H₂O diffusion models in rhyolitic melt with new high pressure data
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Water diffusion in silicate melts is important for understanding bubble growth in magma, magma degassing and eruption dynamics of volcanos. Previous studies have made significant progress on water diffusion in silicate melts, especially rhyolitic melt. However, the pressure dependence of H₂O diffusion is not constrained satisfactorily. We investigated H₂O diffusion in rhyolitic melt at 0.95–1.9 GPa and 407–1629 °C, and 0.2–5.2 wt.% total water (H₂Ot) content with the diffusion-couple method in a piston-cylinder apparatus. Compared to previous data at 0.1–500 MPa, H₂O diffusivity is smaller at higher pressures, indicating a negative pressure effect. This pressure effect is more pronounced at low temperatures. Assuming H₂O diffusion in rhyolitic melt is controlled by the mobility of molecular H₂O (H₂Om), the diffusivity of H₂Om (D_{H₂Om}) at H₂Ot ≤ 7.7 wt.%, 403–1629 °C, and ≤ 1.9 GPa is given by

\[
D_{H₂Om} = D_0 \exp(aX),
\]

with \( D_0 = \exp\left(13.375 + 1.8875P - \frac{12939 + 3625.6P}{T}\right) \),

and \( a = -37.256 + \frac{75884}{T} \).

where \( D_0 \) is in µm²/s, \( X \) is mole fraction of H₂Ot on a single oxygen basis, \( T \) is temperature in K, and \( P \) is pressure in GPa.

H₂O₂ diffusivities (\( D_{H₂O₂} \)) can be calculated from H₂Oₐ diffusivity, or directly from the following expression:

\[
\ln(D_{H₂O₂}/X) = 13.47 - 49.996X + 7.0827\sqrt{X} + 1.8875P - \frac{9532.3 - 91933X + 13403\sqrt{X} + 3625.6P}{T}.
\]

At low H₂Ot content (up to 2 wt.% if an error of a factor of 2 is allowed), H₂O₂ diffusivity is approximately proportional to H₂Ot content:

\[
D_{H₂O₂} = \frac{C}{C_0} \exp\left(9.5279 + 1.8875P - \frac{9698.5 + 3625.6P}{T}\right),
\]

where \( C \) is H₂Ot content in wt.% and \( C_0 \) is 1 wt.%. The new expressions for H₂O diffusion not only reproduce our own data, but also match data in literature from different laboratories and using different methods, indicating good inter-laboratory and multi-method consistency. The new expressions cover a wide range of geological conditions, and can be applied to H₂O diffusion in rhyolitic melts in various volcanic and magmatic processes.

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1. Introduction

Water is a major volatile component in natural silicate melts. The diffusion of water is necessary to the understanding of a series of volcanic processes, such as bubble growth (e.g., Liu and Zhang, 2000).
magma degassing, and magma fragmentation [Zhang, 1999a]. Within natural melts, rhyolite has been the most thoroughly investigated with respect to H2O diffusion due to common occurrences of explosive rhyolitic eruptions. Early workers used measurements involving bulk hydration/dehydration (Shaw, 1974; Friedman and Long, 1976; Jambon, 1979) or the ion microprobe (Delaney and Karsten, 1981; Karsten et al., 1982; Lapham et al., 1984). They demonstrated H2O diffusivity in rhyolitic melt increases with its concentration. Infrared and NMR studies (e.g., Orlova, 1962; Bartholomew and Schreurs, 1980; Stolper, 1982) showed that water is present in silicate melts as at least two species: molecular H2O (H2Om) and hydroxyl group (OH). Therefore, in order to understand the fundamental mechanism of H2O diffusion in melts, it is instructive to understand the role of water speciation in diffusion (Wasserburg, 1988).

Zhang et al. (1991) investigated the dehydration of rhyolite samples with total H2O content (H2Ot) <2 wt.% at low temperatures (403–530 °C), which allows the concentrations of the two H2O species preserved through quenching for infrared determination (Zhang et al., 1995, 1997a; Withers et al., 1999). They concluded that H2Om is the dominant diffusing species, whereas OH is almost immobile and its concentration profile is due to species conversion to maintain equilibrium. Furthermore, they assumed concentration-independent H2Om diffusivity and modeled the concentration profiles well. Later, it was found that the concentration-independent H2Om diffusivity assumption of Zhang et al. (1991) cannot be extended to high H2O content (up to 9.1 wt.%) (Behrens and Nowak, 1997; Nowak and Behrens, 1997). Zhang and Behrens (2000) proposed that H2Om diffusivity increases exponentially with H2O and successfully reconciled all the experimental data covering a fairly wide range of temperature (403–1215 °C), pressure (0.1–810 MPa) and water content (0.1–7.7 wt.%). [The exponential dependence of the diffusivity of a neutral molecular or atomic species has also been observed for CO2 (Watson, 1991) and Ar (Behrens and Zhang, 2001,)] Okumura and Nakashima (2004) reported new H2O diffusion data using in situ measurements of dehydration experiments. Behrens et al. (2007) investigated both H2O and 18O diffusion at 100 MPa from hydration experiments, demonstrating H2Om is the carrier of 18O diffusion. Other natural melts that have been investigated for H2O diffusion include basalt (Zhang and Stolper, 1991; Okumura and Nakashima, 2006), andesite (Behrens et al., 2004, Okumura and Nakashima, 2006), dacite (Behrens et al., 2004, Liu et al., 2004, Okumura and Nakashima, 2006), and trachyte (Freda et al., 2003).

