Hydroxyl and molecular H$_2$O diffusivity in a haploandesitic melt

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Abstract

H$_2$O diffusion in a haploandesitic melt (a high-silica and Fe-free andesitic melt, NBO/T = 0.173) has been investigated at 1 GPa in a piston-cylinder apparatus. We adopted a double diffusion couple technique, in which one couple was composed of a nominally anhydrous glass with 0.01 wt.% H$_2$O and a hydrous glass with 5.7 wt.% H$_2$O, and the other contained the same nominally anhydrous glass and a hydrous glass with 3.3 wt.% H$_2$O. Both couples were annealed in a single experimental run and hence experienced exactly the same P–T history, which is crucial for constraining the dependence of H$_2$O diffusivity on water content. H$_2$O concentration profiles were measured by both Fourier transform infrared (FTIR) microspectroscopy and confocal Raman microspectroscopy. Nearly identical profiles were obtained from Raman and FTIR methods for profile length >1 mm (produced at 1619–1842 K). By contrast, for profile lengths <100 μm (produced at 668–768 K), FTIR profiles show marked convolution effects compared to Raman profiles. A comparison between the short FTIR and Raman profiles indicates that the real spatial resolution (FWHM) of FTIR analyses is about 28 μm for a 7 μm wide aperture on ~200 μm thick glasses.

While the short profiles are not reliable for quantitative modeling, the long diffusion profiles at superliquidus temperatures can be fit reasonably well by a diffusivity model previously developed for felsic melts, in which molecular H$_2$O (H$_2$O$_m$) is the only diffusive species and its diffusivity ($D_{H2O}$) increases exponentially with the content of total water (H$_2$O$_t$). However, there is noticeable misfit of the data at low H$_2$O$_t$ concentrations, suggesting that OH diffusivity ($D_{OH}$) cannot be neglected in this andesitic melt at high temperatures and low water contents. We hence develop a new fitting procedure that simultaneously fits both diffusion profiles from a single experimental run and accounts for the roles of both OH and H$_2$O$_m$ diffusion. With this procedure, $D_{OH}/D_{H2O}$ is constrained to be 0.1–0.2 at 1619–1842 K as H$_2$O$_t$ concentration approaches zero. The obtained OH diffusivity is similar to fluorine diffusivity but is much higher than Eyring diffusivity.

1. INTRODUCTION

As the most abundant and the most important volatile component in silicate melts, the diffusion of water has drawn substantial attention from volcanologists, geochemists and glass scientists (Shelby, 2008; Zhang and Ni, 2010). Since Zhang et al. (1991) laid out a theoretical basis for water diffusion, especially in demonstrating the dominating role of molecular H$_2$O (H$_2$O$_m$) rather than hydroxyl group (OH), water diffusivity has been experimentally determined for a variety of silicate melts (Zhang and Stolper, 1991; Nowak and Behrens, 1997; Zhang and Behrens, 2000; Freda et al., 2003; Liu et al., 2004; Behrens et al., 2004, 2007; Okumura and Nakashima, 2004, 2006; Ni and Zhang, 2008; Behrens and Zhang, 2009; Ni et al., 2009a,b; Wang et al., 2009; Persikov et al., 2010). It has been generally accepted that in felsic melts, water diffusivity increases strongly with increasing concentration of total water (H$_2$O$_t$), but the relationship between diffusivity and H$_2$O$_t$ concentration is less conclusive for silicate melts of intermediate to mafic compositions.

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Water diffusivity in andesitic melts was reported to be nearly independent of water content at superliquidus temperatures of 1558–1848 K (Behrens et al., 2004) and in the intermediate temperature range of 773–948 K (Okumura and Nakashima, 2006). Also at intermediate temperatures, Okumura and Nakashima (2006) found that water diffusivity increases with increasing water content in basaltic and dacitic melts, revealing an unusual behavior of andesite melts. Contrary to previous reports (Behrens et al., 2004; Okumura and Nakashima, 2006), Ni et al. (2009a) and Persikov et al. (2010) demonstrated that, both in the intermediate temperature range and at 1573 K, \( \text{H}_2\text{O} \) diffusivity is significantly enhanced by increasing \( \text{H}_2\text{O} \) concentration in haploandesitic melts. One may attribute this disagreement to the absence of iron in haploandesitic melts, but in both basaltic (Zhang and Stolper, 1991) and haplobasaltic (Persikov et al., 2010) melts, the increase of water diffusivity with increasing water content appears to be consistent. Whether or not water diffusivity depends on water content has a more profound importance than simply a mathematical curiosity – if \( \text{H}_2\text{O} \) diffusivity in andesitic melts at superliquidus temperatures were indeed independent of \( \text{H}_2\text{O} \) concentration as previously suggested (Behrens et al., 2004), this would imply that water diffusion in andesitic melts is not dominated by the transport of \( \text{H}_2\text{O}_m \) as in the case of felsic melts (e.g., Zhang et al., 1991; Zhang and Behrens, 2000; Ni and Zhang, 2008; Ni et al., 2009b).

All post-1990 water diffusion studies have used Fourier transform infrared spectroscopy (FTIR), either by measuring a quenched diffusion profile (e.g., Zhang and Behrens, 2000) or by monitoring in situ the change in bulk water content of a dehydrating melt (e.g., Okumura and Nakashima, 2004, 2006). FTIR measurement is known for its high reproducibility and sensitivity, and with careful calibration it can also achieve high accuracy. However, due to the limited spatial resolution of FTIR spectroscopy, convolution effects may affect diffusion profiles shorter than 200\mu m significantly (Ni and Zhang, 2008). Despite the potential of Raman spectroscopy for measuring \( \text{H}_2\text{O} \) dissolved in glasses, the difficulty in calibrating Raman scattering cross sections has restricted its popularity for many years. In the past decade, increasing needs for analyzing water contents of small melt inclusions have advanced Raman quantification procedures significantly (Chabiron et al., 1999; Thomas, 2000; Behrens et al., 2006; Di Muro et al., 2006; Mercier et al., 2009, 2010). Nonetheless, the high spatial resolution of Raman microspectroscopy has not yet been applied to study water diffusion, for which spatial resolution is often more critical than the accuracy of measured water contents.

