

## Temperature dependence of the speciation of water in rhyolitic melts and glasses

EDWARD STOLPER

Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, U.S.A.

### ABSTRACT

The concentrations of molecular water and hydroxyl groups in rhyolitic glasses and melts depend on temperature as well as total water content. Increasing temperature results in an increase in the proportion of water dissolved as hydroxyl groups at a constant total water content. The temperature dependence of water speciation has been determined experimentally and can be described in thermodynamic terms by using a regular-solution formulation for the interactions between water molecules, hydroxyl groups, and oxygens in the rhyolitic glass or melt. This formulation is also consistent with calorimetric data on hydrous haplogranitic glasses.

The temperature dependence of water speciation in rhyolitic glasses can be used as the basis of a geothermometer for hydrous volcanic glasses. Obsidians from pyroclastic deposits from the ca. 1340 A.D. eruption of the Mono Craters, California, yield temperatures of about 600 °C. These chips may represent samples of the cool glassy margins and roofs of feeder dikes for this eruption. Glass inclusions in quartz phenocrysts from the Plinian deposit of the Bishop Tuff yield temperatures of ~300–600 °C; inclusions in quartz phenocrysts from the Mono Lobe ash-flow deposit of the Bishop Tuff yielded temperatures of ~200–300 °C. These temperatures are interpreted as closure temperatures and suggest that the initially hotter ash-flow deposit cooled more slowly than the Plinian deposit.

### INTRODUCTION

It is well established that water dissolves in silicate glasses in at least two distinguishable forms: hydroxyl groups and molecules of water. For several years, I and my colleagues have been using infrared spectroscopy to measure the concentrations of these two species in natural and synthetic glasses, with the goal of understanding the factors that influence their relative proportions (Stolper, 1982; Newman et al., 1986; Silver and Stolper, 1989; Silver et al., 1989). For all silicate compositions that we have investigated, the major control on the proportions of these two hydrous species is the total dissolved water content. At low total water contents, hydroxyl groups are the dominant species, whereas at high total water contents, molecular water dominates. The anhydrous chemistry of the glass also has an effect, but not a large one. Thus far, we have not detected any dependence of water speciation on the pressure of glass synthesis. For albitic or rhyolitic glasses quenched from melts at elevated temperatures and pressures, increasing the temperature results in a small but measurable increase in the ratio of hydroxyl to molecular water at constant total dissolved water content.

In this paper, I report a series of experiments in which the dependence on synthesis temperature of water speciation in rhyolitic glasses has been explored. Although my colleagues and I have previously demonstrated that the speciation of water in albitic and rhyolitic glasses is a function of synthesis temperature, the magnitude of the effect was not well established. After I characterize the

temperature dependence of water speciation in rhyolitic glasses and melts and show that it can be modeled in terms of a relatively simple thermodynamic treatment, I illustrate the potential of water speciation as a geothermometer for natural volcanic glasses.

### EXPERIMENTAL METHODS

Each experiment consisted of holding a sample of natural rhyolitic obsidian at elevated temperature, followed by rapid cooling to room temperature. Starting materials were all from samples described in Newman et al. (1986, 1988). After cooling, the samples were examined by optical microscopy, and in no cases was devitrification observed. The infrared spectrum of the quenched glass was then obtained on a Cary 17 spectrophotometer or a Nicolet 60SX Fourier-transform infrared spectrophotometer. The concentrations of molecular water and hydroxyl groups were determined from intensities of the 5200  $\text{cm}^{-1}$  and 4500  $\text{cm}^{-1}$  bands, respectively. Details of the spectroscopic techniques can be found in Stolper (1982), Newman et al. (1986), and Silver and Stolper (1989). Glass densities were assumed to be 2360 g/L. In principle, the density of each glass could be measured or approximated from the partial molar volume of water in rhyolitic glasses (Silver et al., 1989); however, the variation in density across the range of compositions that I have studied is expected to be  $\leq 20$  g/L, or less than 1%.

Several categories of heating experiments were conducted.

1. A fragment of hydrous obsidian was ground and

polished to a doubly polished plate, usually 0.05–0.1 cm thick. An infrared spectrum of the unheated sample was obtained. The sample was then placed in a box furnace that was already at the selected temperature (160–660 °C). The sample was placed directly on a Type S thermocouple at the bottom of the furnace, the atmosphere of which was air. After holding at the desired temperature for a selected time, the sample was removed from the furnace, and it cooled to room temperature. Run temperatures were typically low enough that the glass plate did not deform or vesiculate. The spectrum of the glass plate was then taken again, without regrinding or repolishing. For most glass plates, this procedure of heating followed by infrared analysis after cooling was repeated many times, sometimes at the same furnace temperature in order to explore the time required for changes in speciation and sometimes at different temperatures.

2. A problem with the experiments described in the preceding paragraph was that at sufficiently high temperatures (or after extended heating even at relatively low temperatures), water escaped from the polished surfaces of the glass plates. In these cases, the infrared spectrum taken through the glass plate represented the integral of the diffusion profile in the glass after the experiment. As discussed below, this problem did not have a great influence on the results, but in several of the experiments, it was minimized either by experimenting on a coarse glass fragment and grinding and polishing it to a doubly polished plate after the experiment or by regrinding both faces of the polished plate of glass after the heating experiment. In both cases, the diffusive gradients at the margins of the sample were removed, and only the homogeneous interior was analyzed spectroscopically. In one case (POB-82-2-A-8), a doubly polished glass plate was made from a cross section of the sample cut perpendicular to the initially polished faces; the center of the sample was analyzed by infrared spectroscopy and shown to be unaffected by diffusive loss of water.

At the highest temperatures, some samples flowed, resulting in a rippling of the surface, and some samples developed bubbles. After heating, the former samples were typically reground to parallelism prior to infrared analysis, and infrared spectra were taken on bubble-free regions.

These experiments were either conducted in a box furnace as described above or in a vertical tube furnace. In the latter case, the furnace atmosphere was air, temperatures were monitored with a Type S thermocouple adjacent to the sample, and the samples were quenched by dropping into water at room temperature.

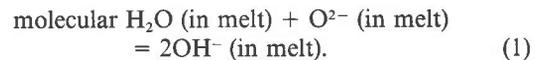
3. Three experiments were conducted on cores of rhyolitic obsidian loaded into Pt capsules and run at 5 kbar in a piston-cylinder apparatus using a NaCl cell. Temperature was monitored with a Type S thermocouple, and the samples were quenched by shutting off power to the internal graphite furnace. In each experiment, the glass run product was ground and polished before infrared analysis.

The conditions of each experiment and the measured concentrations of hydroxyl and molecular water are listed in Table 1. This table also indicates the procedure followed in each experiment and, when applicable, whether the sample was previously held at higher or lower temperature, and thus whether equilibrium was approached from above or below. Note that by using samples previously held at higher and lower temperature, it is possible to determine whether the results are reversible and, if so, what time scales are necessary to approach an equilibrium distribution of species.

### THERMODYNAMIC ANALYSIS

Inspection of Table 1 shows that the ratio of hydroxyl groups to molecules of water in rhyolitic glasses can be readily altered by raising or lowering the temperature of heat treatment. Higher temperatures result in higher hydroxyl to molecular-water ratios at a given total water content.