This study focuses on H2O diffusion in rhyolitic melt. Although H2O diffusion in rhyolite has been investigated extensively, the pressure dependence of H2O diffusivity has not been well resolved, compared to temperature and water concentration dependence, as pointed out by Zhang and Behrens (2000) and Zhang et al. (2007). The majority of the experiments that constrained the dependence of diffusivity on H2O content in Zhang and Behrens (2000) were at 500 MPa. Therefore, application of their model to pressures other than 500 MPa may not be accurate. Behrens et al. (2007) noted that the dependence of H2O diffusivity on H2O content at 100 MPa differs from that predicted by Zhang and Behrens (2000). Because volcanic eruption is a decompressional process as the magma is upwelling, the pressure effect on H2O diffusivity is crucial and needs to be evaluated more accurately. To fulfill such a need, we carried out an experimental investigation on H2O diffusion at 0.95–1.9 GPa and 407–1629 °C, so that the pressure range (0–1.9 GPa) is large enough to constrain the pressure effect and to infer H2O diffusivity at ~0.5 GPa for modeling bubble growth and volcanic degassing. (Diffusion experiments at low pressure such as 0.1 MPa and high H2O content cannot be accomplished because of bubble formation.) Our study makes the rhyolitic system the first for which H2O diffusivity is known as a function of temperature (400–1630 °C), pressure (0–2 GPa) and H2O content (0–8 wt.%).

2. Experimental and analytical methods

2.1. Starting materials

One of the starting materials, the anhydrous rhyolitic glass CIT, is a natural sample from Coso Range, California (Newman et al., 1986), containing small amounts of microlites and bubbles. These imperfections are not expected to have much effect on H2O diffusion. The water content is 0.20–0.22 wt.%. Hydrous rhyolitic glasses with H2O content of 4 to 5 wt.% are synthesized by loading dry glass powder and water into Au80Pd20 capsules in alternating portions and heated at 1000 °C and 500 MPa for 3 days in an internally heated pressure vessel (IHPV) at the University of Hannover. Sample GMR+2 is synthesized at 1400 °C overnight from dry rhyolitic glass from Glass Mountain, California (Hui et al., 2008a). These rapidly quenched (initially 200 °C/min under isobaric conditions) hydrated samples are transparent and free of crystals and bubbles, and contain 2.3 wt.%, 4.0 wt.%, and 5.2 wt.% H2O homogeneously distributed (<3% relative variability). All anhydrous and hydrous rhyolitic glasses are light brown in color, and are analyzed with a Cameca SX100 electron microprobe at the University of Michigan. The dry compositions of all rhyolite samples used in this study are similar, as reported in Table 1, except for a slightly lower silica content for GMR-2. No significant differences in H2O diffusivity between GMR-2 and other samples were noticed. Anhydrous rhyolitic cylinders of 1.2–1.5 mm thickness, and hydrous cylinders of 2.5–2.9 mm thickness were prepared and doubly polished for infrared analysis and subsequent diffusion-couple experiments.

2.2. Diffusion-couple experiments

Diffusion-couple experiments were carried out in a 0.5° end-loaded piston–cylinder apparatus at the University of Michigan. Anhydrous and hydrous rhyolitic glass cylinders of the same diameter (2.4 mm) were placed into a platinum tube that was welded shut. The less dense hydrous half was always on top of the anhydrous half to mitigate convection. Crushable MgO rod and a BaCO3 cell were used as pressure medium inside and outside the graphite furnace, respectively.

The experimental temperature was monitored by a type D thermocouple (Re200W80–Re200W70) and simultaneously recorded by a computer program. In high temperature runs (1118–1629 °C), water diffusion is rapid and only a short duration (2–10 min) is necessary. Therefore, a stepwise heating procedure was programmed with a Eurotherm controller so that it took only ~24 s from the relaxation temperature (200 °C) to the target temperature with only small overheating of 1–4 °C. Because the experimental durations of low

| Table 1 Composition of rhyolitic glasses (wt.% on anhydrous basis) |
|-----------------|-----------------|-----------------|-----------------|
| CIT             | GMR+2           | Rhy4            | Rhy5            |
| SiO2            | 76.93           | 73.12           | 76.87           | 76.05           |
| TiO2            | 0.05            | 0.28            | 0.04            | 0.10            |
| Al2O3           | 13.18           | 14.49           | 13.38           | 13.93           |
| FeO             | 0.94            | 1.35            | 0.97            | 0.75            |
| MnO             | 0.04            | 0.06            | 0.04            | 0.04            |
| MgO             | 0.02            | 0.29            | 0.03            | 0.12            |
| CaO             | 0.44            | 1.30            | 0.55            | 0.87            |
| Na2O            | 4.29            | 4.27            | 4.14            | 4.01            |
| K2O             | 4.62            | 4.36            | 4.65            | 4.22            |
| P2O5            | 0.04            | 0.09            | 0.01            | 0.07            |
| Total           | 100.55          | 99.61           | 100.68          | 100.16          |
| H2O (IR)        | 0.20            | 2.27            | 3.96            | 5.17            |

For each sample, 5 analyses are averaged. Analyses are made on a Cameca SX100 electron microprobe using a scanning beam of 15 kV voltage and 4 nA current. Raw oxide contents are divided by (1–c/100) so as to normalize to dry composition, where c is the water content from infrared analysis in wt.%. 

