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Energetics of water dissolution in trachyte glasses and liquids

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Abstract—Enthalpies of dissolution in HF solutions have been measured at 323 K for a series of hydrous trachyte glasses. Enthalpies of mixing between water and molten trachyte have then been calculated from heat capacity data for the same set of samples and available enthalpy for pure water. The moderately negative enthalpies of mixing suggested at 1 bar by the measurements made on glasses almost disappear when trachyte liquids and water are referred to the same temperature, and particularly so when enthalpies of mixing are calculated for a few kbars pressure. As found for albite and phonolite liquids, trachyte melts thus appear to mix nearly ideally as far as enthalpy is concerned. These results imply that the enthalpy of exsolution of water from magmas is very small or negligible under the *P-T-X* conditions relevant to trachytic volcanism, even for complete degassing of up to 5 wt% H_2O. Furthermore, the viscosity increase associated with exsolution-driven cooling is negligible compared to the decrease caused directly by water exsolution. *Copyright © 2004 Elsevier Ltd*

1. INTRODUCTION

Enthalpies of mixing of water with magmas are important thermodynamic quantities in view of the fundamental role played by volatiles in magma ascent and eruption. For instance they must be known to determine the thermal budgets of water dissolution and exsolution. From a more theoretical standpoint, water dissolves in silicate melts first as hydroxyl ions and then as molecular water (Stolper, 1982). Hence, enthalpies of mixing are not only useful to model water solubility as a function of temperature and melt composition, but they also yield thermochemical information relevant to OH^-/H_2O speciation. Because of experimental difficulties raised by measurements at the kbar pressures required to dissolve significant amounts of volatiles in molten silicates, however, experimental studies devoted to the energetics of H_2O dissolution in silicate liquids and glasses are generally lacking.

An exception is the work by Clemens and Navrotsky (1987) on albite and haplogranite melts. They found negative enthalpies of mixing through a thermochemical cycle that combined relative-enthalpy measurements at 1 kbar and transposed drop-solution calorimetry in lead borate at room pressure and 987 K. For albite "melt" at 1 bar and 298 K, Clemens and Navrotsky (1987) observed a extremum value of about −10 kJ/mol for 3 wt% H_2O. But the results were fraught with relative uncertainties of 15%–30% and the lack of heat capacity data made determinations at the relevant high temperature difficult.

As shown in another work for hydrous albite and phonolite melts (Richet et al., in press), enthalpies of mixing between water and melts can be determined more accurately from hydrofluoric acid solution calorimetry made on glasses at 1 bar. When dissolution of the sample is complete, HF solution calorimetry has several advantages over other possible techniques

for hydrous materials. First, foaming that results from the release of H_2O into solution in oxide-melt solution calorimetry is avoided because samples are dissolved in HF solutions at the low-temperature of 50°C. Second, the high precision of HF solution calorimetry (Hovis et al., 1998) is critical for determining reliably enthalpies of mixing which, for silicate systems, are generally small relative to the enthalpies of solution themselves (e.g., Hovis, 1988; Hovis and Roux, 1993; Roux and Hovis, 1996). Third, and perhaps more important, the possibility of extending the measurements to pure water allows the actual enthalpies of mixing to be accurately determined.

In this work we have investigated a glass series based on trachyte composition (Table 1) with water contents ranging from nominally 0 to 4.9 wt%. There were two main reasons for selecting trachytes for this extensive study. Volcanologically, they are important differentiation products of the alkaline series. Experimentally, they have the additional interest of dissolving readily in HF solutions. Because of the novelty of our approach, we will first describe in some detail how enthalpies of mixing of melts can be derived over wide pressure and temperature ranges from measurements made on glasses near room temperature. We will then derive the mixing properties of water and trachyte melts and compare these results with the few results available for other silicate compositions (Clemens and Navrotsky, 1987; Richet et al., in press). Finally, the petrological and volcanological implications of these results will be drawn.

2. EXPERIMENTAL METHODS

2.1. Sample Synthesis and Characterization

The present samples were the same as those investigated previously in density and viscosity studies (Richet et al., 2000; Whittington et al., 2001) to which we refer for further details on the synthesis and hydration procedures. The composition was chosen to be close to that of an "average" trachyte as given by Cox et al. (1979). Because of redox changes, incipient crystallization at high enough temperature, or incomplete dissolution, the presence of iron could have raised difficulties in viscosity experiments and in HF solution calorimetry as well.

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Table 1. Water content, pressure of synthesis, molar volume, enthalpy of solution and fictive temperature of trachyte glasses, and enthalpy of solution of water.