In this study, we conduct experiments at 668–1842 K and 1 GPa to investigate water diffusion in a haploandesitic melt (a high-silica and Fe-free andesitic melt) and analyze the diffusion profiles by both FTIR and Raman microspectroscopy. The emphasis is on the mechanism of diffusion (OH contribution in particular) and the comparison between FTIR and Raman analyses.

### 2. EXPERIMENTAL AND ANALYTICAL METHODS

#### 2.1. Starting material

Powders of oxides and carbonates, mixed in proportions to reproduce the glass composition used in Ni et al. (2009a), were fused twice at 1773 K in a 0.1 MPa furnace to obtain compositionally homogeneous anhydrous haploandesitic glass (HAD-DRY in Table 1). For the synthesis of hydrous glasses, dry glass powders with distilled water were sealed in a Pt capsule and heated and pressurized to 1323–1423 K and 0.15–0.19 GPa in TZM vessels at the Bayerisches Geoinstitut for a week.

The anhydrous glass is crystal-free but contains some air bubbles. The two hydrous glasses (HAD-H3 and HAD-H6

<table>
<thead>
<tr>
<th>Chemical analysis of andesitic glasses used in ( \text{H}_2\text{O} ) diffusion studies (in wt.%)</th>
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<tr>
<td></td>
</tr>
<tr>
<td>SiO(_2)</td>
</tr>
<tr>
<td>TiO(_2)</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
</tr>
<tr>
<td>FeO(_2)</td>
</tr>
<tr>
<td>MgO</td>
</tr>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>Na(_2)O</td>
</tr>
<tr>
<td>K(_2)O</td>
</tr>
<tr>
<td>Total</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} ) (IR)</td>
</tr>
<tr>
<td>NBO/T</td>
</tr>
</tbody>
</table>

For the glasses used in this study (with similar composition as those used in Ni et al., 2009a), each value is an average of 25–30 points analyzed by a JOEL JXA-8200 electron microprobe using a defocused beam of 15 kV, 15 nA, and 5 \( \mu \)m across. Water content of the anhydrous glass is based on FTIR analysis and the absorption coefficient of the 3550 cm\(^{-1}\) band calibrated by Mandeville et al. (2002). Oxides contents of the two hydrous glasses are normalized to anhydrous basis – divided by \((1 - \text{C}/100)\), where \( \text{C} \) is water content (in wt.%) measured by FTIR based on the calibration of Vetter et al. (2006) for the 5220 and 4500 cm\(^{-1}\) bands. NBO/T is the number of non-bridging oxygen atoms per tetrahedron with Si, Al, and Fe\(^{3+}\) taking tetrahedral sites (for AndDC, Fe\(^{3+}\) is assumed to be 1/3 of total Fe).
in Table 1) both contain small amounts of microcrystals and bubbles, which are not expected to have a significant effect on water diffusion (Zhang et al., 1991; Zhang and Behrens, 2000). FTIR analyses yield homogeneous total water (H$_2$O) concentration in each glass (within 3% relative): 0.01 wt.% in the nominally anhydrous glass using the calibration of the 3550 cm$^{-1}$ band by Mandeville et al. (2002), and 3.36 ± 0.05 wt.% and 5.77 ± 0.06 wt.% in the hydrous glasses using the calibration of the near-infrared (NIR) bands by Vetere et al. (2006). The anhydrous composition of these glasses (Table 1), determined by electron microprobe analyses, is similar to those used in previous studies of viscosity (Richet et al., 1996) and H$_2$O diffusivity (Ni et al., 2009a). But compared to the Fe-bearing andesite (Behrens et al., 2004) and haploandesite (Persikov et al., 2010) with NBO/T (non-bridging oxygen atoms per tetrahedron) of 0.3, our glass composition is more polymerized, with NBO/T of ~0.173 and silica content of ~62 wt.% (Table 1).

2.2. Diffusion experiments

Glass cylinders of 2.5 mm diameter were prepared, with 1.5 mm length for the anhydrous glass and 2.5 mm length for the hydrous glasses. An anhydrous glass cylinder and a hydrous one, with their polished surfaces in contact, formed a diffusion couple. The diffusion couple was placed inside a Pt tube of 3.0 mm outer diameter and 0.2 mm wall thickness, and then the tube was sealed by welding.

Diffusion experiments were carried out in a 3/4" piston-cylinder apparatus at the Bayerisches Geoinstitut. A sketch of the sample assembly is illustrated in Fig. 1, involving a tapered graphite heater and pressure media of talc, Pyrex glass and crushable alumina. Temperature was monitored by a Pt-Pt$_{90}$Rh$_{10}$ thermocouple. Based on the temperature distribution for a straight graphite heater in a piston-cylinder apparatus calibrated by Hui et al. (2008), Ni and Zhang (2008) applied temperature corrections of 29, 19–23, and 7–9 K for their H$_2$O diffusion experiments under nominal temperatures of 1873, 1573, and 673–873 K, respectively. For a tapered or stepped graphite heater, the central section, with a larger cross section area, has a smaller electrical resistance and dissipates less power as heat (Dunn, 1993). Therefore, the thermal gradient in our assembly using a tapered heater is expected to be lower than that in Ni and Zhang (2008). In this study we have applied temperature corrections of 20, 15, and 5 K for nominal temperatures of 1822, 1604, and 663–813 K, respectively (Table 2). The 2σ uncertainty in temperature is estimated to be 20 K for the superliquidus runs (1604–1822 K) and 10 K for the intermediate temperature runs (663–813 K). In each run, two diffusion couples were loaded side by side; the only difference between the two couples was the H$_2$O concentration in the hydrous half. This double diffusion couple design not only promotes efficiency, but also guarantees that the same $P$–$T$ history is experienced by both diffusion couples, which is useful for constraining the H$_2$O dependence of water diffusivity. The sample assembly was first pressurized to 1.0 GPa (after 9% friction correction). For the runs at 663–813 K, temperature was increased to the target value and maintained for 7–18 days. For the runs at 1604–1822 K, it was necessary to increase temperature rapidly to minimize diffusion during heating. Therefore, heating power was manually increased so that a plateau temperature was reached within one minute, at which the sample dwelled for several minutes before quenching. The complete thermal history was recorded and an effective experimental duration was inferred, using the method described in Zhang and Behrens (2000) and assuming an average activation energy of 100 kJ/mol for water diffusion. Conditions of the diffusion experiments are summarized in Table 2.