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temperature runs (407–609 °C) were relatively long (>24 h), manual heating was applied and it took ~1 min to reach the target temperature from the relaxation temperature of 100 °C. Temperature fluctuation during the experiment was generally within ±1 °C, but spikes of ±5 °C were observed for several brief periods (~5 s) in long experiments. Experimental assemblages were rapidly quenched (with a mean cooling time scale of 8 s based on Zhang et al., 2000) by chilled water after turning off the power. A typical thermal history of high temperature runs, including relaxation, dwelling, and quenching, is plotted in Fig. 1. Effective duration accounting for diffusion during heating and cooling was estimated to be 12–16 s by assuming an activation energy of 100 kJ/mol for water diffusion, based on the method described in Zhang and Behrens (2000). Adjustment of about 20 s (including the effect of temperature spikes) for long duration experiments (>24 h) is negligible and not applied. Temperature at the center of the experimental charge is the thermocouple temperature plus a correction based on the calibrated temperature gradient inside the charge (Hui et al., 2008a). The overall uncertainty in temperature is estimated to be 10 K.

The pressure is manually kept at either 1 or 2 GPa using a piston-cylinder apparatus. Due to the precision of pressure based on quartz–coesite transition against the phase boundary determined by Bose and Ganguly (1995). A similar calibration was carried out on another piston-cylinder apparatus in our lab by Hui et al. (2008a), and the correction is 6%. More details about the pressure calibration can be found in Hui et al. (2008a). Uncertainty associated with pressure is ~50 MPa. At about 2 GPa, the hydrous rhyolite, especially those having high water content, readily crystallizes when the temperature is above 480 °C, and the liquidus of dry rhyolite increases with pressure. These considerations significantly limit the experimental temperature range. Details of eight successful experiments can be found in Table 2. Six other runs are deemed unsuccessful and not reported because of partial to complete crystallization of the hydrous half, or poor contact between the two halves.

2.3. Infrared analysis

Water contents of starting samples were measured with Fourier transform infrared (FTIR) spectrometry, in the dry and N2-purged main chamber of the FTIR (Perkin-Elmer Spectrum GX) at the University of Michigan. Doubly polished rhyolite cylinders were attached to a sample holder with pinhole of 531 μm diameter. A NIR source, CaF2 beamsplitter, and liquid nitrogen cooled InSb detector were used for 64 scans from 9000 to 2000 cm⁻¹. After a diffusion-couple experiment the quenched sample in Pt capsule was mounted into epoxy resin and a doubly polished section of 200–250 μm thickness was prepared along the cylindrical axis for FTIR microscopy. The thinness reduces the refractive divergence of the infrared beam inside the sample, while still affording reasonable absorbance at the same time. After high temperature runs the glasses usually become lighter colored than their pre-annealing counterparts. Cracks roughly parallel to the interface in the experimental charge, presumably due to shrinkage during quenching, are always present and are a major source of difficulty and error for the FTIR measurements. For some wide cracks, distances must be subtracted to smooth the concentration profile across the cracks.

The Autoimage microscope system, with an MCT (mercury cadmium telluride) detector cooled by liquid nitrogen, is attached to the Spectrum GX spectrometer for the analysis of H₂O concentrations along the diffusion profile. The aperture is 20 μm wide and 200 μm long, but an edge response analysis shows that the spatial distribution of the infrared signal is roughly Gaussian with a full width at half maximum (FWHM) under analysis conditions being about 30 μm. That is, the spatial resolution is much worse than 20 μm. This convolution effect is important for short profiles (<200 μm long) but negligible for longer profiles (~500 μm long), and will be treated further in the Discussion.

A complete diffusion profile, typically 40–80 points, was acquired with background updated after every 5–10 points. Spectra were hand-fitted with two straight tangential baselines (TT method of Withers and Behrens, 1999) at 5230 cm⁻¹ and 4500 cm⁻¹. Peak heights were measured to calculate molecular H₂O (H₂O₉₉) and hydroxyl group (OH) concentrations, respectively, using the calibration of Withers and Behrens (1999). The sum of H₂O₉₉ and OH is H₂O concentration. Although the calibration of Withers and Behrens (1999) may not be able to retrieve accurate species concentration as that of Zhang et al. (1997b) at relatively low H₂O (≤2.7 wt.%), it can be applied to H₂O₉₉ up to 9.2 wt.% and is less time-consuming for processing a large amount of spectra.

3. Experimental results

Details of the eight successful experiments are listed in Table 2. All H₂O diffusion profiles are illustrated in Fig. 2. Owing to reactions during quench, H₂O₉₉ and OH concentrations from experiments at >780 °C
H2O conditions including data in this and previous studies. The construction of a comprehensive model on H2O diffusivity in rhyolitic and it is necessary to consider the dependence of diffusivity on H2O diffusion in rhyolitic melts. Fig. 3 summarizes the coverage of the region of the anhydrous and hydrous ends and near the capsule, water concentrations may differ from the initial concentrations, attributed to transport along cylinder walls (Zhang and Behrens, 2000). These measured points are excluded from the final data; they are not shown in Fig. 2 and not used for extracting H2O diffusivity. Diffusion profiles at high temperatures are usually longer and better resolved than those at lower temperatures. Because H2O diffusivity depends on water content, the diffusion profiles do not resemble error function curves, and it is necessary to consider the dependence of diffusivity on H2O concentration when modeling these profiles.

This study significantly expands the P–T conditions of H2O diffusion in rhyolitic melts. Fig. 3 summarizes the coverage of P–T–H2O conditions including data in this and previous studies. The extensive investigations on a wide range of temperature (400–1630 °C), pressure (0–2 GPa), and H2O (0–8 wt.%) allow the construction of a comprehensive model on H2O diffusivity in rhyolitic melt, which can be applied to almost all relevant geologic conditions.

