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Partial molar volume of water in phonolitic glasses and liquids

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Abstract The volumes and expansivities of four hydrous phonolitic 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 cm³/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 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 Φ₁H₂O = 22.9 ± 0.6 cm³/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 Φ₁H₂O is constant, with a value of 12.0 ± 0.5 cm³/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 10¹⁰ 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 decomposition 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% H₂O (Behrens et al. 1996). The room-temperature densities of the glasses included in Table 2 were measured by an Archimedes 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 L of the sample as a function of temperature as the difference between the displacement of two SiO₂ rods placed on a sample and on a cylinder of reference SiO₂ 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 x of all samples simply by multiplying the linear coefficient $\alpha_{lin}$ by three:

$$x = 3\alpha_{lin} = 3/L(\partial L/\partial T) = 3\partial \ln(L)/\partial T$$

(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 10¹³ 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

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<th>Table 1 Phonolite glass composition</th>
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<tr>
<td>Oxide</td>
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<tr>
<td>SiO₂</td>
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<tr>
<td>Al₂O₃</td>
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<tr>
<td>MgO</td>
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<tr>
<td>CaO</td>
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<td>Na₂O</td>
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<td>K₂O</td>
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<td>TiO₂</td>
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<th>Table 2 Water contents, densities, thermal expansion of the glasses, liquids and temperature intervals of the measurements</th>
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| Sample | H₂O (wt%) | $ρ^{a}$ (g/cm³) | $x_{g}^{a}$ (10⁻⁵ K⁻¹) | $ρ^{b}$ (g/cm³) | $x_{g}^{b}$ (10⁻⁵ K⁻¹) | Diff. %c | $ΔT$ (K)d | $x_{l}$ (10⁻⁵ K⁻¹) | $ΔT$ (K)

| Phono 0.0 | 0.0 | – | – | 2.457 | 2.531 | – | 300–700 | 7.785 | 875–925 |
| Phono 0.8 | 0.78 | 2.472 | 2.559 | 2.464 | 2.496 | 2.5 | 300–750 | 8.381 | 770–810 |
| Phono 1.6 | 1.59 | 2.460 | 2.885 | 2.458 | 2.598 | 11.0 | 300–650 | 9.509 | 680–720 |
| Phono 2.2 | 2.15 | 2.458 | 2.450 | 2.122 | 3.6 | 3.00–600 | 10.820 | 605–645 |
| Phono 3.2 | 3.20 | 2.438 | 3.324 | 2.433 | – | – | – | – | – |
| Phono 4.2 | 4.72 | 2.412 | – | 2.406 | – | – | – | – | – |

aDensity as synthesized (at 2 kbar and 1,200 °C for Phono 0.8 and Phono 3.2; and at 3 kbar and 1,300 °C for the others)
bDensity after relaxation during dilatometry or DSC measurements
cDifference between the coefficients of thermal expansion of compacted and relaxed glasses [diff. % = ($x_{g}^{b} - x_{g}^{a}$)/$x_{g}^{b}$]
dThe same interval of temperatures was used for compacted and relaxed glasses

*Samples used in DSC experiments (Bouhifd et al., unpublished)