Partial molar volume of water in phonolitic glasses and liquids

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Partial molar volume of water in phonolitic glasses and liquids

Abstract The volumes and expansivities of four hydrous phonolite glasses and liquids have been measured by dilatometry from 300 K up to the glass transition and over a 50 K interval just above the glass transition. The partial molar volume of water is independent of the water content for the glass and liquid phases, with values of about 11.0 ± 0.5 and 17.1 ± 0.9 cm^3/mol at 300 and 800 K, respectively. The partial molar thermal expansivity of water in phonolite glasses is about 8×10^{-5} K^{-1}, a result similar to recently published values for different silicate compositions, and about 36.5×10^{-5} K^{-1} in phonolite liquids. The implications for melt density and water dissolution are discussed.

Introduction

Water is the most important volatile component in the Earth's crust and mantle. It exerts a strong influence on the physical and chemical properties of silicate melts and hence on magma ascent and phase equilibria. Its tremendous effects on viscosity are now rather well documented through measurements on a score of different silicate compositions (e.g., Dingwell et al. 1996; Richet

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et al. 1996; Whittington et al. 2000, 2001). As a light oxide, however, it is clear that water markedly affects the density of the melt. On the basis of their own dilatometry measurements for three materials and the high-temperature, high-pressure measurements of Burnham and Davis (1971) for a hydrous albite-like liquid, Ochs and Lange (1997, 1999) recently reported that dissolved water behaves as other oxides by having a partial molar volume in melts which is independent of composition. For instance, they gave $\overline{V}_{H_2O} = 22.9 \pm 0.6$ cm^3/mol at 1,273 K and 1 bar.

From a review of density data for a great many hydrous glasses, Richet et al. (2000) supported this conclusion at room pressure and temperature since they found that $\overline{V}_{H_2O}$ is constant, with a value of 12.0 ± 0.5 cm^3/mol which is valid for up to 7 wt% contents for polymerized, silica-rich as well as for depolymerized, silica-poor compositions. In view of the database available to Ochs and Lange (1997, 1999), however, it was not clear whether the same conclusion would also apply at higher temperature to melts in the very wide range of geologically important compositions. To expand the composition range of silicate melts dealt with, in this paper we report volume measurements for a series of hydrous phonolite liquids. Taking advantage of a newly developed technique, we show how equilibrium measurements can be performed for hydrous supercooled liquids over significant temperature intervals.

The starting point is the demonstration made by Richet et al. (1996) that physical properties of hydrous supercooled liquids can be measured accurately at 1 bar as long as the viscosity is higher than about 10^{10} Pa.s because the rate of water exsolution then remains negligibly small. As this was also the basis of the dilatometry experiments made by Ochs and Lange (1997, 1999), the distinctive feature of our present measurements is that we follow the procedure set by Toplis and Richet (2000) and Sipp and Richet (unpublished), whereby reversed volume measurements are made on supercooled liquids just above the glass transition. In addition, the good precision of the experiments has allowed us to

determine the influence of decompaction on the apparent thermal expansion of glasses synthesized at a few thousand bars pressure. As a continuation of our systematic study of hydrous melts, we have first investigated the hydrous phonolite glasses and melts which we have already studied by viscometry (Whittington et al. 2001), calorimetry (Bouhifd et al., unpublished), and NMR spectroscopy (Robert et al. 2001).

Experimental methods

The dry sample was prepared from oxide and carbonate mixes through repeated cycles of grinding and fusion as described by Schairer and Bowen (1956). The chemical composition, which is an iron-free analog of a phonolitic composition, was checked by electron microprobe analysis (Table 1). The samples were then hydrated at high temperatures and pressures with the procedure reported by Whittington et al. (2001). The hydration conditions and the water contents measured by Karl-Fischer titration are given in Table 2. Samples of about 10 mg were analyzed in this study, for which the uncertainty on the reported water content is around 0.10 wt% H_2O (Behrens et al. 1996). The room-temperature densities of the glasses included in Table 2 were measured by an Archimedean method with toluene as the immersion liquid, as described by Richet et al. (2000). After each dilatometry measurement, the density of the sample was also measured as a way of determining the extent of volume relaxation. Likewise, we checked by weighing that no water loss occurred during heating at the highest temperatures. For the hydrated glasses, two sets of density are thus available (see Table 2), for the initially compressed glasses and the relaxed glasses after dilatometry or DSC measurements.

The experimental setup used in this work is described in detail by Sipp (1998) and Sipp and Richet (unpublished). Briefly, the furnace is made of two Fibrothal half shells (from Kanthal) and has its temperature regulated with a PID. controller. Temperatures are measured with a Pt–Pt/Rh 10% thermocouple placed near the sample. With a dilatometric technique we measure the length of the sample as a function of temperature as the difference between the displacement of two SiO_2 rods placed on a sample and on a cylinder of reference SiO_2 glass. These measurements are made to within about 0.2 μm with linear variable differential transducers. Silica was chosen as a reference material because its expansivity is approximately zero over the studied temperature intervals.