Quenched samples were embedded in epoxy resin and doubly polished to ~500 μm thickness for Raman analyses, with the top surface approximately at the centerline of the sample. Subsequently the bottom surface of samples was further polished till reaching ~200 μm sample thickness for transmission FTIR analyses. After high temperature (1604–1822 K) runs, the small amounts of bubbles and microcrystals in starting glasses had disappeared, attributed to dissolution into the melt during heating and annealing, and the interface between the two halves of a diffusion couple is difficult to recognize (Fig. 2a). By contrast, in intermediate temperature experimental charges (Fig. 2b), the impurities of starting glasses continue to exist; the interface between two halves remains straight, often with a ~8 μm wide gap in between, likely produced by contraction during quench.

2.3. Raman analyses

Confocal Raman analyses were performed with a Horiba Jobin–Yvon LabRam HR800 spectrometer at the Bayerisches Geoinstitut, using a 514.5 nm argon ion laser of 100 mW input power, a confocal hole of 300 μm diameter,
and an objective of 50× magnification (N.A. = 0.35). For each point of analysis, the laser beam was focused on the top surface of the sample within an error of 2 μm. Because the analyzed glasses were transparent, a volume, instead of an area, was selected by the confocal hole. The diameter of the selected volume was estimated to be 6 μm, about the same as the hole diameter divided by the objective magnification. With a grating of 1800/mm, both the 200–1500 cm⁻¹ region and the 2800–4000 cm⁻¹ region were measured for 218 s in a few windows.

A series of Raman spectra along a diffusion profile are displayed in Fig. 3a. The 2800–4000 cm⁻¹ region contains the 3550 cm⁻¹ stretching band for H₂O analyses. A cubic baseline with base points at 2850, 2950, 3800 and 3950 cm⁻¹ was used to determine peak height. This is similar to the baseline adopted by Mercier et al. (2009), although they did not report the exact frequencies of their base points. For some spectra at low H₂O concentration, the 2950 cm⁻¹ base point had to be shifted to a higher frequency to produce a reasonable cubic baseline. The 200–1500 cm⁻¹ region contains two prominent silicate network bands at ~500 and ~1015 cm⁻¹ and a weak band at ~770 cm⁻¹. Based on Mercier et al. (2009) and references therein, the low-frequency (LF) band at ~500 cm⁻¹ is related to bridging oxygens and the high-frequency band at ~1015 cm⁻¹ is related to non-bridging oxygens. We adopted a cubic baseline with base points at 250, 800, 1200 and 1450 cm⁻¹ to obtain the peak height of both the LF and HF bands. As haploandesite is an intermediate composition (rather than felsic or mafic), either the LF or HF band is strong enough for normalizing the H₂O band to minimize the influence of focusing error or fluctuation of the laser power.

Fig. 4 shows a comparison between Raman intensity profiles based on H₂O peak (I₃550), H₂O/LF peak ratio (I₃550/I₅00), and H₂O/HF peak ratio (I₃550/I₁015), with I denoting the peak height at a certain wavenumber indicated by the subscript. Differences among the three profiles are not large, yet the I₃550/I₁015 profile appears to be smoother than the other two profiles. Furthermore, Mercier et al. (2009) showed that for a fixed melt composition, peak height ratio I₃550/I₁015 had a better linear correlation with H₂O concentration than I₃550/I₅00. Accordingly, we opted to use I₃550/I₁015 for the conversion of Raman data to H₂O concentrations.

### Table 2

<table>
<thead>
<tr>
<th>Run #</th>
<th>T₀ (K)</th>
<th>T&lt;sup&gt;+&lt;/sup&gt; (K)</th>
<th>t&lt;sup&gt;0&lt;/sup&gt; (s)</th>
<th>t&lt;sup&gt;e&lt;/sup&gt; (s)</th>
<th>Initial H₂O&lt;sup&gt;t&lt;/sup&gt; (wt.%)</th>
<th>Final H₂O&lt;sup&gt;t&lt;/sup&gt; (wt.%)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAD-BGI-DC1</td>
<td>1604</td>
<td>1619 ± 20</td>
<td>266</td>
<td>288 ± 10</td>
<td>0.01/5.75</td>
<td>0.02/5.75</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td></td>
<td>0.01/3.31</td>
<td>0.01/3.44</td>
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<tr>
<td>HAD-BGI-DC7</td>
<td>1822</td>
<td>1842 ± 20</td>
<td>149</td>
<td>175 ± 10</td>
<td>0.01/n.a.</td>
<td>0.02/5.77</td>
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<tr>
<td>a</td>
<td></td>
<td>0.01/n.a.</td>
<td>0.02/3.33</td>
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<tr>
<td>HAD-BGI-DC2</td>
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<td>818 ± 10</td>
<td>576,000</td>
<td></td>
<td>0.01/5.72</td>
<td>n.a.</td>
<td>Crystallization</td>
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<tr>
<td>a</td>
<td></td>
<td>0.01/3.36</td>
<td>n.a.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td></td>
<td></td>
<td>0.01/n.a.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HAD-BGI-DC4</td>
<td>763</td>
<td>768 ± 10</td>
<td>828,000</td>
<td></td>
<td>0.01/5.82</td>
<td>n.a.</td>
<td>Crystallization</td>
</tr>
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<td>0.01/3.40</td>
<td>0.02/3.36</td>
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<td></td>
</tr>
<tr>
<td>b</td>
<td></td>
<td></td>
<td>0.01/n.a.</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>HAD-BGI-DC6</td>
<td>663</td>
<td>668 ± 10</td>
<td>1,555,200</td>
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<td>0.01/5.74</td>
<td>0.02/5.72</td>
<td>Partial crystal</td>
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<td>a</td>
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<td>0.02/3.38</td>
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<td></td>
</tr>
<tr>
<td>b</td>
<td></td>
<td></td>
<td>0.01/3.38</td>
<td></td>
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</tr>
</tbody>
</table>

- **a** Two diffusion couples in each experimental run.
- **b** Plateau temperature measured by Pt–Pt₉₀Rh₁₀ thermocouple.
- **c** Temperature corrected for thermal gradient (with estimated 2σ error).
- **d** Dwelling duration at temperatures within 30 K (for HAD-BGI-DC1) or 50 K (for HAD-BGI-DC7) difference from the plateau temperature.
- **e** Duration corrected for the diffusion during heating and cooling (with estimated 2σ error).
- **f** Total H₂O concentrations of two halves measured by FTIR before and after diffusion run.