In previous work, I and my colleagues have analyzed data on the speciation of water in glasses quenched from melts in terms of reactions of the following type among dissolved species:



In rhyolitic glasses and melts, there are probably several distinguishable types of oxygens (i.e., bridging oxygens between adjacent Si-bearing tetrahedra as opposed to those between Si- and Al-bearing tetrahedra; Al-O-Si bridges charged-balanced by various cations; and so on) that react with water molecules to differing extents to generate hydroxyl groups. In addition, there is a range of bonding environments (e.g., of hydrogen bond strengths) for hydroxyl groups and water molecules. Moreover, melt species may be most accurately described in terms of polymeric units covering a range of sizes and shapes, and the energetics of their interactions may be complex. There are thus many possible approaches to the development of thermodynamic descriptions of homogeneous equilibria in rhyolitic melts. As shown by Silver and Stolper (1989), several such approaches, some of which attempt to deal with aspects of the complexities alluded to in this paragraph, can account well for the observed speciation of water in albitic glasses.

In the absence of a complete structural description of hydrous rhyolitic melts and glasses that can serve as a guide to modeling their thermodynamics, I employ in this paper the regular-solution model described in Silver and Stolper (1989) and Silver et al. (1989). The melt (or glass) is treated as a strictly regular solution (Guggenheim, 1952) comprising three species: water molecules, hydroxyl groups, and oxygen atoms (abbreviated in subscripts as mol.H<sub>2</sub>O, OH, and O). Their interactions are described in terms of three temperature- and pressure-independent binary interaction parameters (or “interchange energies” as defined in Hildebrand and Scott, 1950, p. 144) with

units of energy:  $W_{\text{mol.H}_2\text{O-O}}$ ,  $W_{\text{mol.H}_2\text{O-OH}}$ , and  $W_{\text{O-OH}}$ . The activities of these species are (Silver and Stolper, 1989)

$$a_{\text{mol.H}_2\text{O}}^m = X_{\text{mol.H}_2\text{O}}^m \exp\{(1/RT) \cdot [X_{\text{O}}^m X_{\text{OH}}^m (W_{\text{mol.H}_2\text{O-O}} - W_{\text{O-OH}} + W_{\text{mol.H}_2\text{O-OH}}) + (X_{\text{O}}^m)^2 W_{\text{mol.H}_2\text{O-O}} + (X_{\text{OH}}^m)^2 W_{\text{mol.H}_2\text{O-OH}}]\}, \quad (2.1)$$

$$a_{\text{OH}}^m = X_{\text{OH}}^m \exp\{(1/RT) \cdot [X_{\text{mol.H}_2\text{O}}^m X_{\text{O}}^m (W_{\text{mol.H}_2\text{O-OH}} - W_{\text{mol.H}_2\text{O-O}} + W_{\text{O-OH}}) + (X_{\text{mol.H}_2\text{O}}^m)^2 W_{\text{mol.H}_2\text{O-OH}} + (X_{\text{O}}^m)^2 W_{\text{O-OH}}]\}, \quad (2.2)$$

$$a_{\text{O}}^m = X_{\text{O}}^m \exp\{(1/RT) \cdot [X_{\text{mol.H}_2\text{O}}^m X_{\text{OH}}^m (W_{\text{O-OH}} - W_{\text{mol.H}_2\text{O-OH}} + W_{\text{mol.H}_2\text{O-O}}) + (X_{\text{mol.H}_2\text{O}}^m)^2 W_{\text{mol.H}_2\text{O-O}} + (X_{\text{OH}}^m)^2 W_{\text{O-OH}}]\}, \quad (2.3)$$

where  $X_i^m$  refers to the mole fraction of species  $i$  in the melt (m). The activities of these species are related via an equilibrium constant:

$$K_1 = \frac{[a_{\text{OH}}^m]^2}{[a_{\text{mol.H}_2\text{O}}^m][a_{\text{O}}^m]}. \quad (3)$$

Substitution of the activity expressions (Eqs. 2.1–2.3) into Equation 3, followed by rearrangement, yields the following expression:

$$\ln[K_1(T)] = (W_{\text{mol.H}_2\text{O-O}}/RT)(X_{\text{OH}}^m - 1) + (2W_{\text{O-OH}}/RT) \cdot (1 - X_{\text{mol.H}_2\text{O}}^m - \frac{3}{2}X_{\text{OH}}^m) + (2W_{\text{mol.H}_2\text{O-OH}}/RT) \cdot (X_{\text{mol.H}_2\text{O}}^m - \frac{1}{2}X_{\text{OH}}^m) + \ln\{(X_{\text{OH}}^m)^2 / [(X_{\text{mol.H}_2\text{O}}^m)(X_{\text{O}}^m)]\}. \quad (4)$$

Silver et al. (1989) have presented speciation data for rhyolitic glasses with between 0.7 and 5.1 wt% dissolved total water, all synthesized by rapid quenching from liquids saturated with water vapor at 850 °C and pressures between 50 and 1500 bars. Assuming that the pressure dependence of  $K_1$  is negligible (as demonstrated previously for albitic glasses quenched from liquids synthesized between 1 and 25 kbar; Silver and Stolper, 1989), they used an expression related to Equation 4 to solve for three parameters (which they called  $A'$ ,  $B'$ , and  $C'$ ) that are linear functions of  $K_1$  (850 °C),  $W_{\text{mol.H}_2\text{O-O}}$ ,  $W_{\text{mol.H}_2\text{O-OH}}$ , and  $W_{\text{O-OH}}$ . Assuming a value of  $W_{\text{mol.H}_2\text{O-O}} = 0$ , the best-fit values of  $A'$ ,  $B'$ , and  $C'$  given in Silver et al. (1989) yield values of  $W_{\text{mol.H}_2\text{O-OH}} = -2.8$  kcal/mol,  $W_{\text{O-OH}} = -11.6$  kcal/mol, and  $\ln[K_1(850 \text{ °C})] = -11.495$ . The assumption that  $W_{\text{mol.H}_2\text{O-O}} = 0$  is arbitrary, but leads to the convenient simplification that  $a_{\text{mol.H}_2\text{O}}^m \rightarrow X_{\text{mol.H}_2\text{O}}^m$  as  $X_B \rightarrow 0$  (where  $X_B$  is the mole fraction of total dissolved water expressed on a single oxygen basis; Silver and Stolper, 1989).

By using Equation 4 and the values of the parameters given in the previous paragraph, a value of  $\ln(K_1)$  was calculated for the results of each experiment reported here. These values are listed in Table 1. Note that even if species concentrations at a given total water content were independent of temperature,  $K_1$  would still vary with temperature because it enters into Equation 4.

Examination of values of  $\ln(K_1)$  at different temperatures as a function of run duration and the direction from which equilibrium was approached indicates that no experiments conducted at temperatures less than 400 °C reached equilibrium. Only for run durations greater than about 2 d at 400 °C is equilibrium approached, and even then, it may not be reached. At a temperature of 450 °C, the reversed POB-82-2-F experiments indicate that 3 h is sufficient to reach equilibrium for samples with 1.6–1.7 wt% water. On the basis of reversed results, all experiments conducted at temperatures above 450 °C appear to have been run for sufficient time to have closely approached equilibrium. At 620 °C, 50 min appears to be sufficient time to reach an equilibrium distribution of species.