Water content		P (kbar)	V^a (cm^3/mol)	$\Delta H_s(\bar{T})$ (kJ/mol)	$\bar{T}^b$ (K)
wt %	mol %				
Trachyte glasses					
0	0	10^{-3}	26.211	−166.67	972
				−166.94	
0.57	2.01	2	25.593	−160.98	883
				−162.45	
0.83	2.90	2	25.518	−161.30	838
				−160.28	
1.12	3.89	3	25.221	−153.07	807
				−154.11	
1.19	4.12	2	25.361	n.d.	
1.58	5.42	3	25.055	−155.47	771
				−155.56	
2.19	7.40	3	24.774	−151.04	733
				−150.51	
2.61	8.73	2	24.633	−147.83	713
				−148.59	
2.90	9.64	3	24.413	−147.10	699
				−145.61	
3.06	10.13	2	24.469	−144.63	693
				−146.19	
4.92	15.59	3	23.674	−133.80	628
				−133.77	
Water				−0.19	

^{a} From the densities listed by Richet et al. (2000). For 0.36 and 0.83 wt% H$_2$O samples, 1-bar relaxed volumes of 25.68 and 25.69 cm^3/mol, respectively.
^{b} Derived from viscosity measurements for seven samples (Whittington et al., 2001); interpolated temperatures for the other four samples.

This element was thus replaced in the trachyte by Ca and Mg in such proportions as not to change the Ca/Mg atomic ratio. The nominal composition of the anhydrous starting glass prepared at 1 bar from an oxide and carbonate mix is SiO$_2$: 69.00; Al$_2$O$_3$: 10.54; MgO: 4.66; CaO: 6.15; Na$_2$O: 6.95; K$_2$O: 2.30; TiO$_2$: 0.40 mol%. It was verified to within analytical uncertainty by electron microprobe. For the anhydrous silicate end member of our binary system, the molar mass used to report the calorimetric results thus is 64.324 g.

After hydration under a few kbar water pressure at 1200 or 1300°C in internally heated vessels, the samples were analyzed by Karl Fisher titrations which yielded water contents accurate to within 0.1 wt% (e.g., Behrens et al., 1996). Along with electron microprobe analyses and infra-red spectra, these titrations did not reveal any inhomogeneity in chemical composition. Likewise, the measured densities (Richet et al., 2000) and viscosities (Whittington et al., 2001) indicate homogeneous dissolution of water in the samples.

We also checked homogeneity by near-infrared (NIR) spectroscopy measurements made with the setup of the Institüt für Mineralogie, Hannover (see Withers and Behrens, 1999). Further technical details will be presented elsewhere. It suffices here to say that spectra were recorded on ~ 500 μm thick doubly polished chips with a spot which was typically ~100 μm in diameter. The spectra were averaged from 100 scans and recorded at five different places for each chip with a spectral resolution of 2 cm^{-1}. Following Stolper (1982), we determined the concentrations of OH$^-$ and molecular H$_2$O from the peak areas of the relevant bands, using the molar absorption coefficients determined from the Karl Fischer water contents.

2.2. Solution Calorimetry

The measurements have been made with the calorimetric setup described by Hovis and Roux (1993) and Hovis et al. (1998). As

demonstrated in the latter paper, this system enables the measurement of highly precise enthalpies of solution for samples that are two orders of magnitude smaller than those studied 20 yr ago. Indeed the small quantities of hydrated samples for the present study limited individual sample sizes to between 18 and 33 mg for individual calorimetric experiments; it was only for the anhydrous compositions that bigger samples could be investigated. Each sample was dissolved in 910.1 g (about one liter) of 20.1 wt % hydrofluoric acid (HF) at 50°C with an internal sample container under isoperibolic conditions, i.e., with the constraint that the temperature of the medium surrounding the calorimeter was held constant (Waldbaum and Robie, 1970).

Either one or two dissolution experiments were performed in each liter of acid solution. The results obtained on a J/g basis were then converted to J/mol with the molar masses calculated from that of the silicate end member and the measured water contents. As observed in previous studies, multiple runs in the same solution had no detectable effect on the results, in all likelihood due to the high dilution of dissolved ions in the acid. Because the samples dissolved rapidly, the calorimetric experiments were conducted on crushed, but not ultrafine material, to avoid the possibility of heat effects associated with extremely small grain sizes (Nitkiewicz et al., 1983). This sample size also limited the risks of losing slight amounts of water before the solution experiments.

2.3. Precision of the Reported Enthalpies

To gain a sense for calorimetric precision, we have computed twice the standard deviation of the heats of solution for all experiments on each sample, then divided that number by the average enthalpy of solution for the sample. The imprecision calculated in this way for the various samples ranges from 0.07 to 1.80% of the heat-of-solution values. The average 2σ reproducibility among all samples is 0.93%, which translates to about ± 0.7 kJ/mol. This precision is somewhat lower than that experienced with previously investigated systems such as feldspars and feldspathoids (e.g., Hovis and Roux, 1993). This likely results from the smaller size of the samples and from a small degree of water adsorption by the glasses during weighing procedures for the calorimetric experiments. Even so, the data are accurate enough to reveal even small enthalpies of mixing. Moreover, the ± 0.7 kJ/mol average uncertainty is of low magnitude relative to the 33 kJ/mol spread among the heats of solution for the hydrous trachytes, and especially to the 166 kJ/mol enthalpy difference between the trachyte and water end members of the series.