Because glasses and liquids are isotropic, we obtained the volume coefficient of thermal expansion α of all samples simply by multiplying the linear coefficient α_{lin} by three:

$$\alpha_g = 3\alpha_{lin} = 3/L(\partial L/\partial T) = 3\partial ln(L)/\partial T \qquad (1)$$

where L is the length of the sample and T the temperature. To determine the coefficients of thermal expansion of glasses and liquids we have adopted two different strategies. For glasses, we heated the samples continuously from room temperature to a temperature corresponding to a viscosity of 10^{13} Pa.s (T_{13}), known from our previous viscosity experiments, at a constant rate of 2 K/min. For liquids, the temperature T_{13} was taken as a reference temperature, and the sample held at this temperature until a constant length was obtained. The temperature of the sample was then increased or decreased by 10 K steps at 2 K/min and kept constant until a new equilibrium length was reached. Different temperatures over a range of 50 degrees were studied in this manner. The time spent at each temperature was variable, more time being required at lower temperatures (cf. Fig. 1). An important feature of this protocol is that two or more length changes can be measured for each temperature (i.e., upon heating and cooling), providing checks that the measured lengths represent equilibrium values.

This is the procedure described by Toplis and Richet (2000) for anhydrous samples, with the exception that a measurement at T_{13} was not made after the measurements at each other temperature, in order to limit the duration of the experiment and thus the risk of water exsolution. Actually, it is the slowness of water exsolution in the temperature interval investigated that makes accurate measurements possible in the supercooled liquid state just above the glass transition. Because length changes are measured with high precision, the expansivities are generally determined to better than 3% (Toplis and Richet 2000). In this work we set a conservative upper limit of 5% for the experimental uncertainty.

Results

Thermal expansion of hydrous glasses

The thermal expansion of hydrated glasses was investigated with a heating rate of 2 K/min from 300 K up to

Table 1 Phonolite glass composition

Oxide	Phonolite	
	Wt%	Mol%
SiO_2	58.82 (29)	65.40
Al_2O_3	19.42 (18)	12.72
MgO	1.87 (06)	3.10
CaO	2.35 (05)	2.80
Na_2O	9.31 (31)	10.03
K_2O	7.44 (05)	5.28
TiO_2	0.79 (08)	0.66

Table 2 Water contents, densities, thermal expansion of the glasses, liquids and temperature intervals of the measurements

| Sample	H_2O (wt%)	ρ^a (g/cm³)	α_g^a (10^{-5} K⁻¹)	ρ^b (g/cm³)	α_g^b (10^{-5} K⁻¹)	Diff. %[c]	ΔT (K)[d]	α_l (10^{-5} K⁻¹)	ΔT (K)
Phon 0.0	0.0	–	–	2.457	2.531	–	300–700	7.785	875–925
Phon 0.8	0.78	2.472	2.559	2.464	2.496	2.5	300–750	8.381	770–810
Phon 1.6	1.59	2.460	2.885	2.458	2.598	11.0	300–650	9.509	680–720
Phon 2.2[e]	2.15	2.458	–	2.450	–	–	–	–	–
Phon 3.2	3.20	2.438	3.234	2.433	3.122	3.6	300–600	10.820	605–645
Phon 5[e]	4.72	2.412	–	2.406	–	–	–	–	–