Figure 1a shows  $\ln(K_1)$  vs.  $1/T$  ( $T$  in kelvins) for those experiments run for sufficient time to have reached or closely approached an equilibrium distribution of species (including the 400 °C experiments). Also shown is a best-fit line through these data, constrained to pass through the 850 °C value from the fit described above to the rapid-quench cold-seal experiments of Silver et al. (1989). The equation for this line is

$$\ln(K_1) = (-12881/T) - 0.0261. \quad (5)$$

The slope of this line gives a value of  $\Delta H_r^{0,m} = 25597 \pm 73$  cal/mol, where  $\Delta H_r^{0,m} = 2H_{\text{O}}^{0,m} - H_{\text{mol.H}_2\text{O}}^{0,m} - H_{\text{O}}^{0,m}$  is the standard-state enthalpy change of Reaction 1, assumed in this treatment to be independent of temperature.

Figure 1b compares the best-fit line with the results of experiments that approached equilibrium from “above” (i.e., from an initial  $X_{\text{mol.H}_2\text{O}}^m/X_{\text{OH}}^m$  ratio lower than the equilibrium value at the temperature of the experiment, in most cases generated by previously holding the glass at a higher temperature). Figure 1c compares this line with the results of experiments that approached equilibrium from below (i.e., from an initial  $X_{\text{mol.H}_2\text{O}}^m/X_{\text{OH}}^m$  ratio higher than the equilibrium value at the temperature of the experiment, in all cases generated by previously holding the glass at a lower temperature). The results of the experiments plot near the best-fit line regardless of the direction from which equilibrium was approached, illustrating the reversibility of the results and that an equilibrium distribution of species was closely approached for the experiments used to construct Figure 1.

Although it is not apparent in my data, I would expect a change in the slope of  $\ln(K_1)$  vs.  $1/T$  to occur at the glass transition because a change in  $\Delta H_r^{0,m}$  is expected at this point. Moreover, the temperature at which the break in slope occurs would vary with the water content of the glass because the glass transition is probably dependent

TABLE 1. Experimental data on temperature dependence of water speciation in rhyolitic glasses

Sample	Experiment	T (°C)	Duration* (min)	No. of spectra†	H <sub>2</sub> O as molecu- lar H <sub>2</sub> O (wt%)	H <sub>2</sub> O as OH (wt%)	Total H <sub>2</sub> O (wt%)	ln(K) <sub>‡</sub>	Calcu- lated T§	Comments**
GM	EXP#1††	547	126	2	0.33	0.72	1.05	-15.73	548	1
GM	EXP#2‡‡	597	79	2	0.31	0.73	1.04	-14.89	572	1
GM	EXP#3§§	642	60	3	0.30	0.74	1.04	-14.19	601	
MC84-bb-3a	EXP#1††	547	126	2	0.50	0.88	1.38	-15.60	597	1
MC84-bb-3a	EXP#2‡‡	597	79	2	0.06	0.38	0.44	-14.88	571	1
MC84-bb-3b	EXP#1††	547	126	2	0.45	0.82	1.28	-15.68	569	1
MC84-bb-3b	EXP#2‡‡	597	79	2	0.50	0.90	1.40	-14.76	624	1
MC84-bb-3e	EXP#1††	547	126	2	0.45	0.84	1.29	-15.60	598	1
MC84-bb-3e	EXP#2‡‡	597	79	2	0.37	0.80	1.17	-14.79	616	1
MC84-t	EXP#1††	547	126	2	0.17	0.55	0.72	-15.77	533	1
MC84-t	EXP#2‡‡	597	79	2	0.15	0.57	0.72	-14.81	604	1
MC84-t	EXP#3§§	642	60	6	0.14	0.58	0.72	-14.04	677	1
PAN-82-bb-3d	1	—	—	3	0.44	0.88	1.32	—	(650)	2
PAN-82-bb-3d	2	434	58	1	0.48	0.77	1.25	-18.06	(488)	3
PAN-82-bb-3d	3	434	57(115)	2	0.49	0.78	1.28	-18.05	(493)	1, 4
PAN-82-bb-3d	4	497	59	1	0.47	0.79	1.26	-16.71 ↑	511	3, 4
PAN-82-bb-3d	5	507	64	1	0.49	0.80	1.28	-16.53 ↑	511	1, 4, 5
PAN-82-bb-3d	6	539	118	1	0.41	0.80	1.21	-15.80 ↑	573	3, 4
PAN-82-bb-3d	7	496	75	1	0.46	0.76	1.22	-16.79 ↓	492	3, 4
PAN-82-bb-3d	8	543	52	3	0.41	0.80	1.20	-15.75 ↑	568	1(1),3(2),4
PAN-82-bb-3d	9	595	61	1	0.33	0.80	1.13	-14.74 ↑	652	1, 4, 6
POB-82-2-1		700	180	3	0.69	1.05	1.75	-13.28	690	1, 7
POB-82-2-3		500	263	2	0.80	0.87	1.68	-16.83	457	1, 7
POB-82-2-5		900	168	2	0.77	1.12	1.89	-11.31	727	1, 7
POB-82-2-A	0	—	—	1	0.76	0.96	1.72	—	(553)	2
POB-82-2-A	1	160	180	1	0.77	0.98	1.75	-27.55	(569)	3
POB-82-2-A	2	254	~180	1	0.77	0.98	1.75	-23.06	(569)	3, 4
POB-82-2-A	3	353	204	1	0.82	0.92	1.74	-20.03	(493)	3, 4
POB-82-2-A	4	400	180	1	0.87	0.88	1.75	-18.97	(448)	3, 4
POB-82-2-A	5	455	132	1	0.78	0.89	1.67	-17.63 ↑	479	3, 4
POB-82-2-A	6	502	198	1	0.66	0.90	1.56	-16.53 ↑	541	3, 4
POB-82-2-A	7	549	120	2	0.55	0.87	1.43	-15.67 ↑	560	3, 4, 6, 8
POB-82-2-A	8	400	258	3	0.73	0.78	1.51	-19.18 ↓	(397)	3, 4
POB-82-2-A	8'	400	258	1	0.87	0.85	1.72	-19.09 ↓	(416)	9
POB-82-2-B	0	—	—	1	0.75	1.01	1.76	—	(606)	2
POB-82-2-B	1	512	43248	2	0.21	0.64	0.85	-16.24	591	10
POB-82-2-E	1	—	—	1	0.69	0.95	1.64	—	(574)	2
POB-82-2-E	2	400	5	1	0.77	0.91	1.68	-18.78 ↓	(504)	3
POB-82-2-E	3	400	5(10)	1	0.77	0.91	1.68	-18.80 ↓	(499)	3, 4
POB-82-2-E	4	400	10(20)	1	0.78	0.90	1.68	-18.84 ↓	(487)	3, 4
POB-82-2-E	5	400	25(45)	1	0.82	0.89	1.71	-18.92 ↓	(462)	3, 4
POB-82-2-E	6	400	44(89)	1	0.82	0.87	1.68	-18.98 ↓	(446)	3, 4
POB-82-2-E	7	400	86(175)	1	0.82	0.84	1.65	-19.08 ↓	(422)	3, 4
POB-82-2-E	8	400	156(331)	1	0.83	0.83	1.66	-19.12 ↓	(410)	3, 4
POB-82-2-E	9	400	341(672)	1	0.84	0.82	1.65	-19.17 ↓	(399)	3, 4
POB-82-2-E	10	400	857(1529)	1	0.79	0.79	1.58	-19.24 ↓	(383)	3, 4
POB-82-2-E	11	400	1314(2843)	1	0.77	0.77	1.53	-19.28 ↓	(373)	3, 4
POB-82-2-E	12	400	2666(5509)	1	0.73	0.75	1.48	-19.29 ↓	371	3, 4
POB-82-2-E	13	400	5665(11074)	1	0.63	0.70	1.34	-19.35 ↓	356	3, 4
POB-82-2-E	14	400	11368(22442)	1	0.56	0.68	1.24	-19.35 ↓	354	3, 4
POB-82-2-F1	0	—	—	1	0.68	0.94	1.63	—	(572)	2, 11
POB-82-2-F1	1	400	184	1	0.78	0.86	1.64	-18.97 ↓	(450)	3
POB-82-2-F1	2	450	189	1	0.73	0.85	1.58	-17.81 ↓	459	3, 4, 12
POB-82-2-F2	0	—	—	1	0.76	1.01	1.77	—	(605)	2, 11
POB-82-2-F2	1	500	158	1	0.70	0.93	1.63	-16.53 ↓	552	3
POB-82-2-F2	2	450	189	1	0.76	0.87	1.63	-17.77 ↓	470	3, 4, 12
POB-82-2-F3	0	—	—	1	0.76	0.98	1.75	—	(577)	2, 11
POB-82-2-F3	1	450	189	1	0.78	0.88	1.67	-17.77 ↓	471	3, 12
POB-82-45-A	1	—	—	1	0.26	0.65	0.91	—	(528)	2
POB-82-45-A	2	400	5	1	0.27	0.65	0.92	-18.77 ↓	(524)	3
POB-82-45-A	3	400	5(10)	1	0.26	0.65	0.91	-18.79 ↓	(517)	3, 4
POB-82-45-A	4	400	10(20)	1	0.27	0.65	0.92	-18.77 ↓	(524)	3, 4
POB-82-45-A	5	400	25(45)	1	0.27	0.65	0.92	-18.80 ↓	(514)	3, 4
POB-82-45-A	6	400	44(89)	1	0.27	0.64	0.91	-18.85 ↓	(497)	3, 4
POB-82-45-A	7	400	86(175)	1	0.27	0.64	0.91	-18.85 ↓	(497)	3, 4
POB-82-45-A	8	400	156(331)	1	0.27	0.63	0.91	-18.88 ↓	(487)	3, 4