4. Discussion

4.1. Modeling diffusion profiles

The equation describing the diffusion of total H2O (H2O₂) is as follows:

\[
\frac{\partial X}{\partial t} = \frac{\partial}{\partial x} \left( D_{H2O} \frac{\partial X}{\partial x} \right),
\]

where X is mole fraction of H2O on a single oxygen basis (Stolper, 1982; Zhang, 1999b) and is calculated as \( X = C/18.015 \) [\( C/18.015 + (100–C)/32.49 \)] with C being H2O content in wt.%, \( t \) is time, \( x \) is distance, and \( D_{H2O} \) is H2O diffusivity which depends on H2O concentration (and therefore depends on \( x \)). A common approach for obtaining the concentration dependence of the diffusivity is to use the Boltzmann–Matano method. This method is independent of presumptions of the relation between diffusivity and concentration, but the precision of this method is not high (Zhang and Behrens, 2000). An alternative approach is to assume a diffusivity concentration relation, and whether such an assumption is reasonable can be judged from the quality of the fitting. Because molecular H2O (H2O₂m) and hydroxyl (OH) may contribute distinctly to H2O diffusion, the mechanistic approach to H2O diffusion is to consider the contribution of the two water species (H2O₂m and OH) separately:

\[
\frac{\partial X}{\partial t} = \frac{\partial}{\partial x} \left( D_{H2O₂m} \frac{\partial X_{H2O₂m}}{\partial x} + D_{OH} \frac{\partial X_{OH}/2}{\partial x} \right),
\]

where \( D_{H2O₂m} \) and \( X_{H2O₂m} \) are diffusivity and mole fraction of molecular H2O, and \( D_{OH} \) and \( X_{OH} \) are diffusivity and mole fraction of hydroxyl group. Zhang et al. (1991) and Zhang and Behrens (2000) concluded that H2O₂m is the dominating diffusion species, and OH is almost immobile. Then Eq. (2) reduces to

\[
\frac{\partial X}{\partial t} = \frac{\partial}{\partial x} \left( D_{H2O₂m} \frac{\partial X_{H2O₂m}}{\partial x} \right).
\]

If the reaction H2O₂m + O = 2OH is in equilibrium, \( X_{H2O₂m} \) can be determined from X using Eq. (13) in Zhang (1999b). The equilibrium constant was determined by Zhang et al. (1997b). By comparing Eqs. (1) and (3), one can find the relation between \( D_{H2O₂m} \) and \( D_{H2O₂m} \):

\[
D_{H2O₂m} = \frac{\partial X_{H2O₂m}}{\partial x}.
\]

Zhang and Behrens (2000) proposed that molecular H2O diffusivity depends exponentially on total H2O content:

\[
D_{H2O₂m}(\alpha) = D_0 \exp(\alpha x),
\]

where \( \alpha \) is a parameter depending on temperature and pressure. They used a trial and error method to estimate the value of \( \alpha \). This model fits all the diffusion profiles well. Furthermore, diffusivity of molecular species such as CO₂ and Ar has been shown to depend on H2O exponentially (Watson, 1991; Behrens and Zhang, 2001).

We will also assume Eq. (5) in treating H2O diffusion profiles. The program code of Zhang and Behrens (2000) is revised so that the parameter \( \alpha \) is determined from the fitting rather than by trial and error. Because of this improvement, the uncertainty on the parameter \( \alpha \) can also be evaluated (which was the main purpose of revising the code). Hence, in the new code, \( \alpha \) and \( D_0 \) are to be determined by fitting the profile, among which \( \alpha \) is largely determined by the shape of the diffusion profile, and \( D_0 \) largely by the length of the diffusion profile (and the value of \( \alpha \)). In the new fitting, the Levenberg–Marquardt algorithm (Press et al., 1992) is adopted to calculate new values of the fitting parameters in each iteration until the sum of the squares of residuals is minimized.

The new fitting procedure was successfully applied to the six diffusion profiles acquired at ~1100 °C and all are well fit. Two other profiles (Rhy-DC06-8 and Rhy-DC06-9) are not sufficiently long compared to the spatial resolution of FTIR microscope (~30 μm in terms of FWHM). Hence, they are likely distorted and prolonged by the convolution effect (Ganguly et al., 1988) and cannot be used to extract best-fit \( \alpha \). To maintain consistency and find the errors of the best-fit \( \alpha \) values, we also applied the new fitting procedure to the profiles at 250–500 MPa in Zhang and Behrens (2000). All best-fit \( \alpha \) values (Table 3) apparently form a linear trend with \( 1/T \) (Fig. 4A), without much dependence on pressure. A weighted linear regression yields

\[
\alpha = (–37.256±1.863) \times \frac{75884±2286}{T},
\]

where \( T \) is in K. The above equation differs from the expression of \( \alpha \) in Zhang and Behrens (2000), who noticed a dependence of \( \alpha \) on pressure with data for a small pressure range. With a larger pressure coverage by combining this study and previous studies, the pressure dependence of \( \alpha \) is within experimental uncertainty. With \( \alpha \) values from Eq. (6), all diffusion profiles, including those reported in Zhang et al. (1991) and Zhang and Behrens (2000), are refit to find the best \( D_0 \).

For the two short profiles (Rhy-DC06-8 and Rhy-DC06-9), the fitting procedures differ from the other profiles, to examine the convolution effect. A convoluted profile is computed from the theoretical profile by assuming a Gaussian distribution of infrared signal with FWHM = 30 μm. The convoluted profile is then used to fit the measured profile. The excellent fitting (Fig. 2) further verifies the effect of convolution. Similar convoluting procedure is also tested on long profiles such as Rhy-DC07-12, and the difference is negligible and therefore not applied.