### Fig. 2

Photomicrographs of two samples (positioned with increasing water content to the right) after diffusion experiments. (a) HAD-BGI-DC1a, quenched from 1619 K; (b) HAD-BGI-DC6b, quenched from 668 K.
In converting the $I_{3550}/I_{1015}$ ratio to H$_2$O concentration, we used the FTIR-determined H$_2$O concentrations in the flat regions of the two halves of the diffusion couple (i.e., the regions not affected by diffusion) as constraints. Following previous studies (e.g., Behrens et al., 2006; Di Muro et al., 2006), a linear correlation between $I_{3550}/I_{1015}$ and H$_2$O (in wt.%) was assumed. Unlike FTIR that can be used to independently quantify H$_2$O species concentrations once the appropriate molar absorptivities are properly calibrated, Raman data must be calibrated for each specific profile.

2.4. FTIR analyses

Water contents of the starting glass cylinders were measured by a Bruker IFS 120HR FTIR spectrometer at the Bayerisches Geoinstitut, involving a NIR source, a CaF$_2$ beamsplitter, and a liquid-nitrogen cooled MCT detector. Diffusion profiles of doubly polished experimental charges were acquired using the Autoimage microscope on a PerkinElmer Spectrum GX FTIR spectrometer at the University of Michigan. Because a thicker sample would reduce the spatial resolution due to beam divergence in the section, and a thinner sample would be prone to breakage (especially when there were cracks) and weaken infrared absorption, a thickness of ~200 μm was chosen as a compromise for measuring diffusion profiles. For each point, we made 64 scans through 7800–2000 cm$^{-1}$ with a rectangular aperture of 7 × 200 μm in the focus plane. Representative FTIR spectra along a diffusion profile together with the baselines for three H$_2$O bands are shown in Fig. 3b.

At low H$_2$O concentrations, the strong 3550 cm$^{-1}$ band (Fig. 3b) is used to obtain H$_2$O$_{2}$ concentration with the calibration of Mandeville et al. (2002). At high H$_2$O$_{2}$,

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**Fig. 3.** Vibrational spectra along the diffusion profile in HAD-BGI-DC1a (T = 1619 K, t = 288 s, maximum H$_2$O$_{2}$ = 5.75 wt.%). (a) Smoothed Raman spectra. The indicated coordinates (x in μm) are consistent with the profiles in Figs. 4–7. Cubic baselines for the silicate network bands at 500 and 1015 cm$^{-1}$ and the H$_2$O band at 3550 cm$^{-1}$ are shown for selected spectra. (b) Smoothed FTIR spectra, vertically shifted for clarity. Water content and coordinate for each spectrum are approximately the same as those for the Raman spectrum of the same color. Straight tangential baselines are applied to all three water bands. Peak heights (dashed lines) are adopted to compute water contents for both Raman and FTIR. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
concentrations, the 3550 cm⁻¹ band becomes oversaturated and the weaker NIR bands at 4500 cm⁻¹ (representing OH) and 5220 cm⁻¹ (representing H₂O₂) are well resolved. Hence, the heights of the two NIR bands are used to obtain OH and H₂O₂ concentrations using the calibration of Ve-tere et al. (2006), which sum to the H₂O₂ concentration. In the transition from “low” to “high” H₂O₂, which occurs at 0.6 ± 0.2 wt.% H₂O₂, both MIR and NIR calibration methods give similar H₂O₂, verifying the self consistency in the FTIR data along diffusion profiles.

3. RESULTS AND DISCUSSION

In total five experiments containing 10 diffusion couples at 1.0 GPa were successfully performed (Table 2). However, both samples at 818 K (HAD-BGI-DC2a,b) and one sample at 768 K (HAD-BGI-DC4a) showed heavy crystallization in the hydrous half, and could not be analyzed. In comparison with previous dehydration experiments at 0.1 GPa and 743–873 K (Ni et al., 2009a), the substantial crystallization in this work can be attributed to the higher pressure (e.g., Hui et al., 2008; Ni and Zhang, 2008; Wang et al., 2009) and the higher water contents (3–6 wt.% versus 2 wt.%). We measured four diffusion profiles from superliquidus runs (HAD-BGI-DC1a,b and HAD-BGI-DC7a,b) and three from intermediate temperature runs (HAD-BGI-DC4b and HAD-BGI-DC6a,b) using both Raman and FTIR methods.

3.1. Comparison between FTIR and Raman

Sample preparation for Raman analyses is less time-consuming than that for FTIR. Raman only requires polishing one side of a sample (although in this study we initially polished both sides to 500 μm thickness), whereas FTIR profiling requires doubly polishing the sample. Furthermore, it is crucial for FTIR measurements to determine accurate sample thickness along a diffusion profile, which is difficult in practice if the sample contains many cracks or is not polished evenly.

Consistent results are obtained from FTIR and Raman for the four diffusion profiles quenched from superliquidus temperatures. Two examples are shown in Fig. 5a and b. When a sample contains cracks, it appears that Raman measurements are less affected than FTIR measurements (Fig. 5b). This difference is particularly important if the cracks are curved or the crack surfaces are not perpendicular to the polished surfaces.

