Diffusion of water in rhyolitic glasses

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Abstract—Water dehydration experiments on rhyolitic glasses have been carried out at 400–550°C under a N2 atmosphere. Concentration profiles of both H2O molecules and OH groups were measured by Fourier transform infrared spectroscopy. As found in previous studies of water diffusion in rhyolitic melts, the measured total water concentration profiles do not match expectations based on a single constant diffusion coefficient for total water.

The diffusion of total water is described by considering the diffusion of both H2O molecules and OH groups and the reaction between them. The concentration relationship between the two species has been obtained from direct infrared measurement on quenched experimental charges. The quench is inferred to be rapid enough to preserve concentrations of both species at experimental temperature based on experimental results designed to examine reaction kinetics. The measured species concentrations along diffusion profiles show that local equilibrium between H2O and OH is approximately reached at high temperatures and high water contents. However, at lower water content or lower temperature, local equilibrium is not reached. In treating the diffusion problem, this disequilibrium effect is partially compensated by using empirical relationships between H2O and OH concentrations based on measurements, instead of using an equilibrium relationship. It is thus possible to obtain diffusion coefficients for both species from their concentration profiles. The diffusion coefficient of OH is found to be negligible compared to that of H2O at 403–530°C (DOH < 0.02D H2O and could be much smaller); i.e., H2O is the dominant diffusing species even at total water concentration as low as 0.2 wt%. The variation of OH concentration along the diffusion profile is inferred to be due to the local interconversion between OH groups and H2O molecules; the reaction also provides the diffusing H2O species. D H2O values are found to vary by less than a factor of 2 over a total water concentration range of 0.2 to 1.7 wt%. This simple model, coupled with the assumption of local equilibrium between H2O and OH, yields a very good fit to the data from diffusion-couple experiments of LAPHAM et al. (1984) at 850°C. When our data are combined with DH2O obtained from that fit, DH2O (in m²/s) is given by

\[
\ln D_{H2O} = (-14.59 \pm 1.59) - (103000 \pm 5000)/RT
\]

673 K ≤ T ≤ 1123 K

where T is temperature in K and R is the gas constant in J K⁻¹ mol⁻¹. This equation also approximates well DH2O values calculated from previous measurements of concentration-dependent bulk water diffusion coefficients of KARSTEN et al. (1982). The diffusion of H2O is also compared to the diffusion of the noble gas elements. The activation energy for diffusion in rhyolitic glasses is well correlated with neutral species radii of He, Ne, H2O, and Ar. This supports the contention that the diffusing species for “water” is neutral molecular H2O. The role of speciation may also be important in understanding the diffusion of many other multi-species components, and the effect can be treated in a similar fashion as that during water diffusion.

INTRODUCTION

DIFFUSIVE TRANSPORT OF WATER in silicate liquids and glasses plays an important role in a number of phenomena of interest in the geological and materials sciences. For example, the rate of water diffusion in silicate liquids is a critical factor in the growth of bubbles in ascending magmas, and thus may influence the degree to which magmas can dehydrate on ascent and the availability of compressed vapor in bubbles to power explosive volcanic eruptions. Hydration and dehydration of silicate glasses in geological and man-made environments are also limited by water diffusion, and relate to several important issues including the chemical stability of glasses, the mechanical strength of glass fibers, water-rock reaction, and to applications such as obsidian hydration dating.

It has been known for several decades that the chemical diffusion coefficient of “water” in silica glass and other compositionally simple silicate glasses increases strongly with the water content of the glass (e.g., DRURY and ROBERTS, 1963; COCKRAM et al., 1969; BURN and ROBERTS, 1970; LANFORD et al., 1979; HOUSER et al., 1980; Tsong et al., 1980; NOGAMI and TOMOZAWA, 1984). More recently, similar behavior has been documented for rhyolitic liquids with water contents up to 6 wt% (SHAW, 1974; JAMISON, 1979, 1983; Delaney and KARSTEN, 1981; LAPHAM et al., 1984; STANTON et al., 1985). There has been much speculation on the cause of this strong concentration dependence of water diffusion in amorphous silicates. Some authors have suggested that it is related to the interdiffusion of cations and water molecules or hydroxonium ions (COCKRAM et al., 1969; DOREMUS, 1975; LANFORD et al., 1979; HOUSER et al., 1980; Tsong et al.,
different H-bearing species to water diffusion. We also present concentration and transport problem. Our data differ from most previous studies in that we have determined the concentrations in natural rhyolitic glasses in order to understand the special diffusion profiles by infrared spectroscopic measurement.

Several authors have suggested that, although there are two hydrate species, only H2O molecules are mobile in the melt or glass while OH and H2O contents are related by interconversions between OH and H2O (Doremus, 1969, 1973; Ernserberger, 1980; Smets and Lommen, 1983; Nogami and Tomozawa, 1984; Wasserburg, 1988; Wakahayashi and Tomozawa, 1989). Olbert and Doremus (1983) suggested that during dehydration the diffusing species is molecular H2O but that during hydration the diffusion is via alkali-hydronium interdiffusion. Stanton et al. (1985) proposed that at low temperature OH is the diffusing species and at high temperature H2O is the diffusing species. Chekirmir et al. (1988) assumed that OH is the dominant diffusing species below 0.4 wt% water (hereafter, % refers to weight percent unless otherwise specified) and that diffusion of H2O becomes more important with increasing water content. We note that, although most of the recent treatments focus on the importance to diffusion of the presence of both OH and H2O in the glasses or melts, few of them (Scholze et al., 1975; Olbert and Doremus, 1983; Stanton et al., 1985) actually determined contents of both species and only Stanton et al. (1985) determined species concentration profiles in hydrous silicate glasses.

In this paper, we present new data on the diffusion of water in natural rhyolitic glasses in order to understand the hydration and transport problem. Our data differ from most previous studies in that we have determined the concentrations of both H2O molecules and OH groups along the experimental diffusion profiles by infrared spectroscopic measurement of samples quenched to room temperature. Such data are basic for evaluating the importance of the presence of different H-bearing species to water diffusion. We also present a general theoretical treatment of the problem of the diffusion and local equilibrium of H2O molecules and OH groups (similar to those of Wasserburg, 1988, and Chekirmir et al., 1988) and show how data on concentration gradients in these species can be used to extract quantitative constraints on their diffusion coefficients. The role of speciation in diffusion is interesting not only because of its importance in understanding water transport but also because other components may be present in silicate glasses and melts in several different forms. Thus, insights obtained from working on the water diffusion problem may provide a basis for understanding the diffusion of other components in amorphous and crystalline silicates and for relating them to their structures and properties (Zhang et al., 1990b).

**EXPERIMENTAL AND ANALYTICAL METHODS**

**Dehydration Experiments**

The basic approach used in this work was to study the diffusive transport of water from an initially uniform, approximately semi-infinite source with a boundary condition of zero concentration at its planar interface. Experiments were conducted by holding polished wafers of natural rhyolitic glass (with a variety of initial water concentrations and speciation) in a N2 gas stream at 1 atm total pressure at temperatures of 403-520°C for periods of 10-50 days. After quenching, the samples were sectioned perpendicular to the polished face, and infrared spectroscopy was used to measure the concentrations of hydrous species in the glass as a function of distance from the interface through which water diffused out of the sample over the course of the experiment.

The samples of glass used as starting materials came from the Mono Craters in central California and had initial water contents between 0.2 and 1.7% (see Table 1 and Newman et al., 1986, 1988). Natural glasses were used because large synthetic glass chips with uniform and high water concentrations were not readily available. Fragments of these natural glasses were cut into chips and then ground and polished on parallel surfaces to a typical final thickness of 1 to 4 mm prior to the experiment (Table 1). The width and length of these polished wafers were usually greater than 10 mm, so they can be treated as infinite in these dimensions. Based on infrared analyses, the starting materials were homogeneous to within 5% of the total water present. The speciation of water (i.e., the concentrations of H2O and OH) in these starting glass chips differed in some cases among chips with the same water concentration. We attribute this difference to differences in thermal history. These differences in initial speciation had little effect on experimental results because a quasi-equilibrium speciation was reached in a relatively short time during experiments. Most starting glasses contained bands of microphenocrysts (~20 μm), tentatively identified by optical microscopy as plagioclase, biotite, and magnetite, but MC3b glasses were almost free of microphenocrysts. Starting glasses usually contained bubbles, with the number

<table>
<thead>
<tr>
<th>Table 1. Experimental runs for water diffusion</th>
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<tr>
<td>Glass, w% H2O, w% OH</td>
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<tr>
<td>-----------------------</td>
</tr>
<tr>
<td>KS-b**</td>
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<tr>
<td>KS-D5</td>
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<td>PD-D5</td>
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<td>PD-D2</td>
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<tr>
<td>PD-D3</td>
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<td>KS-45A</td>
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<tr>
<td>MC3b-D4</td>
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<tr>
<td>MC3b-D4</td>
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<tr>
<td>KS-D4A</td>
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* Number in parentheses indicates the number of analyses.

** For the big chip KS-b, some small pieces from corners of the big chip were measured before the experiment, one water was cut and 4 points measured after the experiment. Consequently the initial and the final measurements were made on pieces that are about 5 mm apart.