All fitting results are reported in Table 4. The precision of diffusion-couple experiments are generally better than dehydration experiments. Fits of profiles from this work are plotted as solid curves together with data points in Fig. 2, and they match excellently.

\( D_0 \) values (in μm²/s) in Table 4 are plotted in Fig. 4B. At a fixed pressure, the temperature dependence follows the Arrhenius relation despite crossing the glass transition. \( D_0 \) decreases from...
0.1 MPa to 0.5 GPa to 1.9 GPa, and this negative pressure effect is more pronounced at low temperatures, but becomes minimal at $>1200$ °C. Hence, at a given pressure, $\ln D_0 = \ln A - \frac{E_a}{(RT)}$, where $E_a$ is the activation energy, $R$ is the gas constant, and $A$ is the pre-exponential factor. When the pressure dependence is examined, not only is the activation energy dependent on pressure, but...
also lnA. We fit lnD₀ as a function of temperature and pressure as follows:

\[
lnD₀ = \left( 13.375 \pm 0.483 \right) + \left( 1.8875 \pm 0.5179 \right) \frac{P}{T} + \left( 129.39 \pm 489 \right) + \left( 3625.6 \pm 647.2 \right) \frac{1}{P}.
\]  

(7)

where \( D₀ \) is in \( \mu m^2/s \), \( T \) is in K, and \( P \) is in GPa. Eq. (7) reproduces all lnD₀ data with a 2σ error of 0.49 and a maximum error of 0.63. If we were to fit lnD₀ without the extra pressure term (the dependence of Table 3

<table>
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<tr>
<th>Run #</th>
<th>T (°C)</th>
<th>P (GPa)</th>
<th>t (s)</th>
<th>a</th>
<th>( R² )</th>
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<tr>
<td>Rhy-DC07-12</td>
<td>1321</td>
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<td>248</td>
<td>13.53 ± 1.43</td>
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<td>31.76 ± 8.49</td>
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<td>Rhy-DC3</td>
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<td>1360</td>
<td>7.07 ± 1.19</td>
<td>0.9993</td>
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</table>

Errors of parameter \( a \) are given at 2σ level. Source of data: (1)=this work; (2)=refit of data in Zhang and Behrens (2000).

Fig. 3. Coverage of experimental conditions from this work (solid circles) and previous work (open circles) of Zhang et al. (1991), Nowak and Behrens (1997), Zhang and Behrens (2000), Okumura and Nakashima (2004), and Behrens et al. (2007).

Fig. 4. (A) Best-fit \( a \) values (Table 3) from experiments of this work at 0.95–1.9 GPa and those of Zhang and Behrens (2000) at 0.25–0.5 GPa. The straight line is from Eq. (6). Three values at 0.1 GPa from Behrens et al. (2007) are also shown for comparison. (B) Best-fit lnD₀ values reported in Table 4. Straight lines are from Eq. (7).
Table 4
Least-squares fitting results

<table>
<thead>
<tr>
<th>Run #</th>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>H2Om (wt.%)</th>
<th>lnD (µm²/s)</th>
<th>R²</th>
<th>Source</th>
</tr>
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<tr>
<td>KS-D2</td>
<td>530</td>
<td>0.1</td>
<td>0.84</td>
<td>−2.69 ± 0.21</td>
<td>0.9884</td>
<td>1</td>
</tr>
<tr>
<td>PD-D5</td>
<td>530</td>
<td>0.1</td>
<td>0.82</td>
<td>−2.62 ± 0.15</td>
<td>0.9887</td>
<td>1</td>
</tr>
<tr>
<td>KS-D3</td>
<td>490</td>
<td>0.1</td>
<td>0.82</td>
<td>−3.59 ± 0.10</td>
<td>0.9944</td>
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<tr>
<td>PD-D4</td>
<td>490</td>
<td>0.1</td>
<td>0.19</td>
<td>−3.33 ± 0.23</td>
<td>0.9890</td>
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<tr>
<td>KS-D5A</td>
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<td>0.82</td>
<td>−4.38 ± 0.15</td>
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<tr>
<td>3b-D4</td>
<td>403</td>
<td>1.68</td>
<td>0.86</td>
<td>−5.78 ± 0.15</td>
<td>0.9927</td>
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<tr>
<td>3b-D4</td>
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<td>0.80 ± 0.08</td>
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<td>KS-D4A</td>
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<tr>
<td>KS-D14</td>
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<td>0.77 ± 0.18</td>
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<td>KS-D13P</td>
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<td>0.81</td>
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<td>KS-D19P</td>
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<td>−5.15 ± 0.11</td>
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<td>−3.36 ± 0.14</td>
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<td>−5.15 ± 0.11</td>
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<td>SRhy-Dar2</td>
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<td>3.02 ± 0.10</td>
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The fitting assumes D_{ref} = D_{exp}[−37.256 + 75884/T] where D_{ref} is to be determined from fits. *1 The theoretical profile is convoluted first and then used to fit experimental data (see text). Source of data: (1)=Zhang et al. (1991); (2)=Zhang and Behrens (2000); (3)=this work. Errors for lnD_{ref} are from least squares fitting and are given at 2σ level.

\[ \text{lnA on P)} \), the 2σ error would be 1.35, too large to be tolerated. The activation energy (E_a) of D_o increases from 108±4 kJ/mol at 0.1 MPa to 123±5 kJ/mol at 0.5 MPa to 165±11 kJ/mol at 1.9 MPa.