[a]Density as synthesized (at 2 kbar and 1,200 °C for Phon 0.8 and Phon 3.2; and at 3 kbar and 1,300 °C for the others)
[b]Density after relaxation during dilatometry or DSC measurements
[c]Difference between the coefficients of thermal expansion of compacted and relaxed glasses [diff.% = $(\alpha_g^a - \alpha_g^b)/\alpha_g^b$]
[d]The same interval of temperatures was used for compacted and relaxed glasses
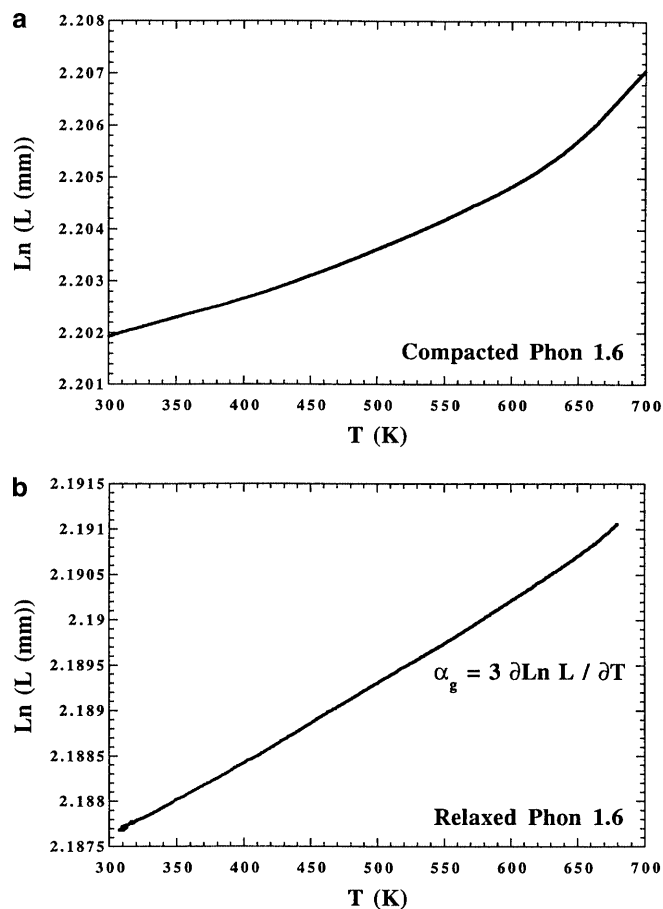[e]Samples used in DSC experiments (Bouhifd et al., unpublished)
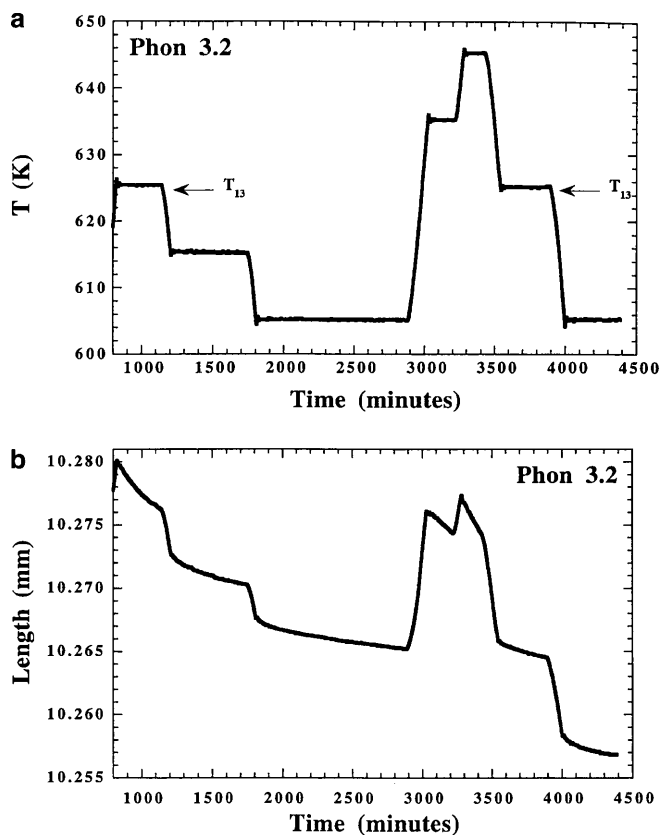
Fig. 1 a Typical temperature–time path followed for hydrated phonolite samples, in this case Phon 3.2, where the *arrow* indicates the reference temperature T_{13}. b Variation of the sample length in response to the temperature changes shown in a. The length variation ΔL_i corresponds to the temperature change ΔT_i

Fig. 2a, b Difference between the expansion [ln (L) vs. T] of compacted a and relaxed b glasses at a heating rate of 2 K/min. Note that a constant slope is observed up to T_{13} once a sample hydrated at a high pressure has relaxed to the 1-bar configuration

T_{13}. After the first measurement on an initially compacted glass, we observed a decrease in the density of the sample due to relaxation towards its equilibrium density at 1 bar pressure (cf. Table 2) without any mass change. A second measurement was then performed with the same heating rate on the relaxed sample. No density or mass variations were observed after this second measurement. Typical experiments are shown in Fig. 2, where a distinct behavior is observed for compacted and relaxed glasses.

For relaxed glasses, the length varies linearly with temperature up to T_{13}. For compacted glasses, in contrast, an anomalously high dilation is observed when the density begins to relax to the 1 bar values. This happens at temperatures at which the viscosity would be around 10^{16} Pa.s as indicated by extrapolation of the viscosity measurements of Whittington et al. (2001). For each glass we calculated the thermal expansion coefficient between room temperature and the highest temperature up to which expansion was linear. For relaxed glasses, this took place up to T_{13}. For compacted glasses, this was observed only up to the onset of volume relaxation. Even when excluding the data affected by relaxation, one finds that the coefficients of thermal expansion of compacted glasses are systematically higher than those of relaxed glasses by about 3–11%. This demonstrates that differences in fictive pressures of only 2 or 3 kbar have minor but detectable effects on the coefficient of thermal expansion.