TABLE 1—Continued

Sample	Experiment	T (°C)	Duration* (min)	No. of spectra†	H <sub>2</sub> O as molecular H <sub>2</sub> O (wt%)	H <sub>2</sub> O as OH (wt%)	Total H <sub>2</sub> O (wt%)	ln(K <sub>1</sub> )‡	Calculated T§	Comments**
POB-82-45-A	9	400	341(672)	1	0.27	0.63	0.91	-18.89 ↓	(482)	3, 4
POB-82-45-A	10	400	857(1529)	1	0.28	0.62	0.90	-18.96 ↓	(460)	3, 4
POB-82-45-A	11	400	1314(2843)	1	0.29	0.61	0.89	-19.03 ↓	(438)	3, 4
POB-82-45-A	12	400	2666(5509)	1	0.28	0.59	0.88	-19.09 ↓	422	3, 4
POB-82-45-A	13	400	5565(11074)	1	0.28	0.59	0.87	-19.12 ↓	412	3, 4
POB-82-45-A	14	400	11368(22442)	1	0.28	0.57	0.85	-19.16 ↓	401	3, 4
POB-82-45-A	15	485	378	1	0.24	0.55	0.79	-17.25 ↑	411	3, 4
POB-82-45-A	16	529	128	1	0.21	0.58	0.78	-16.17 ↑	496	3, 4
POB-82-45-A	17	487	261	1	0.23	0.58	0.81	-17.06 ↓	456	3, 4
POB-82-45-A	18	580	62	1	0.18	0.61	0.79	-15.08 ↑	600	3, 4
POB-82-45-A	19	530	123	1	0.20	0.58	0.78	-16.10 ↑	518	3, 4
POB-82-45-A	20	620	58	1	0.16	0.60	0.76	-14.41 ↑	638	3, 4
POB-82-45-A	21	580	61	1	0.17	0.59	0.77	-15.09 ↓	594	3, 4
POB-82-45-A	22	660	45	2	0.14	0.60	0.75	-13.73 ↑	718	3, 4, 6, 8
POB-82-45-A	23	621	50	3	0.15	0.61	0.76	-14.28 ↓	703	1, 4
POB-82-45-A'	14	400	11368(22442)	1	0.28	0.58	0.86	-19.15 ↓	405	3, 13
POB-82-45-A'	17	487	261	1	0.25	0.59	0.84	-17.07 ↑	454	3, 4, 14
POB-82-45-A'	19	530	123	1	0.22	0.60	0.82	-16.09 ↑	520	3, 4, 14
POB-82-45-A'	21	580	61	1	0.19	0.62	0.81	-15.05 ↑	613	3, 4, 14
POB-82-45-A'	23	621	50	1	0.17	0.62	0.79	-14.32 ↑	681	3, 4, 14
POB-82-45-A'	24	430	1499	1	0.24	0.57	0.81	-18.31 ↓	441	3, 4
POB-82-45-A'	26	400	27947	1	0.25	0.54	0.79	-19.20 ↓	390	3, 4
POB-82-45-A'	27	420	11380	1	0.24	0.53	0.77	-18.74 ↑	382	3, 4
POB-82-45-A'	28	431	4100	1	0.24	0.52	0.75	-18.53 ↑	372	3, 4

\* When listed as x(y), x is the duration of this phase of the experiment, and y is the total time the sample was held at this temperature (includes previous experiments).

† Number of analyses averaged to obtain measured concentrations of hydroxyl and molecular water.

‡ Calculated as described in the text using actual temperature of experiment and measured speciation of water in quenched glass; arrows indicate, where applicable, whether sample tended toward equilibrium from higher (↓) or lower (↑) temperature, based on run conditions of the previous experiment on the starting material or its calculated speciation temperature.

§ Temperature in °C calculated as described in text using measured speciation of water in quenched glasses; values in parentheses were not used in regression to determine  $\Delta H_f^m$ .

\*\* (1) Sample ground and polished for infrared spectroscopy after experiment. (2) Unheated obsidian starting material. (3) Spectrum taken on sample after experiment without regrinding or repolishing. (4) Glass from preceding experiment used as starting material. (5) Surface cracks on sample after experiment. (6) Sample flowed during experiment. (7) Experiment run in piston-cylinder apparatus, NaCl cell, 5 kbar. (8) Sample slightly vesiculated during experiment. (9) Sample POB-82-2-A-8, sectioned perpendicular to previously polished surfaces; spectrum taken in center of sample. (10) Sample heated in vacuum furnace while infrared spectra were taken at high temperatures; speciation based on room-temperature spectrum after heating cycle. (11) Starting materials all cut from a single glass chip. (12) POB-82-2-F1-2, -F2-2, and -F3-1 all run simultaneously. (13) Half of POB-82-45-A-14 sample. (14) Run simultaneously with POB-82-45-A sample.

†† All EXP#1 experiments run simultaneously.

‡‡ All EXP#2 experiments run simultaneously.

§§ All EXP#3 experiments run simultaneously.

on water content (Tomozawa et al., 1983). Assuming that the "softening point" of a glass is closely related to the glass transition, my results suggest that the glass transitions of hydrous rhyolitic compositions occur in the temperature range covered by my experiments: glass with about 0.9 wt% water began to flow at 621–660 °C, whereas glass with about 1.2 wt% water did so at 543–595 °C, and glass with about 1.7 wt% water did so at 502–549 °C (Table 1). More detailed work may reveal the effect of the glass transition on the temperature dependence of speciation.