The extra pressure term in addition to the pressure dependence of the activation energy may be explained in two ways. First, the extra term would result if the activation volume depends on temperature. Starting from (Lasaga, 1998)

\[ \text{lnD = lnA}_0 - \frac{E_a + P \cdot V_a}{RT}, \]  

we have:

\[ \text{lnD = lnA}_0 - \frac{E_a + P (\Delta V_a - mRT)}{RT} = \text{lnA}_0 + mP - \frac{E_a + P \cdot V_a}{RT}, \]

where P is pressure, A_0 is the pre-exponential factor at zero pressure, m is a coefficient, E_a is the activation energy at zero pressure, and \( \Delta V_a \) is the activation volume that is expressed as a linear function of temperature. Because the temperature range in H2O diffusion studies is large (400–1600 °C), the temperature dependence of the activation volume is needed to account for the data. The activation volume for H2O diffusion at low H2O concentrations can be calculated from −RTlnD_{ref}0P using Eq. (7), and is 30±5 cm³/mol at 0 K and linearly decreases to about 15 cm³/mol at 875 K and to 0 at 1921 K. In comparison, Nagami and Tomozawa (1984) reported huge activation volume of −170 cm³/mol at 465 K and −72 cm³/mol at 623 K for water diffusion in silica glass based on diffusion data in a small pressure range (< 130 MPa).

Another way to explain the extra pressure term is to utilize the “compensation law” (Winchell, 1969; Lasaga, 1998), which states that lnA is positively and linearly related to the activation energy. Hence, a dependence of the activation energy on pressure would result in a dependence of lnA on pressure, as in Eq. (7).

4.2. Diffusivity vs. T, P, and X

In summary, by combining data from this work with that of Zhang et al. (1991) and Zhang and Behrens (2000), molecular H2O diffusivity may be expressed as follows:

\[ D_{\text{H2Om}} = D_0 \exp (aX), \]  

with

\[ D_0 = \exp \left( \frac{13.375 + 1.9875P}{12.939 + 3625 \frac{P}{T}} \right), \]

and

\[ a = -37.256 + \frac{75884}{T}. \]

where T is in K, P is in GPa, D is in µm²/s, and X is mole fraction of H2O (on a single oxygen basis). From \( D_{\text{H2Om}} \) above, total H2O diffusivity can be obtained as (Zhang, 1999b):

\[ D_{\text{H2O}} = D_{\text{H2Om}} \frac{\text{dx}}{dx}, \]

with

\[ \frac{\text{dx}}{dx} = \frac{16X}{b} - \frac{8X^2}{b^2} \left( 8 - 2K + \frac{8K - 2K^2(1 - 2X) - 16KX}{\sqrt{K(1 - 2X)^2 + 16KX(1 - X)}} \right), \]

\[ b = X - K + 2X + \sqrt{K(1 - 2X)^2 + 16KX(1 - X)}, \]

and

\[ K = \exp \left( 1.876 + \frac{3110}{T} \right). \]

This model can be used to calculate H2O and H2Om diffusivity from 403–1629 °C, 0–1.9 GPa, and 0.1–77 wt.% water content. In order to calculate total H2O diffusivity using the above procedures, the H2O diffusivity must be used in conjunction with the speciation model of Eq. (11d) (Zhang et al., 1997b), because unlike H2O diffusivity, H2Om diffusivity cannot be directly extracted from diffusion profiles and its value depends on the expression of K. Since K at low pressures is used and it may not apply to high pressure, \( D_{\text{H2Om}} \) from Eqs. (10a, b, and c) may not be accurate, but \( D_{\text{H2O}} \) is still accurate as long as self-consistency is maintained. If a new expression of K as a function of temperature and pressure is adopted in the future (Hui et al., 2008a), Eq. (11d) should still be used for calculation of \( D_{\text{H2Om}} \) until a new expression of \( D_{\text{H2Om}} \) is obtained using new expressions of K.

The dependence of H2O diffusivity on water content, temperature, and pressure is illustrated in Fig. 5. At low water content (< 2 wt.%), \( D_{\text{H2O}} \) is roughly proportional to water content; this dependence becomes exponential as water content is above 2 wt.%. Temperature dependence is always Arrhenian, and the activation energy (E_a) increases with pressure and generally decreases with water content. At 1 wt.% H2O, E_a increases from −81 kJ/mol at 0.1 MPa to −109 kJ/mol at 0.95 GPa to −138 kJ/mol at 1.9 GPa; At 5 wt.% H2O, E_a increases from −46 kJ/mol at 0.1 MPa to −74 kJ/mol at 0.95 GPa to −103 kJ/mol at 1.9 GPa. Pressure reduces H2O diffusion rate, and the negative pressure effect is more noticeable at low temperatures. For example, at 600 °C H2O diffusivity decreases by about one order of magnitude over 1 GPa, whereas at 1200 °C it only decreases by a factor smaller than 2 over the same pressure range.
Because the above procedure to calculate $D_{\text{H}_2\text{O}_t}$ is fairly complicated, for convenience, the following explicit expression is provided to calculate $D_{\text{H}_2\text{O}_t}$ (in $\mu$m$^2$/s):

$$\ln(D_{\text{H}_2\text{O}_t}/X) = a_0 + a_1X + a_2\sqrt{X} + a_3P - a_4X + a_5\sqrt{X} + a_6P.$$  \hspace{1cm} (12)

with $a_0 = 13.470 \pm 0.035$, $a_1 = -49.996 \pm 0.833$, $a_2 = 7.0827 \pm 0.3524$, $a_3 = 1.8875 \pm 0.0116$, $a_4 = 9532.3 \pm 37.9$, $a_5 = -91933 \pm 913$, $a_6 = 13403 \pm 387$, $a_7 = 3625.6 \pm 12.7$, where $X$ is mole fraction of $\text{H}_2\text{O}_t$ on a single oxygen basis, $T$ is temperature in K, and $P$ is pressure in GPa. Results from Eq. (12) agree with those from Eqs. (10a) to (11d) within 17%, which is smaller than the experimental error. Furthermore, Eq. (12) is independent of the speciation model.