** Comment: a: the slab was not thick enough and the center concentration was altered slightly by diffusive loss or gain; d: deformed during the run; b: hydration experiment; rh: center of the sample turned red-brown during the experiment.

y: experiment to study reaction kinetics; a: surface reaction.
of vesicles per volume increasing with water concentration: PD glass samples (0.2% water) were free of bubbles; MC3b-D5dif and KS samples contained few bubbles; other MC3b samples (>1.2% water) contained up to ~0.4 vol%. The presence of a small quantity of small bubbles and microphenoocrysts had no major effect on experimental results, as evidenced by similar diffusion coefficients obtained for samples with different percentages of bubbles and microphenocrysts.

Experiments were conducted in two horizontal furnaces equipped with automatic temperature controllers. Each furnace was lined with a silica tube through which dry N2 gas flowed from a tank during the experiment, both to inhibit oxidation of the sample by the atmosphere and to ensure that, if surface equilibrium between the sample and the N2 atmosphere was achieved, the concentration of water at the glass surface would be essentially zero. Two or more glass wafers were placed together in the “hot spot” adjacent to a Type K thermocouple; the control thermocouple for each furnace was outside of the silica tube near the furnace windings. Temperature gradients within the silica tube were <0.1°C/mm in the vicinity of the hot spot at ~900°C. When samples were placed in the hot spot, the reading on the thermocouple in the hot spot inside the silica tube initially decreased by up to 50°C, but a steady temperature was reached in less than 5 min, after which time the difference in reading between the thermocouple at the hot spot inside the glass tube and the thermocouple outside the glass tube was typically less than 2°C. Temperature fluctuations over the course of the experiment were within ±5°C at 500°C. All the thermocouples used were calibrated against a thermocouple that had been calibrated against the melting point of gold. The durations of the experiments were chosen to be long enough so that diffusion could be conveniently measured by infrared spectroscopy (on the order of 500 to 1000 μm), but short enough so that diffusion can be approximated as having occurred within a semi-infinite medium, as roughly estimated from previous measurements of the bulk diffusion coefficient of water (KARSTEN et al., 1982). The glass wafers were quenched in ice + water.

**Hydration Experiment**

We also carried out an experiment in which rhyolitic glass was hydrated by exposing it to water vapor at elevated pressure and temperature. A doubly polished glass wafer with 0.2% initial water was placed with doubly distilled water in an annealed platinum capsule, which was then welded shut. The welded capsule was placed in a rapid-quinch cold-seal pressure vessel and brought to 490°C and 250 bars. Excess water was present in the capsule throughout the experiment. Although the amount of water present as vapor in the capsule changed with time, fH2O inside the capsule is assumed to have been constant and the same as the pressure in the pressurizing medium (distilled water). After quenching, H2O and OH concentrations were measured along the diffusion profile in the wafer, allowing us to determine water speciation. Although it was our intention to compare diffusion during hydration to that during dehydration, the initially doubly polished flat glass wafer deformed into a curved wafer with rough and white-powdered surfaces, so a good diffusion profile could not be obtained.

**Experiments to Examine Water Reaction Kinetics**

To determine the effect of quenching upon speciation, experiments were also conducted to examine the reaction kinetics of the interconversion of H2O and OH in rhyolitic glasses. We used a range of natural glass wafers with different total water concentrations and wafers with similar total water content but different initial H2O and OH concentrations. The wafers were held at elevated temperatures (400–600°C) for different times and then quenched and measured for H2O and OH concentrations. We put fewer and smaller wafers in the furnaces in this set of experiments so that the temperature drop when the wafers were put into the furnaces was small (<1°C) and a steady temperature was reached within 1 min or less than ¼ of run duration, whichever is shorter. Some results are presented here to examine whether species concentrations at experimental temperatures can be preserved after quench. The details of the experiments will be published elsewhere.

**Infrared Analysis**

After quenching, the wafer was sectioned perpendicular to its polished surface near its center (Fig. 1). This provided a glass slice with a complete diffusion profile. The slice was then polished on both sides and analyzed by infrared spectroscopy, in general following the procedures of Newman et al. (1986). In the center of each slice (i.e., in a region of the sample least affected by water loss through the surface), a round aperture (600 μm in diameter) was used to delimit the infrared beam. However, over the region where diffusion was significant, a slit 10 μm wide and 2 mm long (Advanced Laser Systems, Inc., Waltham, Massachusetts, USA) was used. The slit was fixed to a translation stage and then a sample slice was mounted onto the stage. The stage was designed such that the slice could be rotated so that its rim was parallel to the slit, as well as moved in both vertical and horizontal directions by micrometer drives. The rim position of the wafer was determined by seeing it move into the slit with an optical microscope. Once the rim position was determined, the distance away from the rim was determined from the difference between the micrometer reading at the rim and the reading at the position measured: positions measured in this way are reproducible to better than 20 μm in a 1000 μm distance (the positions were independently confirmed by photographs taken after the measurements in a few cases; see Fig. 1). Note that although the slice width is only about 10 μm, the infrared beam diverges inside the sample and the effective width of the sample that is exposed to the beam may be considerably larger than 10 μm, depending on the sample wafer thickness. The convolution may affect the measured diffusion profiles (Ganguly et al., 1989). This effect on concentration profiles was examined by analyzing the same sample (PD-D5) thinned to different thicknesses (~600 vs. ~150 μm). No significant differences in the concentration profiles were found, but the data from the thinner wafers were much less precise due to smaller total absorbances and to interference fringes. Therefore, for most samples a thickness of 600 μm or greater was used to analyze the concentration profiles.

Water concentrations were determined from the infrared spectra obtained with a Nicolet 660SX FTIR. H2O and OH concentrations were determined from the peak height of the absorption bands at 523.0 and 451.5 mm⁻¹ using the molar absorptivities of Newman et al. (1986). (All reported band positions vary by up to 1.0 mm⁻¹ from sample to sample or from one point to another in the same sample.) Baselines were fit by smooth curves drawn with a french curve. Local glass densities were calculated iteratively considering the effect of water concentrations (Silver et al., 1990). OH concentrations are reported as weight percent of H2O that is present as OH. Total water contents were obtained by summation of the concentrations of these two species.

When total water concentration is low or the wafer is thin (for wafer thickness ≤ 150 μm), the absorption bands at 523.0 and 451.5 mm⁻¹ may be too weak for their intensities to be determined precisely. In such cases, the peak height of the band at 357.0 mm⁻¹, which includes contributions from both H2O and OH, was used to determine...
total water concentration. We tried to avoid determining water concentrations using this band when the total water content is high (i.e., when both H$_2$O and OH contribute significantly to total water contents) because its molar absorptivity depends on both H$_2$O and OH contents (Newman et al., 1986). However, at low water concentrations ($\lesssim 0.2\%$), total water concentration is assumed to be proportional to the peak height at 357.0 mm$^{-1}$ with a molar absorptivity of 88 L/m mol-cm (Dobson et al., 1989) because H$_2$O concentration can be ignored (for the purpose of determining absorptivity) compared to that of OH at these low water levels. In a few cases a correction was applied for the growth in the detector of an ice band (325.0 mm$^{-1}$) in the course of the measurements.

Based on both the quality of the spectra and the reproducibility of an internal standard (sample POB1) that was analyzed many times along with the diffusion profiles, the relative precision of the analyses for total water and for OH is about 2–3% when a slit is used and about 1% when the 600 $\mu$m circular aperture is used. The relative precision for molecular H$_2$O depends on total water concentration because the fraction of water dissolved as H$_2$O depends strongly on total water concentration (while OH is usually the major species for the total water concentration range we have studied). The relative precision is about 3% at 1.2% water, 5% at 0.8% water, and 10% or worse at 0.3% water when the slit is used. When the 600 $\mu$m round aperture is used, the relative precision in molecular H$_2$O content is better than 2% at 0.8% water or more and about 20% at 0.2% water. Consequently, H$_2$O is difficult to measure near the sample edge (within ~50 $\mu$m) due to low water concentration and because the precision cannot be improved by using a larger aperture. Another difficulty in measuring H$_2$O and OH concentrations near edges is that the edges of the polished slices are never perfectly flat due to chipping during cutting and polishing and/or due to surficial cracks (likely developed upon quenching and worsened during polishing). Therefore, H$_2$O and OH concentrations could usually only be measured at more than ~30 $\mu$m away from the edge, the exact distance depending on the particular glass wafer.

Since water concentrations at the slice edge could not be directly measured due to these limitations, we confirmed that the water concentration at the edge for two charges (KS-D2 and KS-D3, both with initial ~0.8% water) is essentially zero by the following method. The glass wafers were cut parallel to the face of the original polished wafer surfaces through which diffusion occurred and that slice was polished down to about 20 $\mu$m thick, where one side was the original exterior sample face. Average total water concentration in both slices was measured to be ~0.1% based on the 357.0 mm$^{-1}$ peak. (A number of points in KS-D3 were analyzed this way at different wafer thickness and results are shown as dotted squares in Fig. 3d.) Given that water concentration at 30 $\mu$m away from the edge is ~0.3%, this value of ~0.1% is consistent with an approximate surface water concentration of 0%. We therefore conclude that the water concentration at the edge is close to zero, approaching equilibrium with the dry N$_2$ ambient atmosphere.