For the intermediate temperature runs with short diffusion profiles, however, differences between FTIR and Raman profiles are much more pronounced. Due to slow diffusion at intermediate temperatures, and limitation of feasible experimental duration, the generated profiles are less than 100 μm long (Fig. 5c–e). We define the x-axis to be along the traverse direction, the z-axis to be along the sample thickness direction, and the y-axis to be the third mutually perpendicular direction. Because the FTIR aperture is 7 μm (along x) by 200 μm (along y) and the measurement is in transmission mode with sample thickness of about 200 μm, the nominal spatial resolution for the IR measurement is 7 μm along the x-axis, 200 μm along the y-axis, and 200 μm along the z-axis. Along the x-axis, which is the most important for our measurements, the nominal spatial resolutions of the two analytical methods are comparable: 6 μm for Raman and 7 μm for FTIR (aperture width in the focus plane). But compared to Raman profiles, FTIR profiles are smoother and longer, attributed to the convolution effect due to the large incipient angle (17–36°) of the IR beam to the optical axis (the z-direction). The convolution effect causes the actual spatial resolution of FTIR in this study to be much larger than 7 μm. In the y- and z-axes, the spatial resolution of Raman is also estimated to be 6 μm, but the spatial resolution of FTIR is about 200 μm in our measurements so as to transmit enough photons and produce large enough absorbance.

Assuming that the convolution effect is negligible for the Raman profiles, we made an effort to estimate the actual spatial resolution of FTIR analyses by convoluting Raman profiles to match FTIR profiles. For each Raman profile, a smooth discretized profile at 1 μm interval was first created. The discretized profile was then numerically convoluted based on the principle of Gaussian density function (Ganguly et al., 1988). For all three intermediate temperature samples, using a Gaussian with a standard deviation of 12 μm to convolute the Raman profiles produces good matches with FTIR profiles (Fig. 5c–e). If the spatial resolution is defined to be the full width at half maximum (FWHM) of the Gaussian, the actual spatial resolution of FTIR microspectroscopy is approximately 28 μm (2.35 standard deviations). Ni and Zhang (2008) found that with a 20 μm wide aperture on a sample thickness of ~200 μm, the actual spatial resolution of FTIR is about 30 μm. Therefore, reducing the aperture width from 20 to 7 μm does not appear to have improved the spatial resolution of FTIR significantly.
3.2. The experiments at intermediate temperatures

As discussed above, because the H$_2$O$_t$ concentration profiles at intermediate temperatures of 668–768 K are <100 µm in length, the smooth profiles from FTIR analyses (Fig. 5c–e) do not reflect the true profile shape and length. Raman spectroscopy has better spatial resolution, but the quality of Raman spectra is significantly degraded by the partial crystallization in the hydrous half, and by the gap (~8 µm wide) between the two halves. While the gap was most likely produced by contraction during quench, the possibility of poor contact between the two halves cannot be completely ruled out. Furthermore, the gap may have been widened during polishing, and there is no accurate way of subtracting the gap distance from the short Raman profiles (Fig. 5c–e).

Fig. 5. Comparison between FTIR (blue) and Raman (red) measurements. (a) Nearly identical profiles are obtained for a long profile with few cracks in the sample; (b) The Raman profile is less susceptible to cracks than the FTIR profile; (c–e) For profiles with <100 µm length, FTIR profiles show a marked convolution effect compared to Raman profiles. Green curves represent profiles convoluted from Raman profiles to match FTIR profiles (see text for detail). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Along a water diffusion profile produced at some intermediate temperature, $H_2O$ speciation may reach equilibrium at high water contents, but there can be disequilibrium at low $H_2O$ (Zhang et al., 1991). In fact, in the dry half of HAD-BGI-DC6a (18 days at 668 K), FTIR spectra of some points close to the gap contain the 5220 cm$^{-1}$ $H_2O_m$ band but the 4500 cm$^{-1}$ OH band is negligible. This suggests that $H_2O_m$ is the mobile species at 668 K, and that the conversion of $H_2O_m$ to OH is too sluggish to reach equilibrium at low $H_2O$.

In principle, all these problems could be alleviated by experiments performed at higher temperatures. However, our attempt was unsuccessful: at 818 K nearly complete crystallization occurred in both diffusion couples in HAD-BGI-DC2. Considering the poor quality of both FTIR and Raman profiles and the complexities associated with the intermediate temperature runs, we decided not to use these profiles to obtain diffusivity. The intermediate temperature results are presented in this study only for underlining the remarkable difference between Raman and FTIR, and for estimating the actual spatial resolution for FTIR analyses.

### 3.3. A modified speciation-based diffusion model for superliquidus experiments

We have focused on studying the four diffusion couples quenched from 1619 and 1842 K. The obtained water concentration profiles cannot be satisfactorily fit using an error function (an example is shown in Fig. 6a). This suggests that $H_2O$ diffusivity in andesitic melt must be dependent on total $H_2O$ concentration, which is in contrast to Behrens et al. (2004) but is consistent with Persikov et al. (2010). Assuming $H_2O$ diffusivity proportional to $H_2O$ concentration roughly fits the profiles, but there are considerable misfits at low $H_2O$ (Fig. 6a). The misfits cannot be attributed to the convolution effect, because these profiles are long and equivalent profiles have been obtained from Raman and FTIR analyses. A third model, first developed by Zhang and Behrens (2000) and later successfully applied in a series of studies (Liu et al., 2004; Ni and Zhang, 2008; Ni et al., 2009a,b), is applied, but the misfits persist (Fig. 6a). The third model is a mechanistic model that explicitly considers the speciation reaction involving $H_2O_m$ and OH, and assumes OH diffusivity to be negligible and $H_2O_m$ diffusivity to increase exponentially with $H_2O$ content. Both the mechanistic model and the proportionality model imply negligible $H_2O_m$ diffusivity as $H_2O$ concentration approaches zero, which is the cause of the misfits at low $H_2O$. Therefore, with decreasing $H_2O$ concentration in superliquidus andesitic melts, even though the $H_2O_m$/$H_2O$ ratio approaches zero and OH becomes the dominant species, $H_2O_m$ diffusivity does not become negligible, indicating that OH diffusivity cannot be neglected. Our experimental data hence offer the opportunity to constrain OH diffusivity, which has never been resolved before.