When $\text{H}_2\text{O}_t$ content is below 2 wt.%, $D_{\text{H}_2\text{O}_t}$ is approximately proportional to $\text{H}_2\text{O}_t$ content, and the following simple equation is obtained for calculating $D_{\text{H}_2\text{O}_t}$:

$$D_{\text{H}_2\text{O}_t} = D_{\text{H}_2\text{O}_t}^0 \frac{X}{X_0} = D_{\text{H}_2\text{O}_t}^0 \frac{C}{C_0} = D_{\text{H}_2\text{O}_t}^0 \frac{C}{C_0} \exp\left(\frac{b_0 + b_1P - b_2 + b_3P}{T}\right).$$ \hspace{1cm} (13)

where $b_0 = 9.5279 \pm 0.0677$, $b_1 = 1.8875 \pm 0.0590$, $b_2 = 9698.5 \pm 74.2$, and $b_3 = 3625.6 \pm 64.7$, $C$ is water content in wt.% and $D^0$ is $\text{H}_2\text{O}_t$ diffusivity at mole fraction of 0.01789 ($X_0$) or 1 wt.% ($C_0$).

4.3. Implication on melt structure

The decrease of $\text{H}_2\text{O}$ diffusivity with increasing pressure may be explained as follows. Increasing pressure reduces free space in melt structure, and hence reduces the mobility of neutral molecular species such as $\text{H}_2\text{O}_m$. This negative pressure effect on diffusivity is consistent with the observation that viscosity of hydrous rhyolite increases with pressure (Hui et al., 2008b). Therefore, hydrous rhyolite behaves like a depolymerized melt, in which diffusion kinetics is slowed by pressure.

Our model results lead to an activation volume of zero at 1648 °C. Above this temperature, $\text{H}_2\text{O}_m$ diffusivity would increase with increasing pressure. It is not clear whether there is qualitative change in the melt structure leading to a change in the diffusion behavior. Our experimental data have not covered such high temperatures and hence cannot verify the behavior. Such high temperatures are also much higher than normal temperatures of rhyolitic melts.

The activation energy is lowered by increasing water content. This has been observed repeatedly before (e.g., Karsten et al., 1982; Zhang et al., 1991; Zhang and Behrens, 2000; Behrens and Zhang, 2001), and may be attributed to increased porosity with more dissolved water. A lower activation energy at higher $\text{H}_2\text{O}$ content is also consistent with the observation that $\text{H}_2\text{O}$ diffusivity increases more rapidly with water content at low temperatures.

4.4. Comparison with other data

In developing the model, some data in the literature was not included. Nowak and Behrens (1997) reported total $\text{H}_2\text{O}$ diffusivity data at 800–1200 °C, 50–500 MPa, and 0.5–6 wt.% water content also based on diffusion-couple technique. Okumura and Nakashima (2004) investigated $\text{H}_2\text{O}$ diffusivity <4.1 wt.% at room pressure based on dehydration with in situ FTIR. Behrens et al. (2007) studied $\text{H}_2\text{O}$ diffusivity at 100 MPa from hydration experiments. In particular, Behrens et al. (2007) showed that their data are different from prediction by the model of Zhang and Behrens (2000) by a factor of 2, and attributed the difference to the uncertainty of the pressure effect in the model of Zhang and Behrens (2000). These experimental data are used to evaluate the applicability of our new model.

The comparison between data in Nowak and Behrens (1997) and Behrens et al. (2007) is straightforward. However, Okumura and
Nakashima (2004) reported diffusion-out diffusivity, which is some average of \(D_{\text{out}}\) over a concentration range. To compare their data with \(D_{\text{out}}\) at a given \(\text{H}_2\text{O}\) concentration (the initial and maximum \(\text{H}_2\text{O}\) mole fraction, \(X_i\)), a conversion factor must be applied. For the case of proportionality between \(D_{\text{H}_2\text{O}}\) and \(X_i\), the correction factor is 0.347 (Wang et al., 1996). For the more general case to higher \(\text{H}_2\text{O}\) concentrations, this factor can be calculated from model profiles at a given temperature, i.e., given parameter of \(a\), equilibrium constant \(K\), and \(X_i\). The mass loss can be found from the model profile of \(\text{H}_2\text{O}\) mole fraction \((X)\) vs. normalized distance \((\xi = x/\sqrt{4D_0t})\) as

\[
M = \int_0^\infty (X_i - X) d\xi.
\]

(14)

It can be derived (Crank, 1975) that the diffusion-out diffusivity \(D_{\text{out}}\) obtained from mass loss is related to \(D_0\) through

\[
\frac{D_{\text{out}}}{D_0} = \pi \left(\frac{M}{X_i}\right)^2.
\]

(15)

Combining Eqs. (4) and (5), \(D_{\text{H}_2\text{O}}\) at \(X_i\) \((D_X)\) is related to \(D_0\) through

\[
D_X/D_0 = \exp(aX_i) \frac{dX_m}{dX)_X}.
\]

(16)

Therefore we find the conversion factor as

\[
D_{\text{out}}/D_X = \frac{\pi M^2}{X_i^2} \exp(aX_i) \frac{dX_m}{dX)_X}.
\]

(17)

The conversion factor thus obtained depends somewhat on temperature, and is \(-0.324\) for 0.7 wt.%, \(-0.207\) to \(-0.243\) for 1.9 wt.%, \(-0.166\) to \(-0.198\) for 2.8 wt.\% \(\text{H}_2\text{O}\), for the temperature range of Okumura and Nakashima (2004). Their \(\text{H}_2\text{O}\) diffusivities at 4.1 wt.% are not included in the comparison because they are similar to or even smaller than those at 2.8 wt.% at the same temperature, which is against the observed general trend of \(\text{H}_2\text{O}\) diffusivity.

