nonbridging oxygens. A second possibility is temperature-dependent coordination changes of cations. Tetrahedral co

ordination of Mg (average coordination number of 4.7 ± 0.3) in high-temperature melts has been suggested by X-ray spectroscopy (WASEDA, 1981).

The chemical complexity of the present join (An-Di) precludes structural conclusions at this time. Simpler systems are under investigation to elucidate the structural origin of the temperature-dependent properties.

CONCLUSION

A method of determining supercooled liquid expansivity and molar volume just above the glass transition temperature has been applied to the anorthite-diopside system. These low-temperature data in combination with volume data obtained from high-temperature densitometry result in the determination of thermal expansivity from just above the glass transition to about 1600°C. The volume fits indicate, in general, a significant negative temperature dependence of the expansivity which results in a 50% decrease in expansivity between 800 and 1500°C for diopside melt. This temperature dependence of expansivity decreases with anorthite content. Anorthite melt has no measurable temperature dependence of expansivity.

The present study solves an existing discrepancy between dilatometric and densitometry data. The improved precision of the method sets the stage for a detailed investigation of the composition dependence of expansivity in silicate melts.

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