The best-fit line shown in Figure 1 can be used as a geothermometer using an iterative technique. For any measured species concentration, a value for  $\ln(K_1)$  can be calculated using Equation 4 given an initial guess of the temperature. A new value of temperature can then be determined by solving Equation 5 for  $T$ . This new value of temperature is then substituted into Equation 4 to calculate a new value of  $\ln(K_1)$ , and so on, until the values of temperature and  $\ln(K_1)$  are unchanged in successive iterations.

## Evaluation of errors

Values of temperature based on the iterative procedure described above were calculated for each of the experimental points shown in Figure 1; these values are listed in Table 1. Figure 2 shows the deviation between the actual and the calculated temperature for the experiments used to constrain the relationship between  $\ln(K_1)$  and temperature. Figure 3 shows a similar plot for the experiments at 850 °C reported in Silver et al. (1989) and used in the fitting procedure to determine the interaction parameters (i.e., the  $W$  values) for the thermodynamic model and the value of  $\ln(K_1)$  at 850 °C.

To evaluate the sensitivity of calculated temperature to errors in the speciation measurements, I have recalculated temperatures for hypothetical glasses with 600 and 850 °C species concentrations (i.e., with speciations corresponding to these temperatures based on Eqs. 4 and 5), assuming that because of measurement error, the hydroxyl and molecular-water contents differed from the actual values by 0.02 or 0.04 wt%, which may be consid-

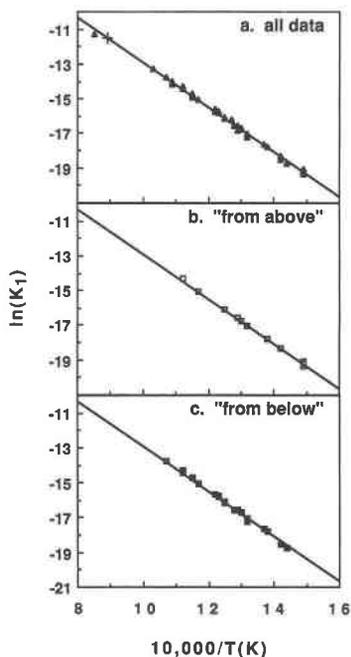


Fig. 1. Plots of  $\ln(K_1)$  for the reaction  $\text{molecular H}_2\text{O (in melt)} + \text{O}^{2-} \text{ (in melt)} = 2\text{OH}^- \text{ (in melt)}$  vs.  $1/T$ , where  $T$  is in kelvins, for experiments on rhyolitic glasses and melts reported in this paper. Only experiments thought to have approached an equilibrium distribution of species are shown; these are indicated in Table 1. For each experiment,  $\ln(K_1)$  was calculated from Equation 4 and the measured species concentrations and temperature of the experiment. (a) Results for all experiments listed without parentheses around the calculated temperature in Table 1. "+" is the value for 850 °C from a fit to rapid-quench cold-seal data reported in Silver et al. (1989). The line is a least-squares best-fit to these data constrained to pass through this 850 °C point. The equation of the line is given in the text as Equation 5. The slope of the line corresponds to a temperature-independent value of  $\Delta H_f^{\circ,m} = 25.6$  kcal/mol. (b) Same as (a), except only data for experiments that approached equilibrium "from above" are shown. These experiments are indicated by a downward-pointing arrow in Table 1. The best-fit line from (a) is shown for reference. (c) Same as (a), except only data for experiments that approached equilibrium "from below" are shown. These experiments are indicated by an upward-pointing arrow in Table 1. The best-fit line from (a) is shown for reference.

ered typical for the infrared measurements (Newman et al., 1986). As shown in Figures 2 and 3 for the results reported in this paper and in Silver et al. (1989), most of the deviations between measured and calculated temperatures can be explained by uncertainties in measurements of species concentrations of 0.02–0.04 wt%. The only significant exception is sample POB-82-2-5, run at 900 °C in a piston-cylinder apparatus; this sample is clearly anomalous, perhaps reflecting a re-equilibration of speciation on cooling or a measurement error (the high total water content compared to POB-82-2-1 and POB-82-2-2, prepared from the same starting material, implies the

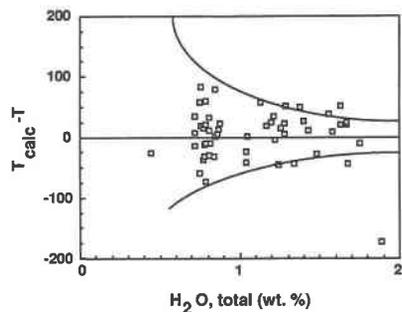


Fig. 2. Calculated temperature ( $T_{\text{calc}}$ ; based on measured species concentrations using Eqs. 4 and 5 as described in the text) minus experimental temperature ( $T$ ) for all experiments used to construct Fig. 1a vs. total water content of the glass. The curves were constructed by first calculating the hydrous-species concentrations for glasses at 600 °C based on Eqs. 4 and 5, then changing the concentrations of molecular water and hydroxyl groups by  $\pm 0.02$  wt%, and then determining  $T_{\text{calc}} - 600$  for these new species concentrations. These curves give an indication of the uncertainties associated with using measured hydrous-species concentrations in rhyolitic glasses for geothermometry.

latter). Figures 2 and 3 also demonstrate that if the absolute uncertainty in species concentrations remains unchanged as the total water content decreases, the errors in temperature increase to such a point that samples with less than about 0.8 wt% water are of little use for constraining thermodynamic models of the temperature dependence of species concentrations or for use in geothermometry. For samples with 2 wt% water equilibrated at 600 °C, uncertainties in temperatures of 25–50 °C will be typical; for samples with 6 wt% water, uncertainties of 10–25 °C can be expected. Since the temperature dependence of speciation is greater at lower temperatures, uncertainties in calculated temperature will diminish with the temperature of equilibration for a given uncertainty in species concentrations.

As explained above, some of the results shown in Figure 1 are based on samples that were ground and polished prior to heating, rather than afterward. These samples lost water through their polished surfaces. Thus, although the bulk of the sample is homogeneous, the measured species concentrations include the water-poor near-surface regions. The effect of this on the results is that, compared to a homogeneous glass with the same total water content as the average value for the zoned samples, zoned samples will have lower  $X_{\text{OH}}^m/X_{\text{mol.H}_2\text{O}}^m$  ratios. This can be seen from Figure 4, which shows the concentration of hydroxyl groups as a function of the total water content at several temperatures based on the best fit to the regular-solution model. Because the curves are concave downward, the effect of averaging between water-rich and water-poor regions of glass will be to measure an apparently low hydroxyl content for the measured total water content.