Fig. 6 compares these experimental data and calculations based on our model, indicating good inter-laboratory and multi-method consistency and therefore demonstrating the reliability of our model. The maximum difference is a factor of 2.3 between our calculation and \(D_{\text{H}_2\text{O}}\) of Nowak and Behrens (1997) using the Boltzmann–Matano method. Such a difference is expected because the precision of the Boltzmann–Matano method is not high. \(\text{H}_2\text{O}\) diffusivities at 1 wt.% \(\text{H}_2\text{O}\) from Behrens et al. (2007) are within a factor of 1.3, and those at 4 wt.% \(\text{H}_2\text{O}\) from Behrens et al. (2007) are within a factor of 1.6 with those predicted by our model. The differences are only slightly larger than the experimental and model uncertainty, and may be attributed to complications in hydration experiments (such as dissolution during the experiment and precipitation during quench). Resolving the pressure effect on \(\text{H}_2\text{O}\) diffusion is the main goal of this study. The good agreement between our new \(\text{H}_2\text{O}\) diffusion model and previous experimental data including those of Behrens et al. (2007) suggests that the pressure effect is now resolved well.

4.5. Applicability of the Einstein or Eyring equation to molecular \(\text{H}_2\text{O}\) diffusion

The Einstein (1905) equation relates diffusivity of a neutral species in a liquid and the viscosity of the liquid, and is derived by considering molecular diffusion as Brownian motion in the liquid continuum. It takes the following form:

\[
D = k T / (\eta L),
\]

(18)

where \(D\) is diffusivity, \(k\) is the Boltzmann constant, \(T\) is temperature in K, \(\eta\) is viscosity, and \(L\) is a length scale and equals 6\(r\) where \(r\) is the radius of the diffusing species. The equation can predict the diffusivity of Ar, Kr and Xe in water to within 30% (Jahne et al., 1987; Fig. 7A). It does not seem that the relation has been applied to silicate melts.

Fig. 7B compares experimental diffusivity of molecular \(\text{H}_2\text{O}\) and Ar with the calculated Einstein diffusivity. The latter is smaller than the
experimental data by many orders of magnitude. Because the uncertainty in the diffusivities is less than a factor of 2, and that in the viscosities is less than a factor of 3, these uncertainties cannot explain the huge discrepancy of the Einstein equation. Therefore, the Einstein equation cannot predict diffusivity of molecular H2O and Ar in rhyolitic melt. Not only do the values not match, but also the slope of logD versus log[1/T] is not −1. Furthermore, the slope is not even a constant (i.e., logD versus log[1/T] is not linear)\textsuperscript{1} The failure of the Einstein equation is likely due to the large size of ionic clusters (such as SiO\textsubscript{4}, SiO\textsubscript{2}\textsuperscript{2−}, etc.) in silicate melts, which are larger than molecular H2O or Ar, meaning that the motion of the molecules in the melt cannot be treated as large molecules moving through a liquid continuum.

The Eyring equation (Glazstone et al., 1941) is based on the transition state theory and assumes that the diffusion and viscous flow involve the same process. The equation has been shown to work for \textsuperscript{18}O and \textsuperscript{30}Si diffusion in some silicate melts (e.g., Shimizu and Kushiro, 1984; Lesher et al., 1996; Tinker and Lesher, 2001; Reid et al., 2003; Tinker et al., 2004), but does not work for, e.g., \textsuperscript{16}O diffusion in hydrolytic rhyolitic melt (Behrens et al., 2007). It takes the same form as Eq. (18), but I is the jumping distance, which is often taken to be the diameter of the diffusing species. Hence, the difference between the Eyring equation and the Einstein equation is about a factor of 10. As can be seen from Fig. 7B, a factor of 10 (or one order of magnitude) is not enough to reconcile the experimental and calculated diffusivities. Hence, the Eyring equation does not work here, which is expected because the process for viscous flow involves motion of the aluminosilicate network, but that of Ar and H2Om diffusion does not.

5. Conclusions

Water diffusion in rhyolite at 0.95–1.9 GPa and 407–1629 °C is investigated to constrain the pressure dependence of H2O diffusivity. High pressure results in a smaller diffusivity, which is attributed to decreased free space in the melt. This negative pressure effect indicates that the process of magma upwelling facilitates bubble growth not only thermodynamically (by reducing H2O solubility), but also kinetically (by increasing H2O diffusivity), although the latter effect is smaller. Based on a model that H2Om dominates water diffusion, two specific H2O diffusivity expressions have been constructed: one for both low and high total H2O contents (up to 7.7 wt.%), and the other simple form is applicable to low H2O contents (up to 2 wt.%). All of the expressions are only applicable when species equilibrium is roughly maintained (Jambon et al., 1992), meaning relatively high temperatures and high H2O contents. For example, at 500 °C, H2O needs to be ≥1 wt.% for the diffusivities to be applicable. With this study, we have resolved the pressure effect on H2O diffusion in rhyolitic melt so that H2O diffusivity can be predicted from 0 to 2 GPa and from 400 to 1600 °C. We recommend the use of these expressions in modeling bubble growth in and degassing from a coesite transition revisited: reversed experimental determination at 500–1200 °C and retrieved thermochemical properties. Am. Mineral. 80, 231–238.