Thermal expansion of hydrous liquids

In order to verify the reproducibility of the observations, two series of experiments were made on each liquid over temperature intervals of 50 K (Fig. 1a). Because of the penetration of the SiO_2 rod into the surface of the sample, the apparent length decreased with time with the steepest slope at the highest temperatures (Fig. 1b). As described in detail by Toplis and Richet (2000), micro-penetration can be easily taken into account to determine the equilibrium length even when, at the highest temperatures, this effect becomes significant. We also note that total penetration was only a few micrometers during a given series of experiments, which represents a very small fraction of the 10-mm initial length of the samples.
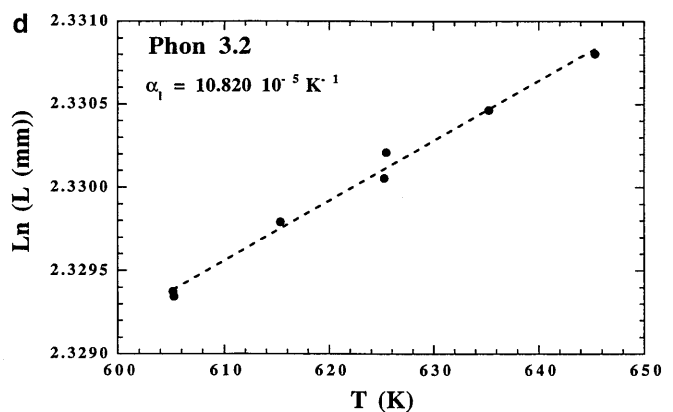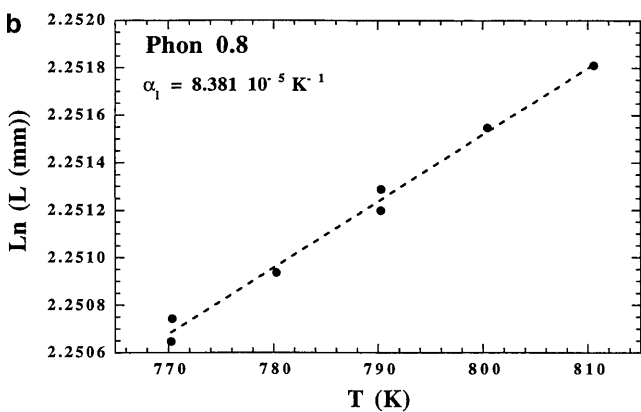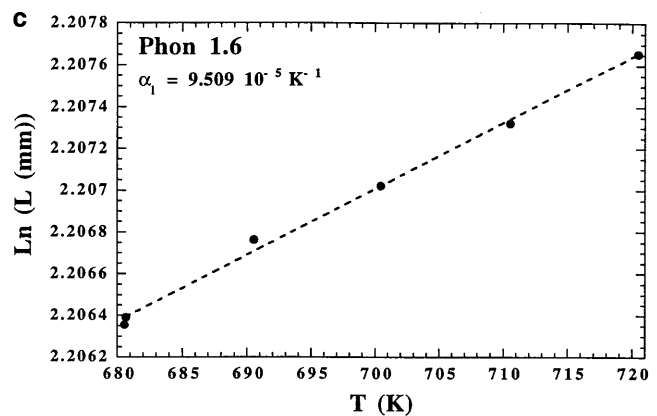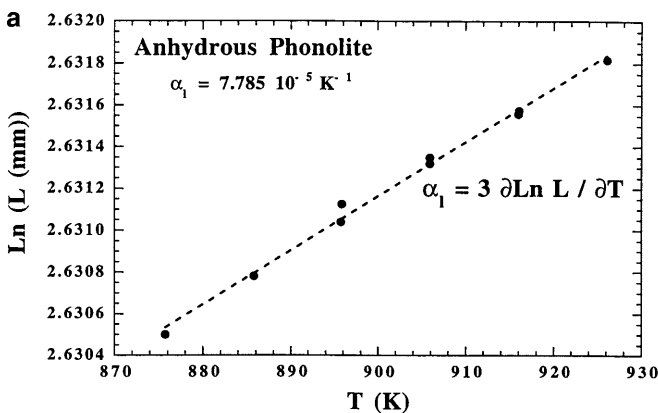
Table 3 Length of hydrous phonolitic liquids as a function of temperature

Phon 0.0		Phon 0.8		Phon 1.6		Phon 3.2	
T (K)	L (mm)	T (K)	L (mm)	T (K)	L (mm)	T (K)	L (mm)
875.8	13.8807	770.3	9.4939	680.7	9.0829	605.2	10.2712
885.8	13.8846	770.4	9.4948	680.5	9.0826	605.2	10.2715
895.8	13.8882	780.3	9.4966	690.5	9.0863	615.4	10.2758
895.9	13.8894	790.3	9.4987	700.5	9.0886	625.2	10.2785
906.0	13.8921	790.3	9.4999	710.5	9.0913	625.5	10.2801
906.0	13.8925	800.5	9.5024	720.5	9.0944	635.2	10.2827
916.0	13.8954	810.6	9.5049	–	–	645.4	10.2862
916.1	13.8956	–	–	–	–	–	–
926.1	13.8990	–	–	–	–	–	–

The observed lengths of the hydrous samples are listed in Table 3 and plotted in Fig. 3. Within the uncertainties of our technique, the logarithm of the length varies linearly with temperature for all supercooled liquids. The slope of these lines thus represents the linear thermal expansion coefficient, which could thus be determined from Eq. (1). These slopes increase with increasing water content, but note that the studied temperature ranges are lower for higher water contents since the glass transition temperature decreases with increasing water content.

Fig. 3a–d Variations of sample lengths with temperature for anhydrous and hydrated phonolite liquids. **a** Anhydrous phonolite liquid between 875 and 925 K; **b** Phon 0.8 liquid (0.78 wt% H_2O) between 770 and 810 K; **c** Phon 1.6 liquid (1.59 wt% H_2O) between 680 and 720 K; **d** Phon 3.2 liquid (3.20 wt% H_2O) between 605 and 645 K