This effect for the zoned samples should express itself by a systematic bias toward lower values for their cal-

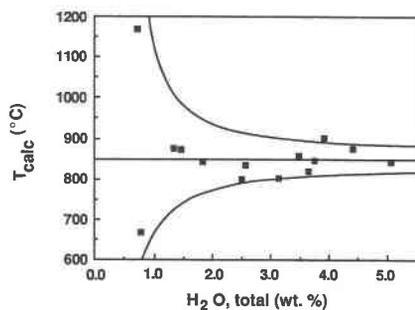


Fig. 3. Calculated temperature based on hydrous-species contents ( $T_{\text{calc}}$ ; see text and caption to Fig. 2) for rapid-quench cold-seal experiments on rhyolitic melts at 850 °C reported in Silver et al. (1989) vs. the total water contents of the glasses. Curves show  $T_{\text{calc}}$  for best-fit hydrous-species contents at 850 °C altered by  $\pm 0.04$  wt%; see Fig. 2 caption for details.

culated temperatures compared to those samples from which diffusive boundaries were removed by grinding and polishing after the experiment. Such a bias is not apparent in the data shown in Table 1. Moreover,  $\Delta H_r^0$  based on fitting only the data for samples that were polished after heating is  $25433 \pm 135$  cal/mol, which, within error, is indistinguishable from the value of  $\Delta H_r^0$  based on the full data set. This value leads to calculated temperatures that are only about 10 °C lower than those based on the fit to the full data set in the 400–600 °C range. For one sample that had clearly experienced diffusive water loss and that had a complex and lengthy thermal history at temperatures up to 550 °C (POB-82-2-A-8), I measured both the average species concentrations including the diffusive boundaries (listed in Table 1 as sample 8), and I sectioned the sample perpendicular to these boundaries after the experiment and measured the species concentrations in the homogeneous interior of the sample (listed in Table 1 as sample 8'). The difference in calculated temperature for the integrated species concentrations (397 °C) and the homogeneous interior (416 °C) is in the direction expected on the basis of Figure 4, but its magnitude is small compared to other sources of error as described above, so I do not believe this effect has had an important influence on the results I have presented or on their interpretation.

### Comparison with calorimetric measurements

One test of the regular-solution model I have adopted to describe the properties of hydrous rhyolitic melts and glasses is to compare the enthalpy of mixing that it predicts with calorimetric measurements on hydrous haplogranitic glasses (Clemens and Navrotsky, 1987). The enthalpy per mole of oxygen atoms of a strictly regular, ternary solution of water molecules, hydroxyl groups, and oxygens is given by

$$H = X_{\text{mol.H}_2\text{O}}^m H_{\text{mol.H}_2\text{O}}^{0,m} + X_{\text{O}}^m H_{\text{O}}^{0,m} + X_{\text{OH}}^m H_{\text{OH}}^{0,m} + X_{\text{O}}^m X_{\text{OH}}^m W_{\text{O-OH}} + X_{\text{mol.H}_2\text{O}}^m X_{\text{OH}}^m W_{\text{mol.H}_2\text{O-OH}} + X_{\text{mol.H}_2\text{O}}^m X_{\text{O}}^m W_{\text{mol.H}_2\text{O-O}} \quad (6)$$

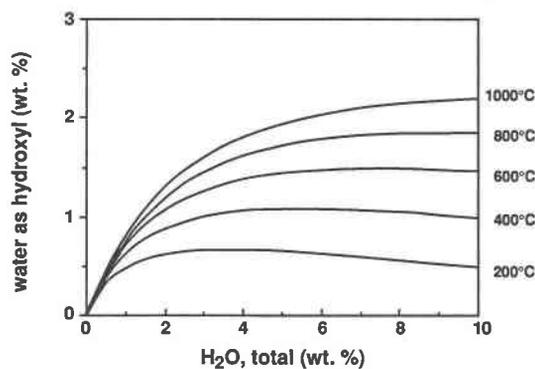


Fig. 4. Concentration of water dissolved in rhyolitic glasses and melts as hydroxyl groups vs. total dissolved water content calculated over a range of temperatures by using the regular-solution model described in the text.

Taking  $H_{\text{O}}^0 = H_{\text{mol.H}_2\text{O}}^0 = 0$ , noting that  $\Delta H_r^0 = 2H_{\text{OH}}^{0,m} - H_{\text{mol.H}_2\text{O}}^{0,m} - H_{\text{O}}^{0,m} = 25597$  cal/mol on the basis of the linear fit to Figure 1, and using the values for the interaction parameters given above (based on an assumed value of  $W_{\text{mol.H}_2\text{O-O}} = 0$ ), results in a reduction of Equation 6 to

$$H = 12799X_{\text{OH}}^{0,m} - 11608X_{\text{OH}}^{0,m}X_{\text{O}}^{0,m} - 2801X_{\text{mol.H}_2\text{O}}^m X_{\text{OH}}^{0,m} \quad (7)$$

where  $H$  is in calories per mole.

On the basis of a series of calorimetric measurements, Clemens and Navrotsky (1987) calculated the enthalpy change that would accompany conversion of hydrous haplogranitic glasses into liquid water and anhydrous glass at 298 K, 1 atm. Measurements were made on three glasses that had been synthesized at 1–5 kbar and 813–1087 °C in an internally heated pressure vessel with water contents of 0.69, 3.19, and 7.80 wt%.

The data reported by Clemens and Navrotsky (1987) are not directly comparable with the enthalpy of mixing given by Equation 7. I have converted their data into a form comparable with my calculation via the following procedure: Their reported  $\Delta H_{m,298}$  was first corrected to 1123 K. This temperature is in the range at which their glasses were synthesized, and I assume that the species distributions in their glasses preserve those appropriate to such temperatures. The correction procedure assumes that the molar heat capacity for hydrous melt/glass can be described by  $X_B \bar{C}_{P,\text{H}_2\text{O}} + (1 - X_B) \bar{C}_{P,\text{O}}$ , where  $\bar{C}_{P,\text{H}_2\text{O}}$ , the partial molar heat capacity for the total water component of the glass, is assumed to be  $19.8 \pm 1.1$  cal/(mol·K) on the basis of their data for hydrous albitic melts, and where  $\bar{C}_{P,\text{O}}$ , the partial molar heat capacity per oxygen for the anhydrous component, is taken to be the same as the average heat capacity for the anhydrous glass. The enthalpy difference between steam at 1123 K and 1 atm and liquid water at 298 K and 1 atm was taken from Robie et al. (1978).

The enthalpy of mixing of Clemens and Navrotsky (1987) refers to the enthalpy difference between  $X_{\text{O}}^m$  moles

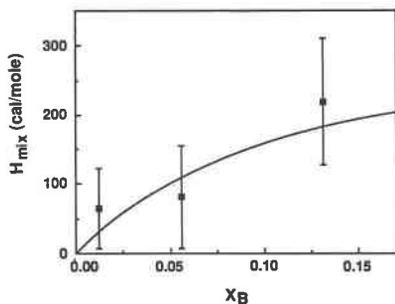


Fig. 5. Comparison of calorimetry with the regular-solution model. Enthalpy of mixing ( $H_{mix}$ ) vs. mole fraction of total dissolved water ( $X_B$ ; expressed on a single oxygen basis) for hydrous rhyolitic or haplogranitic compositions.  $H_{mix}$  is the enthalpy of the hydrous melt per mole of oxygen atoms minus  $(1 - X_B)$  times the enthalpy of anhydrous melt per mole of oxygen atoms minus  $X_B$  times the enthalpy per mole of molecular water in its standard state in the melt. The filled squares are calorimetric measurements for haplogranitic compositions from Clemens and Navrotsky (1987), modified as described in the text. Error bars are based on 2 standard deviations of the mean from their experimental results. The curve is calculated from the regular-solution model described in the text, assuming a distribution of hydrous species appropriate for 850 °C.