Water concentration measured at the sample center after the experiment usually showed a slight (~5%) apparent increase, which we tentatively attribute to a small dependence of the molar absorptivities of H$_2$O and OH bands on thermal history. These small changes in molar absorptivities do not affect our interpretations of the diffusion profiles since these are based nearly entirely on relative concentrations, and small changes in speciation do not affect our results significantly. However, until these effects of thermal history are better understood, caution should be exercised in interpreting small variations (a few percent relative) of species concentrations in rhytholitic glass samples.

**EXPERIMENTAL RESULTS**

**Water Concentration Profiles**

A total of nine successful diffusive dehydration experiments were conducted at temperatures between 403 and 550°C on glasses with initial water contents between 0.2 and 1.7%. Experimental conditions are listed in Table 1. A series of representative spectra covering the concentration profile generated in sample KS-D3 measured with a 10 $\mu$m slit is shown in Fig. 2. Profiles in the concentrations of H$_2$O molecules, OH groups, and total water for all of the experiments are shown in Fig. 3. In all profiles, concentrations of both H$_2$O molecules and OH groups decrease towards the rim of the sample, but H$_2$O/OH ratios decreased with decreasing total water contents.

The smoothness of the profiles shown in Fig. 3 illustrates the precision of both the position and concentration measurements. Another test of the quality of our data is based on the fact that each slice prepared from experimental glass wafers has two edges through which water diffused during the experiment, and the diffusion profiles inward from both edges should be symmetric. Profiles inward from both edges were analyzed in two experimental charges (KS-D3 and PD-D5) and the data are superimposed in Fig. 3. In both cases, concentration profiles measured away from both edges are identical within a few percent, again illustrating the precision and internal consistency of both our concentration and position measurements.

We also measured major oxide concentrations across the water diffusion profile in KS-D2 (530°C, 11.4 d) using an electron microprobe. The concentrations of Na$_2$O and K$_2$O are plotted in Fig. 4 and show no systematic variations across the profile.

**Potential Complications**

Visible changes, including bubble formation and growth, deformation, and discoloration, occurred for samples with high initial water concentration over the course of some experiments. Data obtained on these samples were not used in our efforts to quantify water diffusion. New bubbles formed and/or old bubbles grew for samples with initial water concentrations > 0.7% at 550°C, >1.0% at 530°C, >1.2% at 490°C, and >2% at 403°C. These wafers also deformed to irregular shapes. Discoloration (possibly due to oxidation of ferrous iron to ferric iron by dissolved water) occurred for samples with initial water concentrations > 1.2% at 450°C, >1.5% at 403°C. If these effects proceeded too far, the experiments would be difficult to interpret, so we limit further  

![Fig. 2](image-url) A series of spectra from edge to center for KS-D3 (490°C, 18.6 d). H$_2$O and OH bands are at 530.0 and 451.5 mm$^{-1}$, respectively. Distances from the edge are 40, 120, 200, 530 $\mu$m. H$_2$O and OH concentrations (wt%) are given below the bands.
discussion of our experiments to the water concentration ranges reported in Table 1. For all samples reported in this paper, bubble sizes did not increase noticeably, and only one sample (3b-D4N, 1.7% initial water, 403°C) was slightly discolored after the experiment. Our best data were obtained on the KS samples, which have initial water concentrations high enough (~0.8%) for us to measure both H₂O and OH precisely but low enough so that there are few bubbles before or after the experiments. Moreover, neither did these glasses deform nor were they discolored over the course of the experiments. For the PD samples, although they are clear, free of bubbles, and uncolored after the experiments, their H₂O concentrations could not be precisely determined before or after the experiments. Hence, data from them did not play a decisive role in the development of our water diffusion model.

The Effects of Quenching

Water speciation may be altered during quench of the experiments (STOLPER, 1989; SILVER and STOLPER, 1989; SILVER et al., 1990; DINGWELL and WEBB, 1989, 1991). Since both H₂O and OH concentrations are used in our modelling, knowledge of the extent of quench effects is essential for this study. It would be desirable to measure diffusion profiles at the experimental temperatures, but this is not routinely possible at present. Several experiments were run to study the kinetics of reactions by which OH groups are converted to H₂O molecules and vice versa. In one experiment, an 11 x 12 x 18 mm polished glass parallelepiped (compared to the 1 to 4 mm thick wafers for the diffusion experiments) with 0.8% total water concentration (KS-big in Table 1) was held at 540°C for 5 h and quenched in ice + water. The diffusion distance of water at 540°C in 5 h can be estimated to be ~50 μm based on our diffusion data. Based on thermal
conduction considerations (assuming a thermal diffusivity of $10^{-4}$ m$^2$/s), the center of the parallelepiped cools down to 300°C in ~30 s, while a point 300 μm away from the edge cools down to the same temperature in ~0.1 s. We measured a 4-point profile from the center to about 300 μm away from the edge and found no difference in speciation, demonstrating that for 0.8% water and 540°C the results are independent of average quenching rate between 10 and 2000°C/s. We assume the same result holds for samples with lower water contents and quenched from lower temperatures.

In other experiments designed to address this question, glass wafers with 0.5 to 2.6% dissolved water and with known initial species concentrations were held for various durations at elevated temperatures (400-600°C) and were then measured for H$_2$O and OH content after quenching. Figure 5 shows the variation of the parameter $Q$ vs. time, where $Q$ is defined as

$$Q = \frac{[\text{OH}]}{[\text{H$_2$O}][\text{O}]}.$$  

and O is anhydrous oxygens. Brackets in Eqn. (1) indicate mole fractions of OH and H$_2$O species expressed on a single oxygen basis and $[\text{O}] + [\text{OH}] + [\text{H$_2$O}] = 1$ (for calculation see STOLPER, 1989). At equilibrium, $Q$ is equal to the equilibrium constant, $K$, for the following reaction:

$$\text{H}_2\text{O} + \text{O} \rightleftharpoons 2\text{OH}.$$  

When possible, samples with initially different $Q$ were chosen for this study so that equilibrium was approached from both directions (i.e., from below $K$ and above $K$). At 500°C, parameter $Q$ changed toward $K$ by ~10% in 1 min for the two samples with 1.0 ± 0.1% water shown in Fig. 5a. At ~400°C, the only temperature at which we have samples with more than ~0.85% water, $Q$ changed toward $K$ by ~25% in 1 min for a sample with 2.6% water (Fig. 5b) and changed less than 2% in 5 min for a sample with 1.0% water. The highest initial water content for which we report diffusion experimental results is 1.7% at 403°C. Based on our kinetic data, we can infer that the change of $Q$ toward $K$ in 1 min at 403°C and 1.7% water would be less than 10%. At lower water contents the time to reach equilibrium is much longer (ZHANG et al., 1990a). Since the quench time scale is only several seconds based on thermal conduction considerations, we feel that the effect of quenching on the speciation in all our diffusion experiments can be at most a few percent and can be safely ignored.

**Temperature Dependence of Equilibrium Speciation**

The center of most samples was sufficiently far from the edges that it was unaffected by diffusion over the course of the experiment, but the speciation at the center was affected by reaction (2). All speciation data that are believed to have reached equilibrium based on a variety of criteria are presented in Fig. 6. The details of these equilibrium speciation data will be presented elsewhere. We note here that the speciation depends on temperature and that there is a slight dependence on total water concentration. Based on our studies of quenching effects (ZHANG et al., 1990a), we disagree with the assumption of DINGWELL and WEBB (1989, 1991) that all deviations from simple ideal behavior (i.e., from horizontal isotherms in Fig. 6) are due to speciation changes on quenching, which are enhanced at higher water contents. Our data are in general comparable to those of STOLPER (1989) at similar temperature and water content. These and other equilibrium data on reaction (2) have been fitted to a regular solution model (STOLPER, 1989; SILVER et al., 1990) with resulting parameters (see caption of Fig. 6) different from those of STOLPER (1989) and SILVER et al. (1990). Several calculated isotherms are shown in Fig. 6 and are used below to evaluate departures from local equilibrium along diffusion profiles.
Speciation along Diffusion Profiles and the Approach to Local Equilibrium

To examine whether local equilibrium is reached at each point along diffusion profiles (and at the centers of samples of low initial water concentration), we have compared the speciation along diffusion profiles and as calculated from the regular solution model mentioned in the preceding paragraph. In Fig. 7, we illustrate $Q$ at the centers of experimental charges and along diffusion profiles at various temperatures and compare them with calculated equilibrium isotherm $K$ (the expression for calculating these isotherms is given in the caption of Fig. 6). Note that Fig. 7b compares $Q$ determined along diffusion profiles generated by both hydration and dehydration. Fig. 7 demonstrates clearly that at high water concentration and high temperature, $Q$ in both hydration and dehydration experiments agrees with the equilibrium isotherms within error. However, at low water contents, $Q$ is lower than $K$ during hydration and higher than $K$ during dehydration. Temperature is also an important factor in determining whether equilibrium is reached or not; i.e., for a given run duration, local equilibrium is only reached above a particular water concentration for a given temperature. Specifically, during dehydration, local equilibrium is approximately reached at water concentration $\geq 0.4\%$ at $530^\circ$C (run duration 11.4 d), $\geq 0.5\%$ at $490^\circ$C (18.6 d), $\geq 0.7\%$ at $450^\circ$C (51.7 d), and $\geq 1.2\%$ at $403^\circ$C (39.9 d). During hydration, local equilibrium is approximately reached at $\sim 1.3\%$ water at $490^\circ$C (11.0 d).