3. RESULTS

3.1. Experimental Data and Pressure Effects

We list in Table 1 the enthalpies of solution of all glass samples. To show directly the effect of water on enthalpy we have plotted in Figure 1 the negative of the measured enthalpies of solution because the enthalpy difference between two materials is given by the difference between the negative of their enthalpies of solution. In such a plot concave up relationships indicate negative heats of mixing, i.e., exothermic mixing. For hydrous samples these raw measurements plot linearly against composition. Only the data for the trachyte sample at x_{H2O} = 0.389 lies off this line, probably because of sample problem, as three separate calorimetric experiments gave essentially the same result. Since no sample was left for further investigation, the nature of the problem could not be determined and this discrepant result was discarded in our data analysis.

As already discussed for the density of hydrous glasses (Richet et al., 2000), the effect of the synthesis pressure on properties must be taken into account. Glasses quenched from melts at high pressure are denser than the same materials prepared at room pressure because the high-pressure configuration is frozen in on cooling. This is shown in Figure 2 where
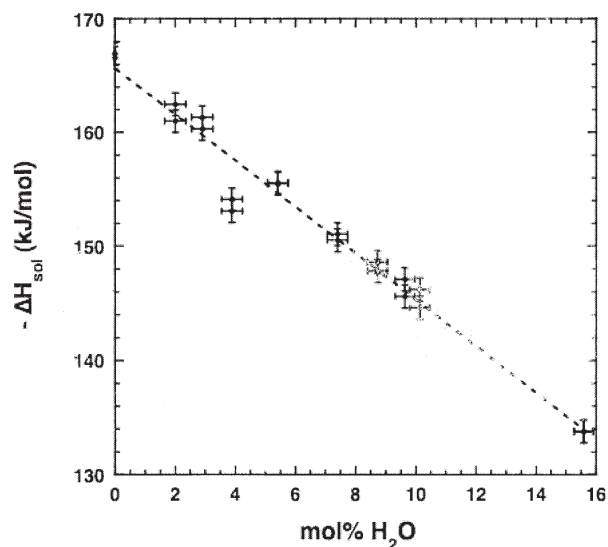
Fig. 1. Negative of the enthalpy of solution of hydrous trachyte glassses against water content.

the molar volumes of trachyte samples prepared at 2 and 3 kbar or relaxed at 1 bar define three separate linear trends against water content.

Similarly, the enthalpy of silicate glasses decreases with synthesis pressure (Ishizaka et al., 1996). Because the experimental uncertainty is greater for enthalpy of solution than for density, however, our results do not allow to distinguish two different trends for the samples hydrated at 2 and 3 kbar (Fig.
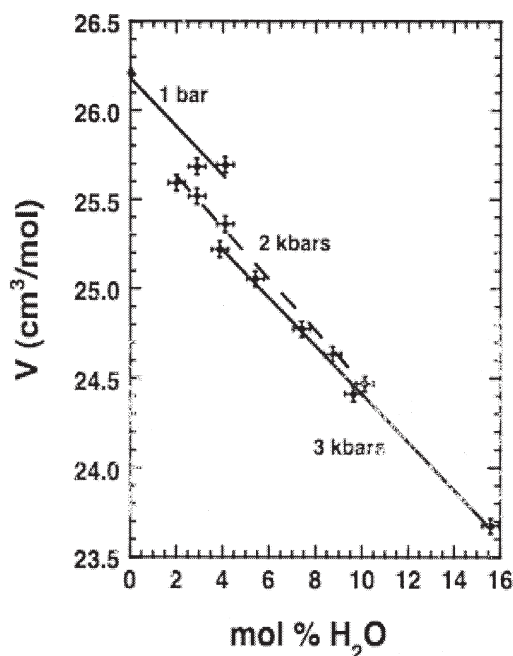
Fig. 2. Room temperature and pressure molar volume of hydrous trachyte glasses synthesized at the pressures indicated (data from Richet et al., 2000). The data plotted for two glasses with low water content refer to samples whose volume had relaxed to 1-bar values at the end of viscosity measurements.

2). Nevertheless, the trend of high-pressure hydrous glasses does not extrapolate to the measurement made on the 1-bar anhydrous sample. The difference of 1 kJ/mol thus represents the average influence of pressure for samples prepared at 2 and 3 kbar. Within experimental errors, the effect appears slightly smaller than found for hydrous albite and phonolite glasses prepared under the same conditions, with values of 3.0 (1.3) and 2.2 (0.4) kJ/mol, respectively (Richet et al., in press).