Possible water loss was a serious concern because the samples were quenched under pressures of 2 or 3 kbar, whereas the solubility of water in silicates at 1 bar is extremely low. We emphasize that no significant changes in sample weights were observed after the experiments. As a more sensitive check, the viscosity of the same supercooled liquids was measured in the same temperature ranges. No influence of thermal history on the measured viscosities was apparent and the variations of the viscosities with temperature are as smooth as for water-free samples (Whittington et al. 2001). Owing to the tremendous influence of water on viscosity, this excellent precision demonstrates unequivocally the lack of significant change in the water content during high-temperature measurements. As long as the viscosity is higher than about 10^9 Pa.s, we thus con-

a Anhydrous Phonolite

$\alpha_l = 7.785 \ 10^{-5} \ K^{-1}$

$\alpha_l = 3 \ \partial Ln \ L / \partial T$

c Phon 1.6

$\alpha_l = 9.509 \ 10^{-5} \ K^{-1}$

b Phon 0.8

$\alpha_l = 8.381 \ 10^{-5} \ K^{-1}$

d Phon 3.2

$\alpha_l = 10.820 \ 10^{-5} \ K^{-1}$

clude that water diffusivity is too small to produce changes in the water content of our samples. Note also that the same behavior was observed during viscosity measurements for andesitic melts which had identical room-temperature infrared spectra of the glasses both prior to and after high-temperature viscometry (Richet et al. 1996).

Partial molar volume of water in glasses under ambient conditions

The densities measured for the compacted and relaxed hydrous glasses are listed in Table 2, where we have added the results for two other hydrated samples studied in differential scanning calorimetry (DSC) experiments over a similar temperature range (namely, Phon 2.2 and Phon 5 of Bouhifd et al., unpublished). A propagation of the errors on both density and chemical analyses indicates an uncertainty on the room-temperature V that ranges from 0.1 to 0.3%. As shown in Fig. 4, the V–x relationship of phonolite is linear to within experimental errors, which implies that the partial molar volume of water in glasses is constant over the composition range investigated. Under ambient conditions $\overline{V}_{H_2O}$ was determined, by the intercept method, to be 11.0 ± 0.5 cm^3/mol from a plot of the volume of relaxed glasses against the mole fraction of H_2O.

Volume of dry and hydrous phonolite compositions

From 300 K to the glass transition temperature, the volume of each glass sample is calculated from:

$$V_g(T) = V_g(300K) \exp[\alpha_g(T - 300)] \qquad (2)$$

where V_g (300 K) is the volume at 300 K, and α_g is the thermal expansion coefficient. The errors on $V_g(T)$ derived from Eq. (2) are given by:

$$\Delta V_{rg}(T) = V_g(T)[\delta V_g(300K)/V_g(300K) + (T - 300)\delta\alpha_g + \alpha_g\delta T] \qquad (3)$$
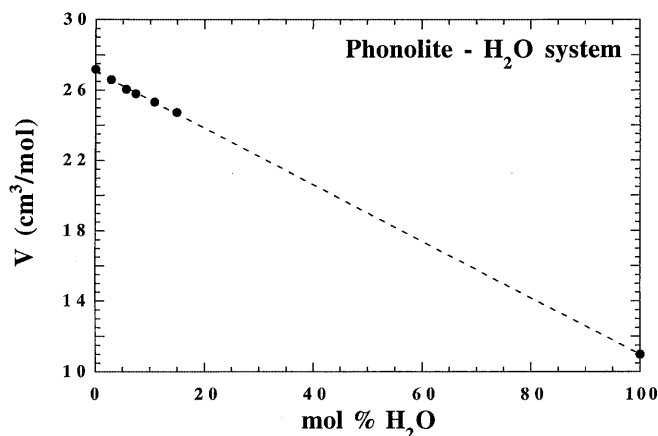

Fig. 4 Room-temperature molar volumes of hydrous phonolite glasses

From this equation it is clear that the uncertainty on $V_g(T)$ is highest around the glass transition temperature T_g. The contribution of $\alpha_g\Delta T$ on $\Delta V_g(T)$ is so small that it can be neglected. For anhydrous phonolite, the error at 875 K (i.e., just below the glass transition temperature) is about 0.04 cm^3/mol, which represents 0.14% of the molar volume. For the three hydrous glasses studied, the error is slightly higher, at about 0.20 cm^3/mol, which represents about 0.7% of V at the glass transition temperatures.

For the liquids, the volume is given by:

$$V_l(T) = V_g(300K) \exp[\alpha_g(T_0 - 300) + \alpha_l(T - T_0)] \qquad (4)$$

where T_0 is the lowest temperature reached during the experiments and α_l is the thermal expansion coefficient of the liquid. The errors on these values are given by:

$$\Delta V_l(T) = V_l(T)[\Delta V_g(300K)/V_g(300K) + (T_0 - 300)\delta\alpha_g + (T - T_0)\delta\alpha_l] \qquad (5)$$

In the investigated temperature ranges they are about 0.1 and 0.5 cm^3/mol for the anhydrous and the hydrous phonolite liquids, respectively. In Eq. (5) we assume $\Delta\alpha_g = \Delta\alpha_l = 5\%$ and we again consider that the contribution of $\alpha_l\Delta T$ to the error is too small to be taken into account. Of course, the errors do not remain acceptable when the data are extrapolated well beyond the range of the measurements because of the $(T - T_0)$ term.

Partial molar volume of water in liquids

The volumes of dry and hydrous phonolite glasses and liquids calculated from Eqs. (2) and (4) and the thermal expansion coefficients determined in this work are reported in Tables 2 and 4 (Vcal are calculated with the parameters in Table 5) and plotted in Fig. 5. For all compositions, the volume increases markedly at the glass transition, and this increase is most important for the highest water contents.