DISCUSSION

Water Diffusion Models

In this section we discuss the calculation of diffusion coefficients ($D_{H_2O}$ and $D_{OH}$) from the experimental data. We treat the diffusion of hydroxyl groups phenomenologically and are not concerned with how charges are balanced in the silicate structure. Given that OH groups and H$_2$O molecules may diffuse through a glass at different rates, characterized by $D_{OH}$ and $D_{H_2O}$, respectively, it is possible to treat the water diffusion process by the following general equation (CHEKHMIR et al., 1988; WASSERBURG, 1988):

$$\frac{\partial \text{[water]}}{\partial t} = \frac{\partial}{\partial x} \left( D_{H_2O} \frac{\partial \text{[H}_2\text{O]} }{\partial x} + D_{OH} \frac{\partial \text{[OH]} }{2 \partial x} \right). \tag{3}$$

where [water], [H$_2$O], and [OH] are the mole fractions of total water, H$_2$O and OH, which, when calculated on a single oxygen basis, are approximately proportional to number densities (number of species per unit volume) of these species. The factor 2 in the above equation accounts for the fact that 2 moles of OH are equivalent to 1 mole of H$_2$O in terms of hydrogen; i.e., [water] = [H$_2$O] + [OH]/2. Given initial and boundary conditions, there are two methods to obtain the diffusion coefficients $D_{OH}$ and $D_{H_2O}$ from measured diffusion profiles and the above equation. The first is to solve Eqn. (3) numerically in a forward manner for [water], [H$_2$O], [OH] profiles as a function of $x/(D_{H_2O})^{1/2}$ given the ratio $D_{OH}/D_{H_2O}$. The solution can then be compared with measured concentration profiles to obtain $D_{H_2O}$ from which $D_{OH}$ can then be calculated. (If Eqn. 3 could be solved analytically, this method would be equivalent to fitting measured diffusion profiles by an analytical solution, such as an error function.) The second method is to use measured diffusion profiles to invert an integrated form of Eqn. (3) to obtain both $D_{OH}$ and $D_{H_2O}$ (the Boltzmann-Matano analysis). We use both approaches and we first discuss the forward solution method.

There are two independent unknowns in Eqn. (3), [H$_2$O] and [OH] (the third concentration variable, [water], is related to [H$_2$O] and [OH] by mass balance), which are to be solved as a function of $x$ and $t$ in a forward solution. Hence,
one additional equation is necessary in order to solve for the concentration profiles given $D_{OH}$ and $D_{H2O}$. If there exists a relationship between $[OH]$ and $[H2O]$, it can be combined with Eqn. (3) to solve the diffusion equation. The simplest calculation that we used was to use a constant $Q$ obtained from the observed $[OH]$ and $[H2O]$ in the interior of the sample (this is equivalent to assuming ideal solution and local equilibrium at all positions along the diffusion profile). The calculated curves were found to match the data quite well for initial water concentrations of more than $\sim 0.8\%$ at $D_{OH}/D_{H2O} = 0$ (see footnote “d” of Table 3). This fit is much improved over what would be obtained by assuming a constant diffusion coefficient for total water. However, for samples with lower initial water concentrations (e.g., PD samples with 0.2%) there are small but substantial deviations. A modified model using $K$ from a regular solution model that is weakly concentration dependent only improves the fit slightly. From Fig. 7 it can be clearly seen that at low total water content (i.e., near the edges of all samples and across the entire profile for samples with low initial water) the hydrous species are not in local equilibrium. Therefore, although these simple treatments are definitely in the right direction, they are not adequate at low water contents and temperatures.

To account for departures from local equilibrium along diffusion profiles, a general approach would combine Eqn. (3) with a knowledge of the temperature and concentration dependence of the kinetics of reaction (2), i.e., with a general equation for, e.g., $\delta[H2O]/\delta t$, containing a diffusive flux term due to the local $H2O$ gradient and a reaction term due to local interconversion of $OH$ and $H2O$. Lacking a sufficiently detailed description of these kinetics, and noting that to a good first approximation all analyses of all dehydration samples at a given temperature fall on a single curve on Fig. 7, we have adopted an empirical description of the $[OH]$ and $[H2O]$ relationship, formulated as $Q$ (defined in Eqn. 1) as a function of [water] at a given temperature. The empirical expressions for $Q$ are obtained from polynomial fits of the speciation data presented in Fig. 7 and are given in Table 2. As can be seen from Fig. 7, the empirical functions adopted are strong functions of water concentration at low water contents and approach the equilibrium distribution of species at speciation, the duration of the experiment, and the position in the diffusion profile. Nevertheless, as illustrated below, this approximation yields very good fits to our diffusion profiles and simple trends among the diffusion coefficients so determined.

Diffusion Eqn. (3) and the empirical speciation relationships obtained above with a boundary condition of zero water concentration were solved numerically by making $D_{H2O}$ a new variable ($\tau$) and given an assumed value of $D_{OH}/D_{H2O}$ ($D_{OH}$ and $D_{H2O}$ were both assumed to be constant over the entire diffusion profile). We used an explicit forward finite-difference method (CRANK, 1975; PRESS et al., 1986) to solve Eqn. (3) with the associated expressions given in Table 2 to relate $[H2O]$ and $[OH]$. (Although implicit methods, such as the Crank-Nicholson method, are more stable and more accurate, they were not used because of the complex relationship between [water], $[H2O]$, and $[OH]$ in Eqn. 3.) Using a time interval $\Delta t$ we calculated the profile at total diffusion time $j \Delta t$ where $j$ is an integer. At each new time step $j + 1$, [water] as a function of $x$ was calculated from $[H2O]$ and $[OH]$ profiles at step time $j$ using a finite difference form of Eqn. (3). Then $[H2O]$ and $[OH]$ at time $j + 1$ were calculated using [water] at time $j + 1$ and the empirical speciation relationship. At each calculation a value of $j$ and $2j$ were fixed for a given $\Delta t$. If there was a significant difference between the graph of [water] vs. $x^{j+1}/2 \Delta t$ and [water] vs. $x^{j+1}/2 \Delta t$, the calculation was repeated with $j_{new} \rightarrow 2j_{new}$ until the results converged for total times $j \Delta t$ and $2j \Delta t$. To insure stability, $(\Delta x)^2/\Delta t$ was chosen between 0.25 and 0.4 in the calculations. The numerical solutions were the same when different $(\Delta x)^2/\Delta t$ (0.25 to 0.4) were used and the solutions are smooth. The calculated diffusion profiles were then fitted to the actual diffusion profiles to obtain $D_{H2O}$ using a nonlinear minimization routine to minimize the following expression (i.e., to fit all three measured profiles by one single parameter $D_{H2O}$):

$$S(D_{H2O}) = \sum_{i} \left[ \left( \frac{[\text{water}] - \langle \text{water} \rangle}{\sigma_{\text{water}}} \right)^2 + \left( \frac{[H2O] - \langle H2O \rangle}{\sigma_{H2O}} \right)^2 + \left( \frac{[OH] - \langle OH \rangle}{\sigma_{OH}} \right)^2 \right].$$

where $\sigma_j$ is error in $[j]$, and quantities with $\sim$ represent the values interpolated (using a second order polynomial) from diffusion profile tables from the forward calculation. $D_{OH}$ is then calculated using the $D_{OH}/D_{H2O}$ ratio assumed in the forward calculation and $D_{H2O}$ obtained from the fit. In the fit, calculated concentrations far away from the edge are forced to be identical to the average of the measured concentrations near centers.