In the following we will first refer all the data to 1 bar. For doing so we will thus add 1 kJ/mol to the negative of the enthalpies of solution of all hydrous glasses. We will then consider a pressure of 3 kbar. A similar adjustment will be made by subtracting 1 kJ from the negative of the enthalpy of solution for the anhydrous end member.

3.2. Glass Transition Effects

On cooling, the temperature-dependent configuration of a melt is frozen in at the glass transition and the loss of configurational degrees of freedom results in a marked heat capacity decrease. Under similar conditions, water markedly depresses the glass transition range of silicates. As a result, the trachyte glasses have fictive temperatures that strongly decrease from 972 K, for the water-free glass, to 628 K for the sample with 15.6 mol% water. When deriving high-temperature enthalpies of mixing from the solution calorimetry, we simply account for this effect by splitting enthalpy integrals in two parts, viz.

$$H_T - H_{323} = \int_{323}^{T_g} C_{pg}\, dT + \int_{T_g}^{T} C_{pl}\, dT \tag{1}$$

where C_{pl} and C_{pg} are the heat capacities of the liquid and glass phases, respectively, and T_g the glass transition temperature taken as the temperature at which the viscosity of the melt is 10^{12} Pa · s (Whittington et al., 2001). Selecting the dissolved glass in HF solution at 323 K and 1 bar as a reference state, we then derive enthalpies of mixing at 1 bar and a given high temperature T from plots of $H_l = -\Delta H_s + (H_T - H_{323})$, where $-\Delta H_s$ is the negative of the enthalpy of solution in HF. We follow the same procedure at a high pressure P by adding to this enthalpy function the relevant variations of enthalpy with pressure as given by thermodynamic tables for water (Haar et al., 1984) and described above for the hydrous glasses.

Because the configurations of different glasses (even if quenched at the same cooling rate) represent the equilibrium configurations of liquids at different temperatures, the effects of such differing fictive temperatures must also be taken into account when examining the 323 K enthalpies of solution. To refer all glass data obtained at 323 K to "isothermal" conditions, the same fictive temperature $\bar{T}_2$ should be chosen. This is why, as obtained from Eqn. 1, an enthalpy of annealing must be included in the glass enthalpy (see Richet and Bottinga, 1986)

$$H_g = -\Delta H_s + \int_{\bar{T}_1}^{\bar{T}_2} (C_{pl} - C_{pg})\, dT \tag{2}$$

where $\bar{T}_1$ is the particular fictive temperature of the glass considered. For evaluating Eqns. 1 and 2, we used the heat capacity–composition relationships from C_p measurements made by Differential Scanning Calorimetry (DSC) on four samples of the trachyte series whose water contents ranged from 0 to 4.9 wt%.

Table 2. Enthalpy of water and hydrous trachyte melts (kJ/mol) and ancillary input data.

x_{H_2O}	C_{pl}	$C_{pl} - C_{pg}$ $(T_g)^a$	T_g	$H_{l1,1000}$	$H_{l1,1300}$	$H_{l3,1300}$
0.00	92.04	4.140	972	214.16	241.77	240.77
2.01	94.12	4.520	883	210.97	239.21	238.21
2.90	93.88	4.672	838	211.94	240.11	239.11
3.89	93.62	4.829	807	205.11	233.19	232.19
5.42	93.22	5.048	771	206.75	234.71	233.71
7.40	92.70	5.286	733	201.63	229.44	228.44
8.73	92.35	5.418	713	198.75	226.45	225.45
9.64	92.12	5.495	699	196.86	224.49	223.49
10.13	91.99	5.533	693	196.08	223.67	222.67
15.59	90.56	5.741	628	187.57	214.73	213.73
100.				68.31	81.25	72.33

ᵃ In J/g atom K.

3.3. Enthalpies of Mixing

Enthalpy of mixing represents the difference between the enthalpy of a given sample and the weighted average of the end-member enthalpies for the same bulk composition. Because it is possible to dissolve pure water in HF solutions, these properties are readily determined from the experimental data of Table 2. Thermodynamically, dealing with mixing between water at 323 K and glasses, even with the same fictive temperatures, would be an inconsistent procedure. Mixing between steam and melts at the same elevated temperature must be considered instead. This will be done first at 1 bar. Since water exsolution begins to take place in magmas at pressures of a few kbar, we will then consider how enthalpies of mixing of supercritical water with trachyte melts depend on pressure.

For H_2O, changing the reference state is easy because the enthalpy of water and steam has long been accurately known over wide temperature and pressure ranges (Haar et al., 1984). Arbitrarily, we have selected temperatures of 1000 and 1300 K to limit C_p extrapolations in evaluating Eqn. 1 for the hydrous silicates. The results obtained are listed in Table 2 along with the input calorimetric data. They are also plotted in Figure 3 for three different P,T conditions. To show enthalpies of mixing more clearly than in Figure 2, we have plotted in Figure 3 the data obtained from fits described below.