In order to obtain OH diffusivity, we start from the general form of the $H_2O$ diffusion equation (Zhang et al., 1991),

\[
\frac{\partial X}{\partial t} = \frac{\partial}{\partial x} \left( D_{H_2O_m} \frac{\partial X_m}{\partial x} + D_{OH} \frac{\partial X_{OH}}{2 \partial x} \right),
\]

where $X = C/18.015/[C/18.015 + (100 - C)/33.84]$ (Ni et al., 2009a) is the mole fraction of $H_2O_m$ in the haploandesitic melt ($C$ is $H_2O$ in wt.%), $X_m$ and $D_{H_2O_m}$ are the mole fraction and diffusivity of $H_2O_m$, $X_{OH}$ and $D_{OH}$ are the mole fraction and diffusivity of OH, $t$ is time and $x$ is distance. Because the temperature is high and hence equilibrium for the speciation reaction $H_2O_m + O = 2OH$ (where O represents an anhydrous oxygen) is expected (e.g., Zhang et al., 1995), comparison with the diffusion equation for a simple component leads to

\[
D_{H_2O_m} = D_{H_2O_m} \frac{dX_m}{dx} + D_{OH} \frac{dX_{OH}}{2dx},
\]

where $D_{H_2O_m}$ is the apparent $H_2O$ diffusivity. The two differential terms in Eq. (2) add up to unity, and the latter is as follows (Wang et al., 2009):
\[
\frac{dX_{\text{OH}}}{2dX} = \frac{1 - 2X}{\sqrt{4X(X - 1)(1 - 4/K) + 1}},
\]

in which \( K \) is the equilibrium constant for the \( \text{H}_2\text{O} \) speciation reaction. For our haploandesitic melt (Ni et al., 2009a), \( \ln K = 1.547 - 2453/T, \)

where \( T \) is temperature in K.

Zhang et al. (1991) assumed \( D_{\text{H}_2\text{O}_\text{a}} \) to be independent of \( \text{H}_2\text{O} \) concentration and \( D_{\text{OH}} \) to be negligible in rhyolitic melts. To reconcile new experimental data at higher \( \text{H}_2\text{O} \) concentrations (>3 wt.%), Zhang and Behrens (2000) revised the model of Zhang et al. (1991) and assumed instead

\[
D_{\text{H}_2\text{O}_\text{a}} = D_0 e^{aX},
\]

with \( D_0 \) and \( a \) being two constants at fixed \( T \) and \( P \), whereas \( D_{\text{OH}} \) was still assumed to be negligible.

Based on the fitting results discussed above and shown in Fig. 6, we find that \( D_{\text{OH}} \) is not negligible in superliquidus andesitic melts. In principle, \( D_{\text{OH}} \) may also depend on \( \text{H}_2\text{O} \) concentration \( (X) \), but the contribution of \( \text{OH} \) diffusion to \( D_{\text{H}_2\text{O}_\text{a}} \) is only expected to be important at low \( \text{H}_2\text{O} \). Moreover, including the dependence of \( D_{\text{OH}} \) on \( X \) would add one additional fitting parameter, which cannot be well resolved because \( D_{\text{H}_2\text{O}_\text{a}} \) also depends on \( X \) (i.e., it is possible to reduce the dependence of \( D_{\text{H}_2\text{O}_\text{a}} \) on \( X \) by increasing the dependence of \( D_{\text{H}_2\text{O}_\text{a}} \) on \( X \)). Hence, we settle for the less ambitious goal of obtaining \( D_{\text{OH}} \) only at low \( \text{H}_2\text{O} \) concentration, and assume

\[
D_{\text{OH}} = \text{constant (at fixed } T \text{ and } P).\]

With this treatment, the dependence of \( D_{\text{OH}} \) on \( \text{H}_2\text{O} \) is convoluted into that of \( D_{\text{H}_2\text{O}_\text{a}} \) on \( \text{H}_2\text{O} \). For fitting a measured diffusion profile, in addition to a small interface adjustment \( \Delta X_\text{OH} \), three free parameters are allowed to vary: they are \( D_0, a, \) and \( D_{\text{OH}}/D_0 \).

We have developed a multivariate least-squares fitting procedure to simultaneously extract the parameters \( D_0, a, \) \( D_{\text{OH}}/D_0 \) and \( \Delta X_\text{OH} \). This modified speciation-based diffusivity model produces a much better fit than all previous models (Fig. 6a). The dependences of \( D_{\text{OH}}/D_0 \) on \( \text{H}_2\text{O} \) concentration for the new model as well as those for previous models are shown in Fig. 6b for the charge HAD-BGI-DC1a. The obtained fitting parameters are summarized in Table 3. The values of \( \Delta X_\text{OH} \) are not reported because they are arbitrary (dependent on the initially chosen coordinates). In Table 3, the errors of \( a \) and \( D_{\text{OH}}/D_0 \) are obtained purely from fitting, but the errors of \( \ln D_0 \) also incorporate the uncertainties of experimental durations.

In general, two diffusion couples in a single run have resulted in similar parameters, as do FTIR profile and Raman profile of the same sample. To fully exploit the fact that two diffusion couples experienced the same \( P-T-t \) history, we have made a further effort to fit two profiles (either two FTIR profiles or two Raman profiles) in a single run simultaneously. This fitting procedure for both profiles has 5 free parameters: \( D_0, a, D_{\text{OH}}/D_0, \Delta X_\text{OH} \), and \( \Delta X_\text{OH} \). The obtained best-fit parameters are also listed in Table 3 (indicated in bold). Again, \( \Delta X_\text{OH} \) and \( \Delta X_\text{OH} \) are not reported for their insignificance. Calculated diffusion profiles using the best-fit parameters are plotted with measured profiles in Fig. 7, which match each other well in most cases.

Modeling two profiles simultaneously adds more constraints to the diffusivity vs. \( \text{H}_2\text{O} \) relationship. At 1619 K, parameter \( a \) using the collective fitting procedure is 15.8 from FTIR profiles and 16.2 from Raman profiles. The difference between these two values is much smaller than if each profile were treated separately. A similar phenomenon has been observed for the profiles at 1842 K, and a parameter \( a \) of ~10.4 is extracted from both FTIR and Raman profiles. These values are much smaller than the \( a \) values of 75–85 at 743–873 K and 0.1 GPa in Ni et al. (2009a). Therefore in haploandesitic melt, as temperature increases, the increase of \( \text{H}_2\text{O} \) diffusivity with \( \text{H}_2\text{O} \) concentration becomes less dramatic. A similar conclusion has been reached by previous work on rhyolitic and dacitic melts (Zhang and Behrens, 2000; Ni and Zhang, 2008; Ni et al., 2009b).