of liquid water (or steam, after correction to 1123 K) plus  $(1 - X_w^m)$  moles of anhydrous glass and a hydrous glass with  $X_w^m$  moles of dissolved water and  $(1 - X_w^m)$  moles of the anhydrous component. The enthalpy of mixing given by Equation 7 in this paper refers to the enthalpy difference between (1)  $X_B$  moles of molecular water in its standard state for hydrous rhyolitic melts plus  $(1 - X_B)$  moles of the anhydrous component and (2) a hydrous glass of the same composition after the reaction between water molecules and the anhydrous component to produce hydroxyl groups has reached equilibrium. In order to compare these two enthalpies of mixing, it is necessary to correct for the difference in enthalpy between steam and molecular water in the melt in its standard state at 1123 K. Following Silver and Stolper (1989) and Silver et al. (1989), who have called this parameter  $\Delta H_{H_2O}^0$  and determined it for water in orthoclasic and albitic melts, this enthalpy difference can be determined from the temperature dependence of the solubility of water in rhyolitic melts. I determined the enthalpy difference in the following way: I used the solubility determinations at 700 bars and 650, 750, 850, and 950 °C from Karsten et al. (1982). For each data point, the speciation of water for the water solubility they reported at the conditions of the experiment was calculated using the parameters given in this paper by iterative solution of Equation A.5 in Silver et al. (1989), which is an alternative form of Equation 4 in this paper. The activity of water at saturation for each experiment was then calculated from Equation 2.1. These values for the activity of water were then fit to Equation 1 in Silver et al. (1989) to determine a value for  $\Delta H_{H_2O}^0$ .  $\Delta H_{H_2O}^0$  was assumed to depend on temperature;  $\bar{C}_{p,mol,H_2O}$

= 19.8 cal/(mol·K) and the heat capacity of steam from Robie et al. (1978) were used. The best-fit value of  $\Delta H_{H_2O}^0$  at 1123 K and 700 bars is  $-4902 \pm 826$  cal/mol. The partial molar volume of molecular water in rhyolitic melts is sufficiently small that the correction to 1 bar is assumed to be minor and is not included. Water fugacities for each experiment were calculated using a modified Redlich-Kwong equation of state (Holloway, 1977). A similar procedure was used in Silver et al. (1989) to determine  $\Delta H_{H_2O}^0$  for albitic and orthoclasic melts, except that  $\Delta H_{H_2O}^0$  was assumed to be independent of temperature; corrected to 1 bar, these values are approximately  $-4.4$  and  $-6.3$  kcal/mol, respectively.

By using the best-fit value of  $-4902$  cal/mol for  $\Delta H_{H_2O}^0$ , the data of Clemens and Navrotsky (1987) were put into a form comparable to the enthalpy of mixing I calculated from Equation 7. The calorimetric values of enthalpy of mixing and the model regular-solution values are compared in Figure 5. The error bars shown on the calorimetric values are based on  $2\sigma$  values given by Clemens and Navrotsky (1987). The calculated regular-solution values assume a speciation of water frozen in at 1123 K. Note that given the correction procedure applied to the data of Clemens and Navrotsky (1987), their corrected values do not depend upon temperature; however, since speciation is temperature dependent, the values calculated with the regular-solution model do depend weakly on temperature. I note that Navrotsky (1987) found that the calorimetric data for hydrous albitic glasses from Clemens and Navrotsky (1987) could be explained by modeling these glasses as ideal mixtures of water molecules, hydroxyl groups, and oxygen atoms provided that  $\Delta H_{H_2O}^0 = 33.8 \pm 4.7$  cal/mol and  $\Delta H_{H_2O}^0 = -10.7 \pm 2.5$  cal/mol; these values are similar to those I have obtained here for a regular-solution model for hydrous rhyolitic melts.

Figure 5 shows that the enthalpy of mixing for hydrous rhyolitic melts calculated with the regular-solution model is in excellent agreement with that from calorimetric measurements. In both cases, the enthalpy of mixing is positive and relatively small, on the order of a few hundred calories or less. It is actually somewhat surprising that the agreement is this good. In the introduction to the thermodynamic modeling, I emphasized the likely complexity of accurate models of the thermodynamic properties of hydrous silicate melts and that the regular-solution model that I have adopted does not explicitly incorporate many of these complexities. Moreover, it is well known (and theoretically expected; Hildebrand and Scott, 1950, p. 135–136) that regular-solution models often account better for deviations from ideality of activity coefficients (i.e., for the free energy of mixing) than for enthalpies or entropies of mixing. In view of these factors, although I consider the comparability of the regular-solution model and the calorimetric data illustrated in Figure 5 to be a demonstration of the utility of the regular-solution approximation for providing a connection between my species measurements and macroscopic

thermodynamic properties, I consider it unlikely that the  $W$  values that I have fit have any actual microscopical significance.

## DISCUSSION

### Temperature dependence of speciation

Figures 4 and 6 show, in somewhat different forms, the calculated speciation of water in rhyolitic melts and glasses over the temperature range 200–1000 °C based on the regular-solution model constrained as described above by data presented in this paper and in Silver et al. (1989). Although the focus of this paper is the temperature dependence of speciation, Figures 4 and 6 illustrate that the temperature dependence is, in fact, not large, though it becomes more pronounced as temperature decreases. Thus, for example, in a melt with 4.0 wt% water at 600 °C, hydroxyl groups account for 1.4 wt% water (34% of the total water); if the temperature is raised to 800 °C, the amount of water dissolved as hydroxyl groups only increases to 1.6 wt% (40% of the total water); if the temperature is decreased to 400 °C, the amount of water dissolved as hydroxyl groups decreases to 1.1 wt% (26% of the total water). Although readily detected by infrared spectroscopic techniques, these are rather small changes, and the overall trends in the speciation of water as a function of total dissolved water content are unchanged by the temperature effect. The small dependence of speciation on temperature is the reason why uncertainties in species concentrations of only a few hundredths of 1 wt% result in uncertainties in temperature of several tens to hundreds of degrees (see Figs. 2 and 3).

An interesting feature of the regular-solution model illustrated in Figures 4 and 6 is that as temperature decreases, a predicted maximum in the hydroxyl-group content with increasing total water content occurs at progressively lower total water contents. Thus, whereas at 1000 °C, the amount of water dissolved as hydroxyl groups is predicted to increase continuously as the total water content rises from 0 to 10 wt% water, the hydroxyl-group content reaches a maximum at ~5.5 wt% total dissolved water at 400 °C and 4.0 wt% total dissolved water at 200 °C. Although a maximum in hydroxyl group concentration has not been directly observed in rhyolitic glasses, such a maximum has been observed by Bartholomew et al. (1980) at <3 wt% total water in Na-Al-Zn-rich silicate glasses synthesized at 300 °C. Hydroxyl-group concentration also decreases with increasing total water contents in anorthite-silica-water glasses with greater than ~9 wt% total water synthesized in internally heated pressure vessels at temperatures of 850–1050 °C (Stewart, 1967; Silver et al., 1989).

### Applications as a geothermometer for hydrous volcanic glasses

I have applied the results of my experiments on hydrous rhyolitic glasses and melts to two suites of volcanic glasses to examine the potential of the speciation of water in hydrous glasses as a geothermometer.

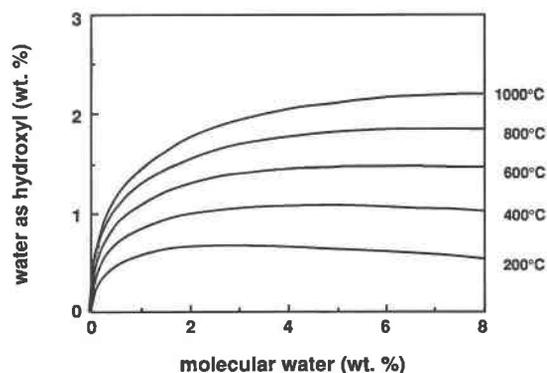


Fig. 6. Concentration of water dissolved in rhyolitic glasses and melts as hydroxyl groups vs. that dissolved as molecular water calculated over a range of temperatures using the regular-solution model described in the text. This figure can be used for graphical determination of the temperature implied by a given speciation of water in rhyolitic glass.