Enthalpies of mixing are slightly negative at 1 bar, either at 1000 or 1300 K, and have practically vanished at 3 kbar and 1300 K. They can be conveniently obtained from regular solution expressions fitted to the results to within their error margins, namely,

$$\Delta H_m = W_H \ (1 - x)x \tag{3}$$

where x is the mole fraction of water and W_H is an adjustable parameter. Enthalpies of mixing thus have a maximum value of only −8 and −3 kJ/mol for 50 mol% H_2O at 1 bar for 1000 and 1300 K, respectively. Note, however, that Eqn. 3 is symmetric with respect to the water and silicate mole fractions. Because the highest water content investigated is 15.6 mol%, we cannot preclude that enthalpies of mixing are asymmetric at higher water content. It follows that Eqn. 3 should be used as a means of data interpolation and comparison. This equation also yields enthalpies of exsolution (or of water dissolution, their negative) with

$$\Delta H_{exsol} = \int_{x_1}^{x_2} W_H x(1 - x)dx \tag{4}$$

where x_1 and x_2 are the initial and final water concentrations, respectively. The value obtained for W_H is −42.7 kJ from the raw data of Table 1 at 323 K. With the adjustments required to yield isothermal data, we find $W_H = -29.8 \pm 6.1$ and -12.7 ± 6.7 kJ at 1 bar for 1000 and 1300 K, respectively, and $W_H = -3.8 \pm 6.6$ kJ at 3 kbar and 1300 K.

The magnitude of enthalpies of mixing decreases with increasing temperatures. It also decreases with increasing pressure up to ∼4 kbar, at which molten trachyte and supercritical water mix ideally as far as enthalpy is concerned, and then slightly increases. These variations are in fact primarily determined by the pressure and temperature dependences of the enthalpy of steam which are several times greater than those of the silicate phases. This is apparent in Figure 4 where the enthalpy of steam is plotted against pressure at a few temperatures.

4. DISCUSSION

4.1. Composition Dependence of Enthalpies of Mixing

With 62 and 20% normative plagioclase and orthoclase, respectively, for the anhydrous sample, our trachyte glasses were expected to dissolve completely in hydrofluoric acid solutions according to previous investigations of materials related to feldspars (Hovis, 1984, 1988; Hovis and Roux, 1993, 1999; Roux and Hovis, 1996). Along with similar observations made for albite and phonolite melts, the results obtained show that HF solution calorimetry is well suited for investigating the energetics of alkali aluminosilicate melts. As a matter of fact, negative enthalpies of dissolution of water into silicate glasses have previously been derived from similar experiments (Epelbaum et al., 1995; Salova et al., 1997), but pure water was not investigated and the lack of C_p data prevented anyway high-temperature determinations of enthalpies of mixing.