Within experimental errors the volume of hydrated phonolite liquids also varies linearly with the mole fraction of water between 600 and 800 K. The V–x relationships yield partial molar volumes of water of 15.32 ± 0.9 and 17.06 ± 0.9 cm^3/mol at 600 and 800 K, respectively (Fig. 6). Considering only the hydrous volume liquids, we obtain from a linear fit to the partial molar volumes of water between 600 and 800 K the following equation:

$$\overline{V}_{H_2O} = 10.17 + 8.82 \cdot 10^{-3} T(K) \qquad (6)$$

The errors on $\overline{V}_{H_2O}$ determined in this manner are about ± 0.9 cm^3/mol. Combining Eq. (6) and the volume equation obtained for the anhydrous phonolite, we have:

$$V_{an.phon.} = 25.61 + 2.26 \times 10^{-3} T(K) \qquad (7)$$

This equation reproduces our experimental data to within 0.5%.

Table 4 Comparison between measured and calculated volumes (cm³/mol)

Sample	T (K)	V_{exp}[a]	V_{cal}[b]	Diff.%
Phon 0.0	875	27.59 ± 0.04	27.33	0.9
	885	27.61 ± 0.04	27.35	0.9
	895	27.63 ± 0.04	27.36	1.0
	905	27.66 ± 0.04	27.38	1.0
	915	27.68 ± 0.04	27.40	1.0
	925	27.70 ± 0.05	27.41	1.0
Phon 0.8	770	26.87 ± 0.20	26.87	0.0
	780	26.89 ± 0.20	26.89	0.0
	790	26.92 ± 0.20	26.91	0.04
	800	26.94 ± 0.20	26.93	0.04
	810	26.96 ± 0.20	26.95	0.04
Phon 1.6	680	26.33 ± 0.18	26.44	−0.4
	690	26.36 ± 0.19	26.46	−0.4
	700	26.38 ± 0.19	26.48	−0.4
	710	26.41 ± 0.19	26.50	−0.3
	720	26.43 ± 0.19	26.52	−0.3
Phon 3.2	605	25.57 ± 0.16	25.77	−0.8
	615	25.60 ± 0.17	25.80	−0.8
	625	25.63 ± 0.17	25.82	−0.7
	635	25.66 ± 0.17	25.85	−0.7
	645	25.69 ± 0.17	25.87	−0.7

[a]Errors on the liquid volumes calculated from Eq. (5)
[b]V_{cal} calculated with the parameters listed in Table 5

Table 5 Parameters of the liquid volume Eq. (8)

Oxide	$\overline{Vi}(cm^3/mol)$	$d\overline{Vi}/dT(cm^3/molK)$	Reference
T_{ref} = 1,073 K			
SiO_2	26.86	0	Lange (1997)
Al_2O_3	37.42	0	Lange (1997)
MgO	9.57	3.27×10⁻³	Lange (1997)
CaO	14.10	3.74×10⁻³	Lange (1997)
Na_2O	23.88	7.68×10⁻³	Lange (1997)
K_2O	38.22	12.08×10⁻³	Lange (1997)
TiO_2[a]	28.32	0	Lange and Carmichael (1987)
T_{ref} = 1,273 K			
H_2O	22.89	9.55×10⁻³	Ochs and Lange (1999)

[a]See text for more details

Discussion

Prediction of liquid volumes

Our results can be compared to the volumes calculated from the model recently proposed by Ochs and Lange (1999), which is an extension to hydrous liquids of the model derived by Lange (1997) for silicate melts from the glass transition to superliquidus temperatures. With oxides as components, the volume of a melt is a given by:

$$V_l(T) = \Sigma x_i[V_i(T_{ref}) + dV_i/dT(T - T_{ref})] \qquad (8)$$

where x_i is the mole fraction of oxide i, $V_i(T_{ref})$ is the partial molar volume of oxide i at T_{ref}, and dV_i/dT is the partial molar thermal expansivity of oxide i. The partial molar volume of TiO_2 is 28.32 and 23.87 cm³/mol in sodium and calcium silicate liquids, respectively (Lange and Carmichael 1987). Because our phonolite is more alkali- than alkaline-earth rich, we have used the former but the latter would yield volumes lower by only 0.1%

because of the low TiO_2 content involved. The volumes calculated in this way reproduce our observations (Table 4) to better than 1%, thus supporting the validity the model of Lange (1997) and Ochs and Lange (1999) for phonolite compositions.