**Best-fit Diffusion Coefficients**

Figures 8a and b compare fits to the experimental diffusion profiles in sample KS-D3 (0.8% initial water, 490°C) for $D_{OH}/D_{H2O} = 1$ and $D_{OH}/D_{H2O} = 0$. Figure 8a ($D_{OH}/D_{H2O} = 1$) corresponds to the case of simple total water diffusion so the calculated total water concentration vs. distance profile is proportional to a complementary error function. It is evident that the fit is a poor one in this case. Figure 8b shows that at $D_{OH}/D_{H2O} = 0$ and constant $D_{H2O}$, the fit to the data is excellent. To illustrate the dependence of the difference

---

**Table 2. Empirical expressions for Q at various temperatures**

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>0.000158</td>
<td>0.1056</td>
<td>0.3310</td>
</tr>
<tr>
<td>530</td>
<td>0.000657</td>
<td>0.1222</td>
<td>-0.5066</td>
</tr>
<tr>
<td>490</td>
<td>0.000489</td>
<td>0.0463</td>
<td>0.8012</td>
</tr>
<tr>
<td>450</td>
<td>0.001235</td>
<td>-0.0680</td>
<td>4.0264</td>
</tr>
<tr>
<td>403</td>
<td>0.001891</td>
<td>-0.0648</td>
<td>1.8264</td>
</tr>
</tbody>
</table>

In this expression for $Q$, $Q$ is infinity at [water]=0 which does not produce difficulty in our calculation because $[H2O]$ and $[OH]$ are both zero.
which upon integration from \( \eta_0 \) to \( \eta \) becomes

\[
D_{\text{H}_2\text{O}} \left( \frac{d[H_2\text{O}]}{d\eta} \right)_{\eta_0} + D_{\text{OH}} \left( \frac{d[\text{OH}]/2}{d\eta} \right)_{\eta_0} = 2 \int_{[\text{water}]_0}^{[\text{water}]_{\eta}} \eta d[\text{water}].
\]  

The integral on the right-hand side and the derivatives on the left-hand side can be evaluated numerically from the measured concentration profiles, although large errors may be associated with the numerical derivatives. Were it not for these large errors, Eqn. (6) could be used to solve for both \( D_{\text{H}_2\text{O}} \) and \( D_{\text{OH}} \) from two nearby points where the composition of the sample is essentially constant, and hence both diffusion coefficients can be regarded as constant. Notice that in order

\[
-2\eta \frac{d[\text{water}]}{d\eta} = \frac{d}{d\eta} \left( D_{\text{H}_2\text{O}} \frac{d[H_2\text{O}]}{d\eta} + D_{\text{OH}} \frac{d[\text{OH}]/2}{d\eta} \right),
\]  

between the model calculated profiles and the observed profiles on the \( D_{\text{OH}}/D_{\text{H}_2\text{O}} \) ratio, we show fits for a range of \( D_{\text{OH}}/D_{\text{H}_2\text{O}} \) in Fig. 9a-c. Clearly the fit improves as the ratio decreases based on the figures. Figure 9d shows \( 1 - r^2 \) (where \( r \) is the correlation coefficient; and \( 1 - r^2 \) is proportional to \( S \) in Eqn. 4) of the fits for different values of \( D_{\text{OH}}/D_{\text{H}_2\text{O}} \), which further illustrates the dependence of the quality of the fit on the \( D_{\text{OH}}/D_{\text{H}_2\text{O}} \) ratio for small \( D_{\text{OH}}/D_{\text{H}_2\text{O}} \) ratios. The minimum of the residuals lies near \( D_{\text{OH}}/D_{\text{H}_2\text{O}} = 0 \) \( (D_{\text{OH}}/D_{\text{H}_2\text{O}} < 0.02) \). The same procedure has been followed for PD-D3 (0.2% initial water, 530°C) and 3b-D4 (1.3% initial water, 403°C), and the minima of \( S \) of both were also found to lie near \( D_{\text{OH}}/D_{\text{H}_2\text{O}} = 0 \). The results for PD-D15 suggest that OH is not the dominant diffusing species even for samples in which OH is overwhelmingly the dominant chemical species. (If OH is both the dominant species and dominant diffusing species, the water profile should be proportional to a complementary error function if \( D_{\text{OH}} \) is constant, which is clearly not the case for our low water samples.) This result is contrary to the assumption of CHEKHMIR et al. (1988) that OH is the dominant diffusing species below 0.4% water content. For samples at lower temperatures, the profiles themselves also clearly show that the OH diffusion coefficient is much smaller than that of H2O (just judging from the length scale of the OH and of the H2O profiles in Fig. 3).

We also employed a second, more direct approach to determining \( D_{\text{OH}} \) and \( D_{\text{H}_2\text{O}} \) from the measured H2O and OH profiles in which we inverted Eqn. (3) using a Boltzmann transformation by replacing both \( x \) and \( t \) with a single parameter \( \eta \) \( (=x/2vt; \text{CRANK}, 1975) \). With this transformation we obtain from Eqn. (3) the following:

\[
-2\eta \frac{d[\text{water}]}{d\eta} = \frac{d}{d\eta} \left( D_{\text{H}_2\text{O}} \frac{d[H_2\text{O}]}{d\eta} + D_{\text{OH}} \frac{d[\text{OH}]/2}{d\eta} \right),
\]  

which is from Table 2. (a) \( D_{\text{OH}}/D_{\text{H}_2\text{O}} = 0.5 \); (b) \( D_{\text{OH}}/D_{\text{H}_2\text{O}} = 0.3 \); (c) \( D_{\text{OH}}/D_{\text{H}_2\text{O}} = 0.1 \); (d) \( 1 - r^2 \) vs. \( D_{\text{OH}}/D_{\text{H}_2\text{O}} \).
to solve for both $D_{HZO}$ and $D_{OH}$ in this way, we would need large variations in the two derivatives that are not proportional. (Note that, from this argument, it is impossible to obtain diffusion coefficients of different species if their concentrations were proportional to each other, as they would be, for example, in CO$_2$-bearing glasses in which both CO$_2$ molecules and CO$_3^{2-}$ are potential contributors to bulk carbon diffusion, but present in roughly constant proportions according to Fine and Stolper (1985). The bulk diffusion coefficient for CO$_2$ in this case would be independent of the total CO$_2$ concentration, consistent with the results of Watson et al. (1982). It is precisely the complicated nonlinear relationship between [H$_2$O] and [OH] that allows us to determine $D_{HZO}$ and $D_{OH}$. However, the two derivatives are always correlated (though not proportional) because of the local near equilibrium between H$_2$O and OH. In order to minimize the influence of these errors, we determined values of the two diffusion coefficients (assumed to be constant) to fit the entire profile using a simple linear least-squares procedure. $D_{OH}/D_{HZO}$ thus determined is very small (e.g., $0.05 \pm 0.10$ for KS-D3). This calculation confirms the conclusion presented above from fitting measured profiles with profiles calculated from Eqn. (3) using a forward difference method. However, the errors for both $D_{HZO}$ and $D_{OH}$ are large with the direct approach compared to the fit of measured profiles to calculated profiles.

We conclude from the above analysis that our data are best explained by $D_{OH}/D_{HZO} = 0$. It follows that the transport of water in rhyolitic glasses in the temperature and water concentration range we have studied is governed by the diffusion of H$_2$O molecules. The OH concentration profile is not due to the diffusion of OH groups, but due to the local interconversion between OH groups and H$_2$O molecules by reaction (7). The interconversion plays a critical role in supporting the local concentration of diffusing H$_2$O molecules. This result is consistent with the models of Doremus (1969), Ernsberger (1980), Smets and Lommen (1983), Nogami and Tomozawa (1984), Wasserburg (1988), and Wakahayashi and Tomozawa (1989). The result from analyzing diffusion profiles that $D_{OH} \neq D_{HZO}$ is supported by comparing speciation during hydration and dehydration (Fig. 7b). During dehydration at low total water concentration the observed H$_2$O concentration at any point along a diffusion profile is lower than the equilibrium H$_2$O concentration, whereas during hydration it is higher. This suggests that during dehydration, H$_2$O is lost from a site (whereas during hydration it is added) and the conversion of OH to H$_2$O (or H$_2$O to OH during hydration) is necessary to bring the H$_2$O concentration to the equilibrium value. When the conversion is not rapid enough at low water concentrations, the H$_2$O concentration would be expected to lower during dehydration and higher during hydration than the equilibrium value, as is observed.

Since $D_{OH}/D_{HZO}$ cannot be distinguished from zero, we adopt the approximation that $D_{OH}/D_{HZO} = 0$ to treat all our data to obtain $D_{HZO}$ values. Table 3 lists the best-fit values for $D_{HZO}$ and the goodness of the fit for all our water diffusion experiments assuming $D_{OH} = 0$. The fits are compared with the measured profiles in Fig. 3. For the PD samples, only total water can be measured accurately from 357.0 mm$^{-1}$

<table>
<thead>
<tr>
<th>Glass#</th>
<th>T (°C)</th>
<th>Initial water</th>
<th>$D_{HZO}$</th>
<th>$D_{HZO}$ range</th>
</tr>
</thead>
<tbody>
<tr>
<td>3b-D5</td>
<td>550</td>
<td>0.80</td>
<td>0.121 (0.005)</td>
<td>0.106-0.126</td>
</tr>
<tr>
<td>KS-D2</td>
<td>550</td>
<td>0.83</td>
<td>0.121 (0.005)</td>
<td>0.106-0.126</td>
</tr>
<tr>
<td>PD-D5</td>
<td>550</td>
<td>0.20</td>
<td>0.074 (0.008)</td>
<td>0.060-0.080</td>
</tr>
<tr>
<td>KS-D3</td>
<td>490</td>
<td>0.80</td>
<td>0.040 (0.001)</td>
<td>0.035-0.044</td>
</tr>
<tr>
<td>KM-L1</td>
<td>490</td>
<td>0.80</td>
<td>0.043 (0.003)</td>
<td>0.038-0.049</td>
</tr>
<tr>
<td>KS-D4</td>
<td>450</td>
<td>0.78</td>
<td>0.051 (0.007)</td>
<td>0.046-0.055</td>
</tr>
<tr>
<td>3b-D4N</td>
<td>403</td>
<td>1.68</td>
<td>0.077 (0.005)</td>
<td>0.072-0.087</td>
</tr>
<tr>
<td>3b-D4</td>
<td>403</td>
<td>1.29</td>
<td>0.073 (0.002)</td>
<td>0.068-0.078</td>
</tr>
<tr>
<td>KS-D2A</td>
<td>403</td>
<td>1.72</td>
<td>0.056 (0.006)</td>
<td>0.050-0.061</td>
</tr>
</tbody>
</table>

All calculations assumed $D_{HZO} = 0$ and used speciation given by fit to Q given in Table 2. $r^2$ is the correlation coefficient of the fit.