Although we did not investigate a range of water content as wide as that studied by Clemens and Navrotsky (1987) for albite glass, the gain in precision is obvious for the 0–5 wt% H_2O interval which is actually relevant for petrological applications. This is apparent in Figure 5 where we compare our
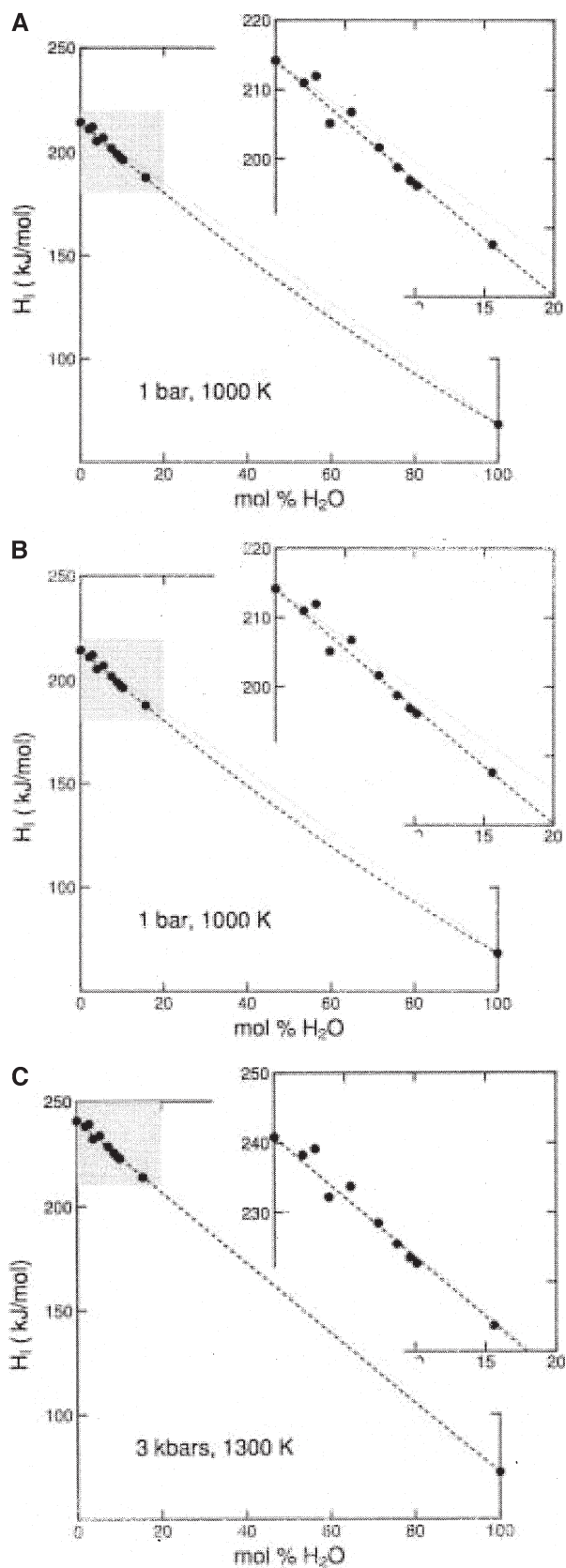
Fig. 3. Enthalpy of mixing between trachyte melts and steam under the conditions indicated.
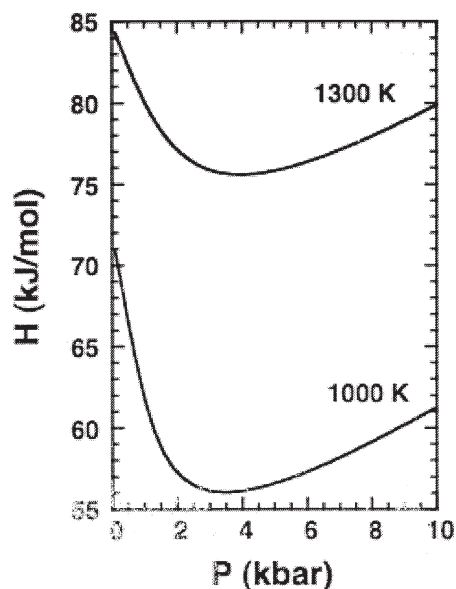

Fig. 4. Enthalpy of steam and supercritical water against pressure at the indicated temperatures. Data from Haar et al. (1984).

apparent enthalpies of mixing for trachyte glass at the same temperature of 298 K for which Clemens and Navrotsky (1987) reported their results for albite and haplogranitic glasses. In this plot the HF solution results have been referred with Eqn. 2 to the same fictive temperatures. Note that such an adjustment is unnecessary for the results of Clemens and Navrotsky (1987) because relaxation was certainly achieved for all their hydrous samples at the temperature of 987 K of the solution calorimetry experiments.

Clemens and Navrotsky (1987) also concluded that the magnitude of enthalpies of mixing decreases with increasing temperature. Our measurements confirm this conclusion. In addition, they allow the temperature, pressure and composition dependences of ΔH_m to be more accurately determined. These variations are similar for the albite, phonolite and trachyte melts investigated by HF solution calorimetry. The magnitude
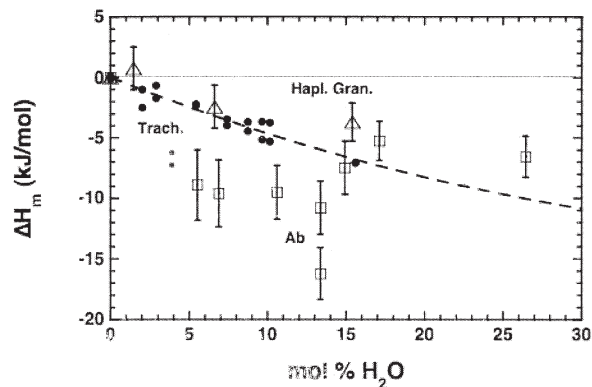

Fig. 5. Comparison between the enthalpies of mixing determined by Clemens and Navrostky (1987) for albite (open squares) and haplogranite (open triangles) glasses and the data of this study for trachyte (solid circles and dotted line).

of enthalpies of mixing is marginally smaller for albite than for phonolite and trachyte melts, the results obtained for the last two compositions being practically indistinguishable.