The \( D_{\text{OH}}/D_0 \) ratio has been constrained to be between 0.1 and 0.2 with large relative errors (Table 3). This means that, at 1619–1842 K and extremely low \( \text{H}_2\text{O} \) concentration, \( \text{OH} \) diffusivity is lower than \( \text{H}_2\text{O} \) diffusivity probably by less than an order of magnitude. This finding is not

<table>
<thead>
<tr>
<th>Run #</th>
<th>Analytical method</th>
<th>( T ) (K)</th>
<th>( a )</th>
<th>( \ln D_0 ) (in m²/s)</th>
<th>( D_{\text{OH}}/D_0 )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAD-BGI-DC1</td>
<td>FTIR</td>
<td>1619</td>
<td>17.4 ± 2.1</td>
<td>22.84 ± 0.16</td>
<td>0.24 ± 0.08</td>
<td>0.997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28.3 ± 5.4</td>
<td>22.93 ± 0.25</td>
<td>0.22 ± 0.10</td>
<td>0.996</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>15.8 ± 2.1</td>
<td>22.99 ± 0.15</td>
<td>0.18 ± 0.06</td>
<td>0.9995</td>
<td></td>
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<tr>
<td></td>
<td>Raman</td>
<td>18.7 ± 4.5</td>
<td>22.64 ± 0.32</td>
<td>0.14 ± 0.13</td>
<td>0.9990</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>21.5 ± 6.6</td>
<td>22.40 ± 0.32</td>
<td>0.09 ± 0.08</td>
<td>0.9986</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.2 ± 3.4</td>
<td>22.41 ± 0.22</td>
<td>0.10 ± 0.07</td>
<td>0.9985</td>
<td></td>
</tr>
<tr>
<td>HAD-BGI-DC7</td>
<td>FTIR</td>
<td>1842</td>
<td>11.9 ± 5.5</td>
<td>21.37 ± 0.42</td>
<td>0.16 ± 0.14</td>
<td>0.9991</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.6 ± 5.3</td>
<td>21.02 ± 0.27</td>
<td>0.16 ± 0.08</td>
<td>0.9996</td>
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<tr>
<td></td>
<td></td>
<td>10.4 ± 4.6</td>
<td>21.26 ± 0.35</td>
<td>0.18 ± 0.12</td>
<td>0.9987</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Raman</td>
<td>11.0 ± 4.1</td>
<td>21.19 ± 0.30</td>
<td>0.10 ± 0.08</td>
<td>0.9992</td>
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<tr>
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<td></td>
<td>9.9 ± 7.3</td>
<td>20.95 ± 0.39</td>
<td>0.10 ± 0.09</td>
<td>0.9992</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>10.4 ± 3.6</td>
<td>21.16 ± 0.26</td>
<td>0.11 ± 0.07</td>
<td>0.9985</td>
<td></td>
</tr>
</tbody>
</table>

Errors are given at 2σ level. Equilibrium constant for reaction \( \text{H}_2\text{O} + \text{O} = 2\text{OH} \) is based on Ni et al. (2009a).

* Both profiles from a given experiment are regressed simultaneously.
completely unexpected. At intermediate temperatures such as 800 K, $D_{\text{OH}}$ has not been resolved from $D_{\text{H}2\text{O}}$ (Ni et al., 2009a), implying that the $D_{\text{OH}}/D_0$ ratio is small.

Because the activation energy for the diffusion of OH, the more sluggish species, is expected to be much higher than that for $\text{H}_2\text{O}_m$ diffusion, $D_{\text{OH}}$ increases more rapidly than

Fig. 7. Diffusion profiles fit by the modified speciation-based diffusion model assuming $D_{\text{H}_2\text{O}} = D_0 e^{\alpha x}$ and $D_{\text{OH}} = \text{constant}$ (solid curves), with fitting parameters in Table 3 (those in bold). Open circles are measurements affected by cracks in the sample, and were not used for fitting.
with increasing temperature. This explains the negligible $D_{OH}/D_0$ ratio at $\sim$800 K and resolvable $D_{OH}/D_0$ ratio at 1619–1842 K.

The relative contribution of OH diffusion to $D_{H2O}$ depends not only on $D_{OH}/D_0$ and $a$, but also on the differential terms in Eq. (2), which further depend on the equilibrium constant $K$ and $H_2O$ concentration. Ni et al. (2009a) found that $K$ increases from rhyolitic to dacitic to andesitic melt at <900 K. If the compositional trend at <900 K can be extrapolated to higher temperatures, at a given $H_2O$ mole fraction ($X$), there is a higher percentage of OH in andesitic melts than in felsic melts. At 1619–1842 K, if the $K$ value from Eq. (4) is used to calculate $X_{OH}/(2X)$, OH will account for 100% of total $H_2O$ at $X=0$, and more than 70% at $X=0.104$ (5.8 wt.% $H_2O$). The differential term $dX_{OH}/(2dX)$, meaning the “weight” of $D_{OH}$ in $D_{H2O}$, is also higher in andesitic melt.

The successful resolution of $D_{OH}$ in this work, compared to negligible $D_{OH}$ in earlier studies, can be attributed to the following: (i) The “dry” half of the diffusion couple in this study contains a very low concentration of $H_2O$ (0.01 wt.%), for which the fraction of $H_2O_m$ and its contribution to water diffusion are minimized. In some previous studies (e.g., Zhang and Behrens, 2000), the “dry” half often contains >0.10 wt.% $H_2O$, 10 times more than in the present study. (ii) It is also possible that $D_{OH}/D_0$ in andesitic melt at superliquidus temperatures is greater than that in rhyolitic and dacitic melts.