$^1$ Water concentration at the center of this water was affected by diffusion and $D_{HZO}$ is calculated based on the forward simulation of diffusion in finite space, to account for the effect. Since the initial center water concentration relative to the final concentration is not known precisely (recall apparent water concentration at the center changes slightly during experiments due to dependence of activities on thermal history, see text), there is an additional error associated with this fit which we do not take into account.

$^2$ $D_{OH}$ is 0.36 × 0.002 if constant $Q_{HZO} = 0.005$ is used (1 = 0.0002); $D_{OH}$ is 0.37 × 0.002 if regular solution $K$ is assumed ($1 = 0.0025$).

Table 3. Diffusion coefficients of molecular H$_2$O
Comparison to Previous Studies and Treatment of Previous Data

Most previous studies of water diffusion in rhyolites have been at higher temperatures than our experiments (i.e., on melts rather than glasses) and used hydration (SHAW, 1974; FRIEDMAN and LONG, 1976; ARZI, 1978; DELANEY and KARSTEN, 1981; KARSTEN et al., 1982; JAMBON, 1983; MICHELS et al., 1983; WHITE, 1983) of diffusion-couple (LAPHAM et al., 1984) experiments instead of dehydration experiments. Another difference with previous experiments is that previous authors determined either total water concentration profiles (DELANEY and KARSTEN, 1981; KARSTEN et al., 1982; JAMBON, 1983; LAPHAM et al., 1984) or total water losses during dehydration or gains during hydration (SHAW, 1974; JAMBON, 1979). When total water concentration profiles are determined, an apparent diffusion coefficient for total water ($D_{\text{water}}$) can be obtained from the following diffusion equation:

$$\frac{\partial [\text{water}]}{\partial t} = \frac{\partial}{\partial x} \left( n_{\text{water}} \frac{\partial [\text{water}]}{\partial x} \right).$$

This approach is equivalent to treating the diffusion of both species, H$_2$O and OH, with a single diffusion coefficient of $D_{\text{water}}^*$ (which has to be a strong function of total water concentration to account for experimental data), and is clearly an oversimplification. When total water losses or gains are determined, a water diffusion coefficient that characterizes the mean transport rate over a range of water concentrations can be obtained. This diffusion coefficient is called $D_{\text{water}}^*$ hereafter. $D_{\text{water}}^*$ is not directly comparable to $D_{\text{water}}$. We now discuss how to treat other published data in the context of our two species diffusion model. We first compare our results with previous $D_{\text{water}}^*$ data, and then treat previous $D_{\text{water}}$ data.

Comparison with previous $D_{\text{water}}^*$ data

In the context of our model (i.e., $\delta_{\text{water}} = 0$), $D_{\text{water}}^*$ and $D_{\text{H2O}}$ are related by (CHEKHIMIR et al., 1988)

$$D_{\text{water}}^* = D_{\text{H2O}} \frac{d[H_2O]}{d[\text{water}]}.$$  \hspace{1cm} (8)

$D_{\text{water}}^*$ at various water concentrations from diffusion profiles have been calculated in hydration (KARSTEN et al., 1982; JAMBON, 1983) or diffusion-couple (LAPHAM et al., 1984) experiments. Using Eqn. (8) we can calculate $D_{\text{H2O}}$ from the published values of $D_{\text{water}}^*$, given knowledge of the relationship between [H$_2$O] and [water]. Assuming local equilibrium at the high temperatures of these experiments, the species relationship was extrapolated from our equilibrium data at low temperatures and our estimate of the standard-state enthalpy change of reaction (2) (formula in caption of Fig. 6). From the $D_{\text{water}}^*$ values of KARSTEN et al. (1982) and of LAPHAM et al. (1984), we have calculated $D_{\text{H2O}}$ at 650 to 950°C at water concentrations of 1 to 3%. These values of $D_{\text{H2O}}$ are shown in Fig. 10 and compared with our results obtained at lower temperatures. It can be seen that they are in reasonably good agreement. We have also calculated $D_{\text{H2O}}$ from $D_{\text{water}}^*$ values of JAMBON (1983) at water contents of 1 to 6% after a hydration experiment at 750°C and 200 MPa water pressure. These $D_{\text{water}}^*$ values are greater than those of KARSTEN et al. (1982, hydration at 7 MPa water pressure) at similar water contents, and the corresponding $D_{\text{H2O}}$ values (not shown) depend strongly on water content and are higher than the $D_{\text{H2O}}$ values shown in Fig. 10.

In addition, we have calculated a fit to the water concentration profile in the diffusion-couple experiments of LAPHAM et al. (1984) using our model of H$_2$O diffusion. We again assumed local equilibrium between H$_2$O and OH to relate the concentrations of the two species. The fit to the profile is shown in Fig. 11 and can be seen to be very good. (The interface in the fit is the Matano interface, instead of the actual interface. The Matano interface is the interface at which mass loss from one side equals the mass gain of the other side. The difference between the positions of the actual interface and the Matano interface is due to the Kirkendall effect; see SHEWMON, 1963.) The value of $D_{\text{H2O}}$ ($9 \times 10^{-12}$ m$^2$/s) at 850°C so determined lies almost exactly on the extension of our diffusion data (Fig. 10). If we combine this data point with all of our data, an activation energy of 103
where \( D_{H_2O} \) is in \( \text{m}^2/\text{s} \), \( T \) is temperature in K, \( K \) is the gas constant in J K\(^{-1}\) \( \text{mol}^{-1} \), and errors are \( 2\sigma \) errors. As LAPHAM et al. (1984) carried out their experiments on hydrous silicate melts while ours were done on glasses, we take the excellent agreement to indicate that there are no detectable discontinuities or nonlinear changes in the \( \ln D_{H_2O} \) vs. \( 1/T \) plot due to a glass-melt transition. This is consistent with the observations of JAMBON and SEMET (1978) that glass-melt transitions in silicate systems are difficult to detect in Arrhenius plots of diffusion data.

Based on our treatment, we can successfully reproduce the water diffusion profiles of LAPHAM et al. (1984) and can estimate the apparent total water diffusion coefficients \( D_{\text{water}}^* \) of KARSTEN et al. (1982) and LAPHAM et al. (1984). However, our model cannot reproduce the details of the water diffusion profiles from the hydration experiments of KARSTEN et al. (1982) and JAMBON (1983); neither can our model estimate \( D_{\text{water}}^* \) values of JAMBON (1983), which disagree with the results of KARSTEN et al. (1982). The profiles in both KARSTEN et al. (1982) and JAMBON (1983) deviate from an error function more than our model predicts, especially near the hydration surface. The failure of our model to predict the details of these water profiles cannot be totally due to the fact that these experiments were run at higher temperature in rhyolitic melts or due to errors in the local equilibrium assumption (which should be very good at these high temperatures anyway), given that we can reproduce well the water profiles produced in the diffusion-couple experiments of LAPHAM et al. (1984), which were conducted at similarly high temperatures. Neither can the failure be due to a contribution of \( OH \) to the diffusion of water in their experiments because this would make the total water diffusion profiles deviate less from an error function.

The discrepancy is possibly due to the very nature of hydration experiments, which differ somewhat from dehydration and diffusion-couple experiments. In dehydration and diffusion-couple experiments, the only major concentration gradients are in the H-bearing species. The gradients for other components are primarily due to dilution or enhancement by the addition or loss of water species. However, during "hydration," especially when the fluid phase is dense (at high pressures or in liquid water), both hydration (water dissolves and diffuses into silicate melt/glass) and leaching (silicates dissolve and diffuse out of the silicate into the fluid) occur due to partitioning of components between the two phases. Therefore, during hydration, both water and silicate components such as alkalies are mobile. Even though care was taken to minimize the dissolution and the leaching of the melt by placing rhyolite powders adjacent to the sample (KARSTEN et al., 1982), the effect might still be significant. Because the silicate components actively take part in the process, there may also be coupling between the diffusive components, in the form of interdiffusion (LANFORD et al., 1979) or multicomponent diffusion (which may show up as uphill diffusion, as observed by KARSTEN, 1982). Additionally, at low temperatures (<100°C), a gel-like reaction layer may form near the water-glass interface during hydration (DOREMUS, 1975). As we noted in the experimental section, in experiments in which we hydrated rhyolitic glasses at 490°C and 250 bars, we observed vapor-glass reaction at the interface (possibly due to dissolution and reprecipitation) and deformation of the interface. All these observations suggest that hydration experiments are more complicated and perhaps more difficult to interpret than dehydration or diffusion couple experiments. The above discussions are supported by the observations that no alkali concentration gradients were observed during dehydration (this study, Fig. 4) or during diffusion-couple experiments (LAPHAM et al., 1984), but that such gradients are generated during hydration experiments (WHITE, 1983; KARSTEN, 1982; and numerous studies on the hydration of commercial glasses e.g., TSONG et al., 1980).