4.2. Water Dissolution in Glass

The partial molar volume of water in silicate glasses at 298 K is composition independent and has the low value 12 cm^3/mol (Richet and Polian, 1998; Richet et al., 2000). Water dissolves as a very dense component because this value is the same as the room-temperature molar volume of ice VII, the densest polymorph of ice. The enthalpy of this polymorph could thus be relevant for a discussion of water dissolution, instead of the liquid phase of water which is not an appropriate end member to determine enthalpies of hydration of silicate glasses. For this reason we have calculated what would be the enthalpy of solution of ice VII in our HF solution. Because the difference between the enthalpies of formation ($\Delta H°_f$) of water and ice VII is equal to the negative of the enthalpies of solution of these phases, we can write

$$\Delta H^o_{f, \text{iceVII}}(-291.1 \text{ kJ/mol}) - \Delta H^o_{f, \text{water}}(-285.8 \pm 0.0 \text{ kJ/mol})$$

$$= \Delta H_{s, \text{water}}(-0.19 \text{ kJ/mol}) - \Delta H_{s, \text{iceVII}}(\text{unknown}) \quad (5)$$

For this calculation the enthalpies of formation at 298.15 K are taken from Robie and Hemingway (1995) for water and from Fei et al. (1993) for ice VII, the latter value being close to the −290.3 kJ/mol reported by Bina and Navrotsky (2000). The negative of the enthalpy of solution of ice VII in 20.1% HF would thus be −5.1 kJ/mol, with an uncertainty that could be ~1 kJ/mol. Without adjustment for the 25 K difference between 298 K and the 323 K temperature of the calorimetric experiments, we will compare this value with that obtained by extrapolation to 100 mol% H_2O of our glass data. For this purpose, the glass enthalpies have all been referred with Eqn. 2, and the ancillary data of Table 2, to a common fictive temperature of 800 K which lies at the middle of the fictive temperature range (Table 1). It happens that a linear fit of these data extrapolates to −4.85 kJ/mol for 100 mol% H_2O. Although the extrapolation is performed over a very large interval, the agreement with the value calculated from thermochemical information is consistent with the conclusion drawn from volume data that there is structural similarity between dissolved water in silicate glasses and the densest polymorph of ice, in particular through the importance of hydrogen bonding in water dissolution (Richet and Polian, 1998).

4.3. Energetics of Water Speciation and Water Solubility Models

Ever since Burnham's (1975) contribution, the ideal or nonideal mixing of water and silicate melts has been a controversial issue. Burnham claimed that mixing was actually ideal if mixing was considered to take place between water and silicates for which formula units with 8 oxygen atoms were selected. For lack of experimental data, however, it has not been possible to determine if thermodynamic ideality would result from zero enthalpies of mixing or from some compensation between the enthalpy and entropy contributions to Gibbs free energies.

Enthalpies of mixing have been derived from thermodynamic analyses of water solubility. Such thermochemical implications of water solubility and speciation has been comprehensively reviewed by McMillan (1994). Since then, more detailed analyses have been published by Sahagian and Proussevich (1996) and Zhang (1999). Using the equation-of-state measurements of Burnham and Davis (1974) for hydrous albite melt, Sahagian and Proussevich (1996) found that enthalpies of exsolution decreased from high values of 15–20 kJ/mol at a few bar pressure and 700 to 1200 °C temperatures to almost zero at 3 kbar before increasing slightly at higher pressure by ~0.6 kJ/mol per kbar. Our results are consistent with their conclusion that these enthalpies decrease with increasing temperature at constant pressure, but indicate considerably smaller values at low pressure. Such elevated values could result at least in part from uncertainties in the input PVT data due to the very small solubilities that prevail under these conditions.

More recently Zhang (1999) has refined this approach for a hydrous rhyolitic melt by setting up a rigorous model which takes into account the influence of water speciation. From spectroscopic studies (e.g., Stolper, 1982; Silver and Stolper, 1989) it is well known that water first dissolves primarily as hydroxyl ions and then, at water contents higher than 3–4 wt%, as molecular water. The crossover between the concentrations of the two species varies with temperature because hydroxyl ion formation is favored by high temperatures through the reaction

$$O_b^{2-} + H_2O = 2OH^-, \quad (6)$$
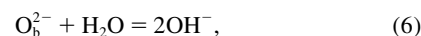
where O_b denotes a bridging oxygen of the silicate framework.

From the observed equilibrium constant of Eqn. 6, Zhang (1999) determined the enthalpy of speciation of the speciation reaction from which he could calculate only the pressure dependence of enthalpies of mixing. He found a large value of ~2 kJ per 100 bars at 850°C, which was ascribed to be an effect of the water speciation reaction. Such values are probably too high, however, for the reasons described above for the results of Sahagian and Proussevitch (1996). As already shown in Figure 4, the major changes in enthalpies of mixing are simply determined by the variations of the enthalpy of pure water. As pointed out by Zhang (1999), the use of directly measured enthalpies of mixing in such rigorous models should in turn improve predictions of water solubility and speciation as a function of temperature, pressure and composition.