Effect of water on α_g and α_l

In Fig. 7 we plot the thermal expansion coefficients of phonolite glasses and liquids against the water content. Within its 5% estimated uncertainty α varies linearly with water content up to 11 mol% H_2O for both phases. For the glasses, the coefficients determined in this work (Table 2) increase from 2.53×10⁻⁵ K⁻¹ for anhydrous phonolite to 3.12×10⁻⁵ K⁻¹ for a hydrated phonolite with 10.9 mol% H_2O, which represents an increase of about 20%. The small pressure dependence on the coefficients of thermal expansion is also apparent in Fig. 7 as the difference between the data for compacted and relaxed glasses. For glasses, the best fit linear equation for thermal expansion for all data is: $10^5\alpha = 2.410+$
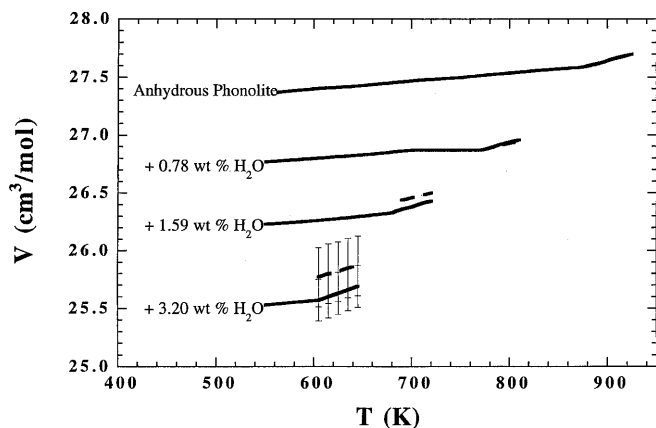
Fig. 5 Molar volumes of hydrous phonolite glasses and super-cooled liquids (*thick solid line*) and calculated values for liquids from the model of Lange (1997) and Ochs and Lange (1999) (*thick dashed line*, see text)
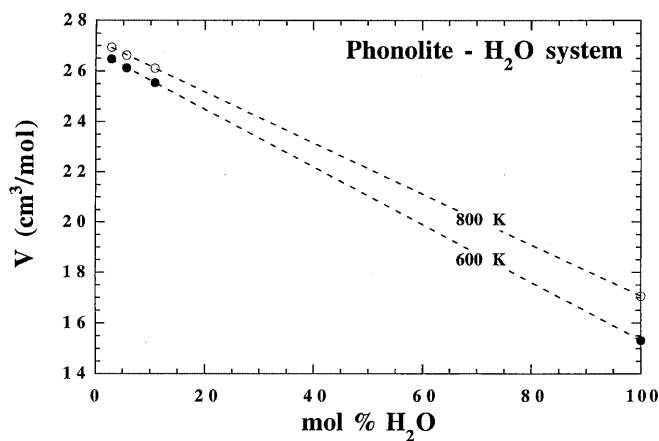

Fig. 6 Molar volumes of hydrous phonolite liquids at 600 and 800 K

$0.0573x_{H_2O}$, which yields a value of 8.1×10^{-5} K^{-1} for the partial molar thermal expansion coefficient of water.

Our results show that the effect of water on the thermal expansion of glasses is not anomalously high. This observation is consistent with the results of Shelby and McVay (1976), Jewell et al. (1990), and Jewell and Shelby (1992), which demonstrate the slight influence of water on thermal expansion for a variety of glasses containing 600 or 1,850 ppm H_2O. More significantly, the observations of Tomozawa et al. (1983) for hydrated $Na_2Si_3O_7$ glasses indicate that α_g is twice as great for a sample with 22 mol% H_2O than for the water-free glass, which actually corresponds to a mean coefficient of about 4×10^{-5} K^{-1} for the water component. Indeed, such a coefficient is comparable to the value of 6×10^{-5} K^{-1} derived from the data of Ochs and Lange (1997) for hydrous albite glasses as a function of water content, or to the value of 8×10^{-5} K^{-1} derived from our experiments.

For the liquid phase, the difference in thermal expansion coefficient is about 40% between the anhydrous
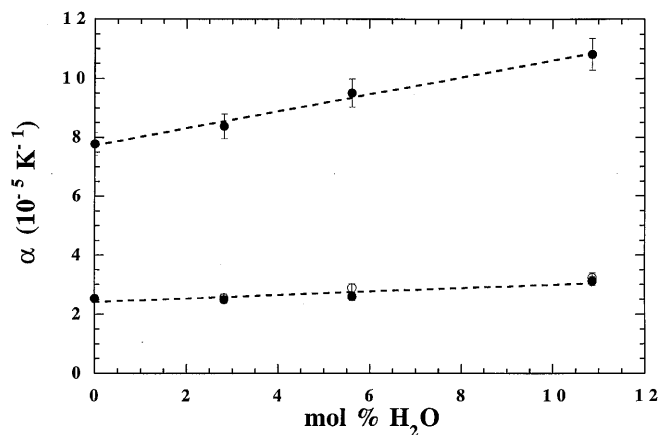
Fig. 7 Coefficients of thermal expansion of hydrous phonolite glasses and liquids. For glasses, the data are shown for compacted (*open circles*) and relaxed glasses (*solid circles*)

sample (7.8×10^{-5} K^{-1}) and that with 10.9 mol% H_2O (10.8×10^{-5} K^{-1}). The best fit to all data is: $10^5\alpha = 7.734 + 0.287x_{H_2O}$, which gives a value of 36.5×10^{-5} K^{-1} for $\overline{\alpha}_{H_2O}^{liq}$ between 600 and 800 K.

Configurational thermal expansion

The differences observed between the expansion behavior of hydrated glasses and liquids in this work reflect the existence of configurational contributions to the liquid expansivities, which are nonexistent in glasses. Since the lack of compositional effects on thermal expansion is a salient feature of glasses just below the glass transition, the complexities affecting melts find their roots in the structural changes which begin to take place at this transition. As extensively discussed for the heat capacity, the thermal expansivity of silicate liquids is made up of vibrational and configurational parts (Richet and Neuville 1992; Lange 1997). Hence one can write that:

$$dV_i/dT = dV_i^{vib}/dT + dV_i^{conf}/dT \qquad (9)$$

where dV_i^{vib}/dT and dV_i^{conf}/dT are the vibrational and configurational contributions, respectively, to dV_i/dT, the latter representing the abrupt jump in thermal expansivity at the glass transition.