We tentatively suggest that, because of diverse complex processes, the hydration results should not be directly compared to diffusion in dehydration or diffusion couple experiments, especially near the vapor-melt or liquid-glass interface. The effects of these complex processes may be more severe under higher water pressures, which may be the reason for the disagreement between the results of KARSTEN et al. (1982) and of JAMBON (1983). Nevertheless, from the agreement of the \( D_{H_2O} \) values calculated from KARSTEN et al. (1982; see Fig. 10), we conclude that the dominant diffusing water species during hydration of rhyolitic melt at high temperatures is probably the same as that during dehydration and diffusion-couple experiments (i.e., molecular \( H_2O \)).

Treatment of \( D_{\text{water}}^* \) values (mean water transport rate)

Many previous authors have studied total water loss during dehydration or gain during hydration and characterized their data in terms of a constant diffusion coefficient for total water, \( D_{\text{water}}^* \) (e.g., MOULSON and ROBERTS, 1961; SHAW, 1974; JAMBON, 1979). Such treatments are complicated by the fact that \( D_{\text{water}}^* \) is in fact not constant along a diffusion profile. In fact, for cases in which \( D^* \) varies with concentration, different values of \( D^* \) could result depending on which of several techniques are used to extract \( D^* \) from total mass gain or loss data (although each is valid for the case in which \( D^* \) is constant along the diffusion profile). These complications may be part of the explanation of why \( D_{\text{water}}^* \) during hydration of silica glasses is higher than that during dehydration under similar conditions (MOULSON and ROBERTS, 1961). We now show that such a discrepancy is to be expected from our treatment of water diffusion even for constant \( D_{H_2O} \) and \( K \).

To obtain \( D^* \) from mass gain or loss data, the following equation, which applies to diffusion in a semi-infinite medium (CRANK, 1975, Egn. 3.15, p. 32), is often used (e.g., JAMBON, 1979; MOULSON and ROBERTS, 1961):

\[
D^* = \frac{\pi}{4t} \left( \frac{M}{c_0 - c_i} \right)^2, \tag{10}
\]

where \( c_0 \) and \( c_i \) are the surface and initial concentrations of the component, \( t \) is the duration of the experiment, and \( M \) is total mass loss or gain per unit area directly measured. \( M \) can also be calculated as follows given a concentration profile:

\[
M = \int_{c_0}^{c_i} (c - c_i) dx. \tag{11}
\]
Assuming $D_{H_2O}$ is constant and defining $\xi = x/2\sqrt{D_{H_2O}}$, we can combine Eqns. (10) and (11) to give the following expression:

$$\frac{\bar{D}_{water}}{D_{H_2O}} = \pi \{ M^* / ([\text{water}]_0 - [\text{water}]) \}^2 \exp \left( \frac{-E^*}{RT} \right),$$

(12)

where $M^*$ is calculated from the $[\text{water}]$ profile from an integration similar to $M$ in Eqn. (11) except that the integration is with respect to $\xi$. Using Eqn. (12), it is possible to relate $\bar{D}_{water}$ and $D_{H_2O}$ during both hydration and dehydration.

We have calculated model water diffusion profiles for both hydration and dehydration assuming $D_{H_2O} = 0$ and constant $K$ and $D_{H_2O}$. $K$ was arbitrarily taken as 0.1. In order to be comparable to Moulson and Roberts (1961) experiments, $[\text{water}]_0$ was taken to be 0.001 and $[\text{water}]$, to be 0 in the hydration calculation and vice versa in the dehydration calculation. Given $K$, $[\text{water}]_0$, and $[\text{water}]$, $[\text{water}]$ as a function of $\xi$ can be calculated and $M^*$ can be found. We then find by applying Eqn. (12) to these two model profiles that $\bar{D}_{water}/D_{H_2O}$ for hydration is a factor of 1.73 times that for dehydration. This is similar to the factor of 2.5 in the values of $\bar{D}_{water}$ for hydration and dehydration reported by Moulson and Roberts (1961). We note that this factor does not depend on $D_{H_2O}$, although it does depend on $K$, $[\text{water}]_0$, and $[\text{water}]$. The small difference between the model and measured factor could be due to our assumption that $K$ is constant and the assumed value of $K$, local disequilibrium during hydration and dehydration (see Fig. 7b and our earlier discussions on disequilibrium), or experimental errors. That $\bar{D}_{water}$ is greater during hydration than during dehydration at the same $D_{H_2O}$ and $K$ can be explained as follows. The interface water concentration and hence $\bar{D}_{water}$ near the interface are high during hydration and low during dehydration, and the interface diffusive flux (which is proportional to $\bar{D}_{water}$ at the interface) controls the water mass gain or loss. Diffusion in the interior also plays a role, of course, and tends, following this line of reasoning, to lessen the difference in $\bar{D}_{water}$ during hydration and dehydration.

Temperature dependence of $D_{H_2O}$. $\bar{D}_{water}$ and $\bar{D}_{water}$

The temperature dependence (i.e., the activation energy) of $D_{H_2O}$, will be approximated well by that of $\bar{D}_{water}$ determined at a fixed water content and by that of $\bar{D}_{water}$ determined under fixed surface and initial water contents even under circumstances in which the speciation of water is not well known. At low water concentrations, both $\bar{D}_{water}$ and $\bar{D}_{water}$ are inversely proportional to $K$, and $\bar{D}_{water}$ can be expressed as follows assuming constant $K$ based on Eqn. (8) (see Doremus, 1969; Wasserburg, 1988):

$$\bar{D}_{water} = \frac{8[\text{water}]D_{H_2O}/K}{1 + \frac{[\text{water}]D_{H_2O}/K}{e^{-(E^*/RT)}}}$$

(13)

where $E$ is the activation energy of $D_{H_2O}$ and $\Delta H^\circ$ is the standard state enthalpy change of reaction (2). Hence the “activation energy” of $\bar{D}_{water}$ at low water content is lower than that of $D_{H_2O}$ by $\Delta H^\circ$, which is $\sim23$ kJ/mol (see caption of Fig. 6). The same applies for $\bar{D}_{water}$ at low water content. At higher water content, the activation energies of $D_{water}$ and $\bar{D}_{water}$ are even more similar to that of $D_{H_2O}$. For example, at equilibrium, based on our regular solution model (Fig. 6), the effect of temperature-dependent $K$ contributes to a spurious “activation energy” of $\bar{D}_{water}$ of only $\sim12$ kJ/mol and of $\bar{D}_{water}$ of only $\sim13$ kJ/mol at 1% total water and about $\sim5$ kJ/mol at 4% total water. Therefore, the activation energies of $\bar{D}_{water}$ and $\bar{D}_{water}$ will typically be 5 to 23 kJ/mol lower than that of $D_{H_2O}$, depending on water concentration.

When the activation energy of $\bar{D}_{water}$ is determined under a fixed $P_{H_2O}$ (e.g., Moulson and Roberts, 1961), it differs from that of $D_{H_2O}$ not only by the temperature dependence in $K$, but also by the temperature dependence of water solubilities. Since $K$ increases with temperature (Fig. 6) and total water solubilities at a fixed $P_{H_2O}$ decrease with temperature (with $\Delta Q_{water}$ of $\sim12$ kJ/mol in silica glasses at $P_{H_2O}$ $\sim0.09$ MPa, Moulson and Roberts, 1961; and $\sim5$ kJ/mol in rhyolitic melts at $P_{H_2O}$ $\sim70$ MPa, Karsten et al., 1982; where $\Delta Q_{water}$ is the standard state enthalpy change for total water dissolution into a silicate), both effects reduce the fraction of $H_2O$ with increasing temperature and hence reduce the “activation energy” of $\bar{D}_{water}$. Depending on the value of $\Delta Q_{water}$ for total water solubilities, the activation energy for $\bar{D}_{water}$ determined at constant $P_{H_2O}$ could thus be significantly lower than that of $D_{H_2O}$. However, due to a low $\Delta Q_{water}$ for total water solubilities in rhyolitic melts, the activation energy of $\bar{D}_{water}$ should also be only slightly lower than that of $D_{H_2O}$.