**Mono Craters obsidians.** Newman et al. (1988) measured the speciation of water in obsidian chips from pyroclastic deposits of the ca. 1340 A.D. eruption of the Mono Craters in central California. Temperatures were calculated on the basis of their species concentrations as described above. Results are shown in Figure 7. Although there is a spread of a few hundred degrees, it is apparent from Figure 7 that this range can be accounted for entirely by the fact that many of the glasses have water contents below 0.8 wt% where the calculated temperatures are very sensitive to uncertainties in the measurements. The results are consistent with all of the glasses having equilibrated near 600 °C.

These temperatures are below those expected for rhyolitic magmas prior to eruption on the basis of coexisting iron-titanium oxides from the Mono Craters domes (Carmichael, 1967) or from other rhyolitic systems (Hildreth, 1981). One possibility is that these glasses erupted as liquids at ~850 °C, but that they cooled sufficiently slowly that the speciation changed on cooling and that 600 °C is a closure temperature. However, as discussed in Newman et al. (1988), I think it unlikely that hydrous melt erupted at 850 °C would be preserved as glass; i.e., given nucleation rates for bubbles in rhyolitic melts (Westrich, 1982), any hydrous melt that erupted at 850 °C would instantly vesiculate and turn to pumice. Such melts could never survive on eruption the relatively slow cooling rates that on single-stage cooling from 850 °C are required to get closure temperatures of about 600 °C (on the order of degrees per second, based on the fact that samples of glass synthesized at 850 °C in air-quenched cold-seal bombs by Silver et al., 1989, record speciation temperatures of ~600 °C). In other words, any melt erupted at 850 °C that cooled rapidly enough to avoid vesiculation would not record a speciation temperature as low as 600 °C. Thus, the very existence of nonvesicular hydrous obsidian chips in pyroclastic deposits is puzzling, and specia-

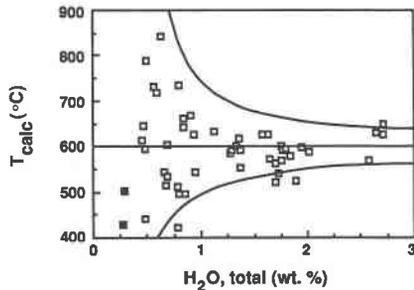


Fig. 7. Calculated temperature based on hydrous species contents ( $T_{\text{calc}}$ ) versus total water content for obsidians from the ca. 1340 A.D. eruption of the Mono Craters (Newman et al., 1988). The average value of temperature of the 32 samples with greater than 0.9 wt% water is 592 °C ( $1\sigma = 36$  °C). Open squares are obsidian chips from pyroclastic deposits; closed squares are for samples from lava domes. Curves were calculated for 600 °C speciation as described in the caption to Fig. 2 for uncertainties in hydrous-species concentrations of  $\pm 0.04$  wt% and give an indication of the uncertainty in  $T_{\text{calc}}$ .

tion temperatures of 600 °C are even more so, unless the chips were already at least this cool when they exited the volcano. As suggested by Newman et al. (1988), a plausible explanation for the existence and low speciation temperatures of these obsidian chips is that they are samples of the glassy margins and roofs of dikes that fed the Mono Craters eruption and that were caught up in the eruption. According to this view, the relatively cool 600 °C speciation temperature would be typical of these glassy margins. It is interesting that during my experiments, 550–650 °C is the range over which the obsidians began to flow; perhaps this softening point defines the interior edge of a rhyolitic dike's glassy margin.

**Glass inclusions in quartz phenocrysts from the Bishop Tuff.** Anderson et al. (1989) measured the concentrations of hydrous species in glass inclusions in quartz phenocrysts from two stratigraphic levels in the Bishop Tuff. The speciation temperatures are shown in Figure 8. Although the uncertainty in species concentrations in these glasses ( $\sim 0.1$  wt%) is typically larger than for larger obsidian chips, total water contents are also higher, so the uncertainty in calculated temperature is still about 50 °C. Speciation temperatures range from  $\sim 300$  to 600 °C for glass inclusions from an air-fall deposit from the Plinian phase of the eruption, whereas those for the later-erupted Mono Lobe ash-flow range from  $\sim 200$  to 300 °C. These temperatures are all significantly lower than the magmatic temperatures for the Bishop Tuff eruption based on coexisting iron-titanium oxides (720 °C for the Plinian phase, 790 °C for the Mono Lobe; Hildreth, 1979). These low temperatures probably reflect slow cooling after deposition. According to this interpretation, the ash-flow unit cooled more slowly than the Plinian air-fall deposit, so that although the ash-flow was initially hotter, both on eruption and deposition, water speciation in its glass inclusions record generally lower closure temperatures.

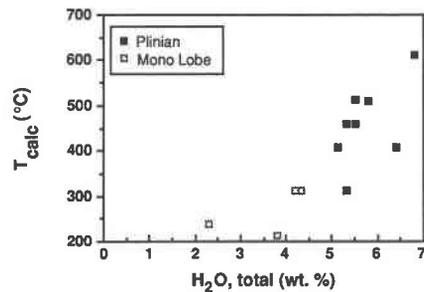


Fig. 8. Calculated temperature based on hydrous-species contents ( $T_{\text{calc}}$ ) versus total water contents for glass inclusions in Bishop Tuff quartz (Anderson et al., 1989). Closed squares are for glasses in quartz from the early, low-temperature Plinian phase of the eruption. Open squares are for glasses in quartz from the later, high-temperature Mono Lobe ash-flow.

## SUMMARY

The proportions of water dissolved in rhyolitic glasses and melts as water molecules and hydroxyl groups depend on temperature as well as total water content. Increasing temperature increases the proportion of water dissolved as hydroxyl groups at a constant total dissolved water content. Although the effect is not large, it is readily measurable by infrared spectroscopy. The effect is also reversible, and, at temperatures  $\geq 400$  °C, speciation can be re-equilibrated on laboratory time scales.

The temperature dependence of water speciation can be described in thermodynamic terms using a regular-solution formulation for the interactions between water molecules, hydroxyl groups, and oxygens in the rhyolitic glass or melt. This formulation is also consistent with calorimetric data on hydrous haplogranitic glasses.

The temperature dependence of water speciation in rhyolitic glasses can be used as the basis of a geothermometer for hydrous volcanic glasses. It has been applied to obsidian chips from pyroclastic deposits from the ca. 1340 A.D. eruption of the Mono Craters and yields temperatures of about 600 °C. On the basis of these low temperatures, which are consistent with the fact that these obsidians did not vesiculate on eruption, it is likely that these chips were already cool when they were erupted. One possibility is that they represent the cool glassy margins and roofs of feeder dikes for the eruption. The thermometer has also been applied to glass inclusions in quartz phenocrysts from Plinian and ash-flow deposits of the Bishop Tuff. Temperatures are as low as  $\sim 200$  °C, suggesting that water speciation reflects slow cooling in these deposits. The temperatures of the ash-flow glasses are generally lower than those of Plinian glasses, suggesting that the initially hotter ash-flow deposit cooled more slowly than the Plinian deposit.

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