Contrary to enthalpies of solution derived from thermodynamic models of water solubility in melts, our results are free from any assumption on ideal or nonideal behavior regarding ideal vs. nonideal behavior, or water speciation. In particular, we note that the cross-over between the concentrations of molecular water and hydroxyl ions is observed within the composition range that we have investigated (Fig. 6). Within this range, the essentially linear enthalpy-composition relationships found for the glasses thus suggest by itself that water speciation does not affect markedly the energetics of hydrous glasses. A similar observation has already been made for volume of mixing (Richet and Polian, 1998; Richet et al., 2000).
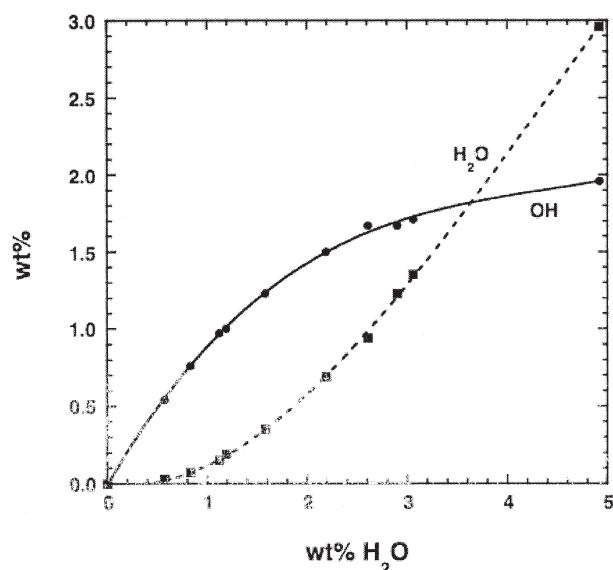
Fig. 6. Speciation of water in the quenched hydrous trachyte glasses investigated as determined from infrared spectroscopy measurements.

4.4. Volcanological Implications

Alkali aluminosilicate melts are particularly prone to explosive volcanic events. The volcanological implications of the present work have been discussed elsewhere (Richet et al., in press). It suffices here to say that the thermal effects of water exsolution can be directly determined from our results since the temperature change due to water exsolution is given by

$$\Delta T = \int_{x_1}^{x_2} W_H x (1 - x) dx / Cp_{x_2} \tag{7}$$

The temperature changes are so small that they do not affect the viscosity compared to the many orders of magnitude increases caused by water exsolution at constant temperature (Fig. 7). For trachyte melts, for instance, a loss of 5 wt% water at 1300 K would result in temperature decreases of a few degrees at most
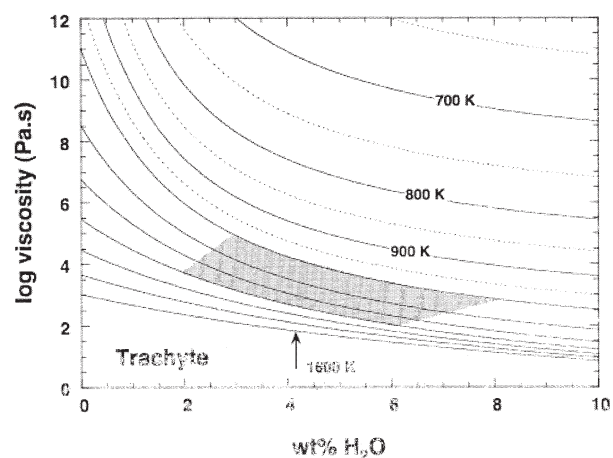

Fig. 7. Effects of dissolved water on the viscosity of trachyte melts between 650 and 1600 K.

up to kbar pressures. From the data of Whittington et al. (2001), it appears for instance that the viscosity change resulting from 5 wt% water loss is more than three orders of magnitude at 1300 K, from $10^{2.32}$ to $10^{5.46}$ Pa · s (and more than seven orders of magnitude at 1000 K, from $10^{3.73}$ to $10^{11.01}$ Pa · s). The additional viscosity increase caused by cooling from 1300 to 1290 K is only 0.1 log units (and 0.3 log units on cooling from 1000 to 990 K).

Whereas water solubility weakly depends on temperature, it is a strong function of pressure (e.g., McMillan, 1994). Clearly, the main factor controlling water solubility is the volume difference, and not the entropy difference between dissolved water and steam or supercritical water. Within this framework, the slight negative departure from thermodynamic ideality tends to counteract water exsolution when the pressure is decreased, but the effect has much too small a magnitude to be significant in explosive volcanism. As discussed by Burnham (1979, 1985), the large volume variation due to the transfer of water from a condensed phase to a gas phase is the main thermodynamic drive for explosions. Recent calculations by Mysen and Wheeler (2000) indicate that the energetics of this process can now be predicted from the equation of state of water and the partial molar volume of dissolved water in magmas.

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