For anhydrous phonolite, the vibrational and configurational contributions to the expansivity are 0.7×10^{-3} and 1.5×10^{-3} K^{-1}, respectively. Combining these values with those of the hydrous samples we find that dV^{vib}/dT and dV^{conf}/dT are 2.0×10^{-3} and 7.3×10^{-3} K^{-1}, respectively, for the water component. With respect to the vibrational contributions of the expansivity, water behaves similarly to alkali oxides (Shelby and McVay 1976; Richet et al. 2000). The partial thermal expansivity of water is between those of alkali oxides (Na_2O and K_2O) and alkaline-earth oxides (CaO and MgO) determined by Lange (1997). For the liquid phase, the configurational contribution to the partial thermal expansivity of water is about 79%, closer to those of

alkaline-earth components [for CaO: 70($\pm$4)% and for MgO: 77($\pm$7)%] (Lange 1997).

Water in aluminosilicate melts

Water is now well known to dissolve in aluminosilicate melts as both hydroxyl groups and molecular water. At low water contents (i.e., less than 3 wt%), hydroxyl groups are the dominant hydrous species. For water contents of 3 to 4 wt% water dissolves in about equal amounts of OH^- and H_2O. Above 4 wt% most of water is dissolved as molecular water (e.g., Stolper 1982; Silver et al. 1990). The formation of hydroxyl groups can be described by the following reaction:

$$H_2O_{mol} + O_b^{2-} = 2OH^- \tag{10}$$

where H_2O_{mol}, O_b^{2-}, and OH^- denote molecular water, bridging oxygens of the silicate framework, and hydroxyl groups, respectively.

Although water speciation is usually measured on quenched glasses, recent studies have shown that the fraction of water present as hydroxyl groups increases on heating above the glass transition temperature (Nowak and Behrens 1995; Shen and Keppler 1995; Sowerby and Keppler 1999; see also the review paper of Kohn 2000). Despite the observation that the equilibrium reaction (10) is shifted to the right with increasing temperature, the effect of water on the viscosity of the hydrated phonolite compositions considered here clearly becomes much less strong with increasing temperature (Whittington et al. 2001). These authors found that, for depolymerized melts, the effect of additional water leads to a very similar viscosity reduction for compositions with similar NBO/T (non-bridging oxygens per tetrahedral cation), irrespective of the identity of the network modifier cations involved (alkali- or alkaline-earth elements). We conclude that the incorporation of water into depolymerized melts is not strongly dependent on the nature of the network modifier cations already present.

The role of hydroxyl groups has been a matter of recent debate, and many different mechanisms have been proposed for dissolution of water in aluminosilicate melts. However, the recent NMR study of Robert et al. (2001) on the same hydrated phonolite compositions indicates that two mechanisms may operate simultaneously, as was suggested by Whittington et al. (2001) on the basis of viscosity measurements on the same compositions. The first mechanism involves breaking the strong T–O–T bonds of the aluminosilicate network, and the second may weaken T–O–T bonds by protonation of the bridging oxygen to create a bridging hydroxyl group.

Regardless of such complexities, the striking fact is that, up to water contents of at least 15 mol%, speciation has no significant effect on both the volume and thermal expansion coefficient of our phonolite glasses and liquids, in agreement with the conclusion of Ochs and Lange (1999) for a hydrous rhyolite and a strongly depolymerized K–Ca silicate. For glasses, this conclu-sion agrees with an extensive review of available data for hydrous silicate glasses covering a wide range of chemical compositions (Richet et al. 2000). As originally noted by Richet and Polian (1998), this indicates that the volume change of reaction (10) is negligible and this is also why this reaction, which is driven by entropy, as also mentioned by Richet and Polian (1998), does not affect the volume of liquids when speciation begins to change above the glass transition.

Within the framework of the Adam–Gibbs configurational entropy theory (Adam and Gibbs 1965; Richet 1984), we finally note that the temperature dependence of the viscosity is mainly determined by changes in configurational entropy. For the hydrous phonolitic melts studied here water enhances non-Arrhenian behavior (Whittington et al. 2001). As a consequence, the configurational entropy and the configurational heat capacity should increase with the amount of water. Indeed, the configurational heat capacity has been found to increase with increasing water content (Bouhifd et al., unpublished). Such correlations between thermodynamic and rheological properties should provide insights into the differences between glasses and melts, and into the restructuring that occurs within and above the glass transition temperature interval.

Conclusions

The results of this paper first reveal the importance of volume relaxation when compacted hydrous samples are heated up at 1 bar. As originally shown for the viscosity, equilibrium measurements are also possible for the volume of hydrous supercooled liquids over a significant temperature interval just above the glass transition. For both phonolite glasses and liquids, the molar volume and thermal expansion coefficient vary linearly with the water content and are thus unaffected by changes in water speciation over the range of water contents investigated. For the liquid phase, the effects of water on volume are consistent with those predicted from the model by Lange (1997) and Ochs and Lange (1999). However, further experiments are required to constrain better and to determine the properties of water over a wide range of temperature and silicate melt compositions.

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