It is thus not surprising that the activation energies for water diffusion in rhyolitic glasses and melts determined from studies of the temperature dependence of $\bar{D}_{water}$ and $\bar{D}_{water}$ are generally similar to but usually lower than our value of 103 $\pm$ 5 kJ/mol (2σ errors); e.g., 54 $\pm$ 13 kJ/mol (Shaw, 1974), 130 kJ/mol (Arzi, 1978), 46 kJ/mol (Jambon, 1979), and 80 $\pm$ 4 kJ/mol (Karsten et al., 1982) (these errors from previous authors are probably 1σ errors). If an adjustment of $\sim10$ kJ/mol is added to the result of Karsten et al. (1982) to account for the difference between $\bar{D}_{water}$ and $D_{H_2O}$, it would bring their activation energy to $\sim90$ kJ/mol, in better agreement with our result. In any case, the difference between our value and that of Karsten et al. (1982) is not much outside the experimental errors, giving an activation energy for molecular $H_2O$ diffusion at 80 to 110 kJ/mol in the temperature range 400 to 950°C.

Diffusion of Hydroxyl

Our diffusion data and our analysis thereof strongly suggest that hydroxyl groups are essentially immobile compared to $H_2O$ molecules under the conditions of our experiments (i.e., $D_{OH}/D_{H_2O} \ll 1$). Although other workers have reached different conclusions (Tomozawa, 1985; Chekhmir et al., 1988) and there may indeed be conditions under which OH diffusion makes an important contribution to water diffusion, a small diffusion coefficient for OH groups is, a priori, a reasonable result because OH groups are charged and may be strongly bound to silicate tetrahedra. If OH groups are bonded to Si or Al (Wasserburg, 1957), the diffusive behavior of the oxygen in the SiOH or AlOH unit and hence of OH (assuming OH diffuses as a whole unit) may be most similar.
to the self-diffusion of other non-bridging oxygens (however, see Kohn et al., 1989, for an alternative view of the local hydroxyl environments in albite glasses). The self-diffusion coefficient of oxygen determined by \(^{16}O\) and \(^{18}O\) exchange experiments in dry diopside melt (in which non-bridging oxygen is dominant) is \(6 \times 10^{-11} \text{ m}^2/\text{s}\) at 1650°C and 15 kbars (Shimizu and Kushiro, 1984). We can estimate the diffusion coefficient of non-bridging oxygens at 500°C in silicate glass to be on the order of \(10^{-20} \text{ m}^2/\text{s}\) by a gross extrapolation using this result and an activation energy of 250 kJ/mol (the activation energy of oxygen diffusion in jadeite melt; Shimizu and Kushiro, 1984). Given that our value for the diffusion coefficient of molecular H\(_2\)O or total water is on the order \(10^{-14} \text{ m}^2/\text{s}\) at 500°C, this would give \(D_{\text{OH}}/D_{\text{H}_2\text{O}} \sim 10^{-6}\); it may thus not be surprising that the diffusion coefficient of OH is many orders of magnitude smaller than that of H\(_2\)O in rhyolitic glass at this temperature.

The relative contribution of H\(_2\)O and OH diffusion to apparent total water “diffusion” is not only related to the diffusion coefficients of H\(_2\)O and OH, but also to the relative proportions of H\(_2\)O and OH. Since the fraction of H\(_2\)O decreases rapidly with decreasing total water content, it can be seen from Eqn. (3) that the contribution of H\(_2\)O to total water “diffusion” becomes smaller when water concentration is lower. At very low water concentration, it may be necessary to consider the contribution due to diffusion of OH even under the conditions of our experiments. In order to evaluate the relative contributions of H\(_2\)O and OH diffusion to total water “diffusion,” we have derived the following by modifying Eqn. (13) to include \(D_{\text{OH}}\) (again assuming equilibrium and constant \(K\) and low water concentrations):

\[
D_{\text{water}}^* \approx D_{\text{OH}} + 8D_{\text{H}_2\text{O}}/K. \quad (14)
\]

Hence, the contribution to \(D_{\text{water}}^*\) (i.e., the flux of total water) due to OH diffusion would be the same as that due to H\(_2\)O diffusion if \([\text{water}] = KD_{\text{OH}}/(8D_{\text{H}_2\text{O}})\). Assuming \(K = 0.1\) (at \(\sim 500^\circ\text{C}\)) and \(D_{\text{OH}}/D_{\text{H}_2\text{O}} \sim 10^{-6}\), then the contribution of OH and H\(_2\)O diffusion would be identical at \([\text{water}] \sim 10^{-6}\). These arguments are in accord with our conclusion that even at total water concentration as low as 0.2%, or \([\text{water}] \sim 0.0036\) (where H\(_2\)O is minute compared to OH), the contribution of OH diffusion to total water “diffusion” is still negligible.

Chekoshik et al. (1988) assumed that at total water concentration lower than 0.4%, OH is the only diffusing species and obtained \(D_{\text{OH}}\) by equating it to \(D_{\text{water}}^*\) at these low water concentrations. They then calculated \(D_{\text{H}_2\text{O}}\) from \(D_{\text{water}}^*\) at higher water contents by subtracting the contribution from OH diffusion. Their calculations based on this assumption would indicate that \(D_{\text{OH}} = D_{\text{H}_2\text{O}} \approx 10^{-10} \text{ poise}\) (Fig. 3 in their paper), which is clearly inconsistent with our experimental results.

**Comparison of H\(_2\)O Diffusion with Diffusion of Other Neutral Species**

The diffusion coefficient of molecular H\(_2\)O can be compared to that of other neutral species, especially the noble gases. Noble gas diffusion coefficients in rhyolitic glasses have been determined previously for He at 192–267°C (Jambon and Shelby, 1980), Ne at 100–400°C in tektites (Reynolds, 1960), Ne at 200–700°C (Matsuda et al., 1989), and Ar at 500–900°C (Carroll and Stolper, pers. comm.; Matsuda et al., 1989). The activation energies for the diffusion of He (35 ± 7 kJ/mol), Ne (65 ± 9 kJ/mol based on regression of the data of Matsuda et al., 1989, excepting two points that lie outside the trend), H\(_2\)O (103 ± 5 kJ/mol, based on this work and one data point from Lapham et al., 1984), and Ar (152 ± 10 kJ/mol, Carroll and Stolper, pers. comm.) are shown in Fig. 12 against their molecular radii. The activation energy \(E\) (kJ/mol) can be expressed as a function of the radii (\(r\) in Å) of these neutral molecular species:

\[
E = 94(r - 0.31)^2. \quad (15)
\]

In agreement with the elastic theory of diffusion (see Jambon, 1982, for a review), although the parameters (94 kJ mol\(^{-1}\) Å\(^{-2}\) and 0.31 Å) are not the same as those of Jambon (1982). The fact that \(D_{\text{H}_2\text{O}}\) follows the same relationship in an \(E\) vs. \(r\) plot as the noble gas elements suggests that molecular H\(_2\)O diffuses in a manner similar to the noble gases, which are generally thought to be relatively unbound species that reside in holes in the glass structure (Shackelford and Masaryk, 1978; Shackelford and Brown, 1981).

**CONCLUSIONS**

Water dehydration experiments on rhyolitic glasses have been carried out under a N\(_2\) atmosphere and various temperatures. Concentration profiles of both H\(_2\)O molecules and OH groups were measured by Fourier transform infrared spectroscopy. As found in previous studies, the measured water concentration profiles do not match expectations based on a single constant diffusion coefficient for total water. We have modelled the diffusion of water by the diffusion of two

![Fig. 12. Activation energies for the diffusion of molecular species He, Ne, H\(_2\)O, and Ar. Error bars represent 2σ errors. Data for He are from Jambon and Shelby (1980); for Ne are from Reynolds (1960) and Matsuda et al. (1989); for H\(_2\)O are from this paper; and for Ar are from Carroll and Stolper (pers. comm.).](image)
species: H$_2$O molecules and OH groups. It is assumed that the local abundance of these species is controlled by an interconversion by the reaction H$_2$O + O $\leftrightarrow$ 2OH, and an empirical relationship between speciation and total water concentration along the diffusion profiles was obtained from infrared measurements. The diffusion coefficients for both species were then calculated from the concentration profiles. Our results indicate that the diffusion coefficient of OH is negligible compared to that of H$_2$O at 400–530°C (D$_{OH}$ < 0.02D$_{H2O}$ and could be much smaller), and OH does not contribute significantly to the diffusion of total water even at water concentrations as low as 0.2%, where the concentration of H$_2$O is minute compared to that of OH. The variation of OH concentration along the diffusion profile is inferred to be due to the local interconversion between OH groups and H$_2$O molecules. The reaction also provides the diffusing H$_2$O species. The conclusion that H$_2$O molecules are the predominant diffusing species at very low to high water concentrations confirms the results of several previous studies. D$_{H2O}$ values vary by less than a factor of two over the total water concentration range of 0.2 to 1.7%. The activation energy for diffusion of molecular H$_2$O is $\sim$103 kJ/mol, and D$_{H2O}$ in m$^2$/s is given by

$$\ln D_{H2O} = -\frac{(14.59 \pm 1.59) - (103000 \pm 5000)/RT}{400°C \leq T \leq 850°C}$$

where $R$ is in J K$^{-1}$ mol$^{-1}$. When compared with diffusion of noble gases, the diffusion coefficient of H$_2$O follows the same trend in an activation energy vs. radius plot. This supports the contention that what we call molecular H$_2$O behaves during diffusion as a neutral molecular species.

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