### 3.4. Comparison between $D_{OH}$ and Eyring diffusivity

Zhang et al. (1991) assumed $D_{OH}$ to be similar to non-bridging oxygen diffusivity or Eyring diffusivity. The Eyring diffusivity ($D_{Eyr}$) is related to melt viscosity ($\eta$) as $D_{Eyr} = kT/\eta L$, with $k$ being the Boltzmann constant and $L$ being the jump distance (~0.28 nm). Our new data allow us to examine whether the assumption of Zhang et al. (1991) is correct. At 1619 K and $\leq$0.1 wt.% $H_2O$, the Eyring diffusivity estimated from the viscosity model of Vetere et al. (2006) for andesitic melt is $1.6 \times 10^{-13}$–$2.0 \times 10^{-13}$ m²/s. The $D_{OH}$ value at low $H_2O$ and 1619 K can be estimated from the values of $D_{OH}/D_0$ and $D_0$ in this study to be $\sim 2 \times 10^{-11}$ m²/s, larger than $D_{Eyr}$ by about two orders of magnitude. The nonequivalence of $D_{OH}$ and $D_{Eyr}$ is not problematic, because for the two to be comparable, a prerequisite is that OH is always bonded to the network formers (Si, Al and Fe³⁺). However, NMR studies have found that OH can also be linked to alkalali or divalent cations in both polymerized and depolymerized melts (Kohn et al., 1989; Xue and Kanzaki, 2004). These “free” OH subspecies are expected to have higher mobility than Si-OH and Al-OH, and their motion is not restricted by the process of viscous flow. The “free” OH subspecies are favored by more depolymerized melts and a higher content of alkaline earth elements (Xue and Kanzaki, 2004). In our rather polymerized haploandesitic melt (NBO/T = 0.173), although the “free” OH subspecies may only account for a fraction of OH, they can still dominate OH diffusion, much the same way as a small fraction of $H_2O_m$ dominates $H_2O$ diffusion (Zhang et al., 1991).

### 3.5. Comparison between $D_{OH}$ and F diffusivity

The $H_2O_m$ and OH diffusivities in nearly anhydrous haploandesitic melt obtained from the Raman data are shown in Fig. 8. $H_2O_m$ has higher diffusivity than OH for being a neutral molecule and interacting less with the melt structure. OH, similar to fluorine ion, has a valence of -1; their size is also comparable – for a coordination number of 4, the ionic radii of OH and F are 0.135 and 0.131 nm, respectively (Shannon, 1976). Because the size and charge of an ion play a major role in controlling its diffusivity (e.g., Zhang et al., 2010), we expect OH diffusivity and F diffusivity to be similar under the same conditions, especially if OH⁻ and F⁻ are bonded to the same cations. F diffusivity has not been measured in andesitic melts, but as shown in Fig. 8, the $D_{OH}$ values at 1 GPa estimated in the present study are close to the measured F diffusivities in basaltic and phonolitic melts at 1 GPa (Alletti et al., 2007; Balcone-Boissard et al., 2009). This good agreement suggests that the OH diffusivity values constrained from our fittings are reasonable.

### 3.6. Comparison with previous studies

$H_2O_m$ diffusivity at 1619–1842 K and 0–6 wt.% $H_2O$ can be calculated using Eqs. (2)–(5) and the parameters reported in Table 3. Fig. 9 illustrates how $D_{H2O}$ varies with temperature and water content based on the Raman data.

Because we only have data at two temperatures, the temperature dependence is not well constrained. Adopting the Arrhenius relationship, the activation energy for $D_{H2O}$ at water contents below 0.1 wt.% $H_2O$ is approximately 146 kJ/mol, decreasing to 126 kJ/mol at 1 wt.% $H_2O$, and to 75 kJ/mol at 5 wt.% $H_2O$. For Fe-bearing andesitic melts (AndDC in Table 1) at 1 GPa, Behrens et al. (2004) determined the activation energy at 1 wt.% $H_2O$ to be 142 kJ/mol. Therefore, our roughly estimated activation
energies are reasonably close. Our $D_{\text{H}_2\text{O}}$ data at 1 wt.% $\text{H}_2\text{O}$ are lower than those of Behrens et al. (2004) by a factor of $\sim 2$ (Fig. 9a). This difference may be attributed to the difference in melt composition – the melt in Behrens et al. (2004) has lower $\text{SiO}_2 + \text{Al}_2\text{O}_3$ content and higher NBO/T of 0.313 (Table 1). At temperatures $\gtrsim 1300 \text{ K}$, $\text{H}_2\text{O}$ diffusivity tends to increase with increasing degree of melt depolymerization (Zhang and Ni, 2010).

Persikov et al. (2010) reported $D_{\text{H}_2\text{O}}$ diffusivity at 1573 K and 0.1 GPa and up to 4 wt.% $\text{H}_2\text{O}$, in a different haploandesitic melt, with much higher alkalis (8.9 wt.% $\text{Na}_2\text{O}$), similar $\text{SiO}_2 + \text{Al}_2\text{O}_3$ (81 wt.%) and higher NBO/T (0.287) compared to the haploandesite in this study (Table 1). Fig. 9b shows that the diffusivities in Persikov et al. (2010) are higher than our values by a factor of 2–5. We attribute this difference to the higher degree of depolymerization and the much higher alkali content of the melt investigated by Persikov et al. (2010). Wang et al. (2009) have shown that $\text{H}_2\text{O}$ diffusivity in peralkaline rhyolitic melt is slightly larger than that in metaluminous rhyolite, supporting our interpretation. The pressure difference between this study and that of Persikov et al. (2010) may also cause some difference.

4. CONCLUSIONS

(1) Raman spectroscopy can be used to measure $\text{H}_2\text{O}$ concentration profiles in silicate melts once the concentrations at the two ends are determined (e.g., by FTIR), and it can achieve a spatial resolution superior to that of FTIR.

(2) The technique of double diffusion couples allows more accurate determination of the dependence of $\text{H}_2\text{O}$ diffusivity on water contents in silicate melts.

(3) $\text{H}_2\text{O}$ diffusivity in haploandesitic melts increases with increasing $\text{H}_2\text{O}$ concentration.

(4) OH diffusivity in superliquidus haploandesitic melts is 10–20% of $D_{\text{H}_2\text{O}}$ diffusivity as water content approaches zero. OH diffusivity is similar to $F$ diffusivity but is much higher than Eyring diffusivity.

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