The speciation of dissolved H$_2$O in dacitic melt

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ABSTRACT

We report the first systematic study of H$_2$O speciation in dacitic melt with total dissolved H$_2$O ranging from 1.4 to 2.6 wt% at temperatures ranging from 1.4 to 2.6 wt% at temperatures ranging from 480–590 °C for certain durations and then quenched in water or air. Species concentrations were measured with Fourier transform infrared (FTIR) spectroscopy. At a given temperature, the equilibrium constant for the reaction, H$_2$O$_m$ (melt) + O (melt) = 2OH (melt), is roughly constant. At the same temperature and water content, the equilibrium constant for the hydrous species interconversion reaction in dacitic melt appears to be slightly greater than in hydrous rhyolitic melt, reflecting a larger proportion of dissolved H$_2$O as hydroxyl groups in dacitic melt. Our results can be applied to model species equilibrium in hydrous dacitic melt, to estimate the apparent equilibrium temperature of natural dacitic glasses, and to investigate viscosity of hydrous dacitic melts.

INTRODUCTION

As the most abundant volatile component in terrestrial magmas, dissolved water in silicate glasses and melts significantly influences the properties of silicate melts and plays a critical role in explosive volcanic eruptions. Most early work on water in silicate melts focused on rhyolitic melt. However, explosive volcanic eruptions with less-siliceous melt compositions are common. To model eruption dynamics and magma evolution, it is necessary to understand the thermodynamic properties of dacitic magma, isotope fractionation, and the H$_2$O diffusivity in dacitic magma. Investigation of H$_2$O speciation is critical to such understandings. Furthermore, because of its high SiO$_2$ concentration, dacitic magma is easy to quench into glass. Hence, speciation data can also be applied to infer apparent equilibrium temperature of natural dacitic glass, as well as cooling rates of the magma at glass transition.

Water dissolves in silicate melts as at least two species: molecular H$_2$O and hydroxyl group (hereafter referred to as H$_2$O$_m$ and OH, respectively) (Stolper 1982a, 1982b). These two species inter-convert according to the reaction:

$$\text{H}_2\text{O}_m\ (\text{melt}) + \text{O} (\text{melt}) = 2\text{OH} (\text{melt}),$$

where O is an anhydrous oxygen.

The speciation of H$_2$O in rhyolitic melts has been investigated extensively (e.g., Zhang et al. 1991, 1995; Ihinger et al. 1999; Withers et al. 1999; Zhang 1999; Nowak and Behrens 2001). The equilibrium constant (K) of Reaction 1 in rhyolitic melts depends only on temperature (lnK = 1.89 – 3120/T) when the total dissolved H$_2$O (hereafter referred to as H$_2$O$_t$) content is no more than 2.5 wt% (Ihinger et al. 1999). Whether K depends on water content at H$_2$O$_t$ > 2.5 wt% remains a topic of debate (Ihinger et al. 1999; Nowak and Behrens 2001). Speciation in basaltic melt also has received considerable attention (Dixon et al. 1995; Ohlhorst et al. 2001). Experiments were carried out at 1200 °C in internally heated pressure vessels. Dixon et al. (1995) showed that the quenched speciation is the same for normal (8 K/s) and rapid quench (calculated as 500 K/s, HOLLOWAY et al. 1992). However, the kinetics of the reaction has not been investigated and the quench effect has not been quantified. Other melt compositions (synthetic Ca-Al-silicate glasses, orthoclase, anorthite, jadeite: Silver et al. 1990; Fe-free andesite: Richet et al. 1996; andesite and dacite: Ohlhorst et al. 2001; andesite and Fe-free andesite: Mandeville et al. 2002) also have been investigated, but these preliminary data also are based on samples quenched from high-temperature experiments (≥850 °C) and probably reflect speciation at the apparent equilibrium temperature (T$_{eq}$). Here we report the first experimental study of H$_2$O speciation in dacitic melt at 480–590 °C and 1 bar using the heat-and-quench technique. It has been shown that reaction of hydrous species during quench from 400–600 °C is negligible in rhyolitic glasses (Withers et al. 1999). Behrens and Nowak (2003) also showed that water speciation data obtained by the quench technique, by in situ IR measurements and by controlled cooling from superliquidus temperature, are in excellent agreement for rhyolitic and albic compositions.

EXPERIMENTAL AND ANALYTICAL METHODS

Starting materials

Hydrous dacitic glasses were prepared by dissolving water into anhydrous glasses at high $T$ and $P$ using an internally heated pressure vessel (IHPV) at Hannover, Germany. Anhydrous dacite with a composition similar to Unzen dacite was synthesized by fusing oxides and carbonates at 1600 °C in air (Ohlhorst et al. 2001). Homogeneous hydrous glass with 1.0–2.5 wt% H$_2$O$_t$ was prepared as follows. Powdered anhydrous glass (mixture of grains <200 μm and 200–500 μm)
and water were loaded into Au–Pd capsules (3 mm in diameter and 30 mm in length) in turn in several portions. Syntheses were performed in a conventional IHP at 1250 °C and 3–5 kbar for 13–48 h. Temperatures measured by two sheathed type-K thermocouples at the top and bottom of the capsule differed by less than 15 °C. Isobaric quenching was achieved by turning off the power of the furnace but keeping the pressure stable by automatically pumping Ar into the vessel. Measured initial cooling rates were ~200 °C/min and decreased to ~100 °C/min near the glass transition of hydrous glasses at 300–600 °C. The activity of metallic Fe in the sample was very low because the high intrinsic oxidation conditions in the IHP (ANNO = ~3, close to the MnO-MnO2 buffer for a water activity of 1) tend to stabilize Fe oxides (Berndt et al. 2002). Furthermore, metallic Fe has low solubility in the Au–Pd alloy. Thus Fe loss during synthesis was negligible (Table 1). Small broken chips from the wall or two ends of the synthesized glass cylinder were polished to a thickness of ~30 μm and checked under an optical microscope. Thin samples have a light brown color. No quench crystals or bubbles were found with optical observations.

Equilibrium experiments

Experiments were conducted on dacitic glasses with two different initial H2O contents (DC55 and DC1, 1.3–1.4 wt%; DC2A and DC2B, 2.3–2.5 wt%) at ambient pressure in a horizontal tube furnace using the heat-and-queue technique. One experiment was carried out at ambient pressure using a sample with 3.6 wt% H2O, but the baseline shape changed after the experiment indicating structure changes such as changes in local environment and/or oxidation state of iron in the sample. This experiment was rejected as unsuccessful. Experimental procedures follow those of Zhang et al. (1991, 1995, 1997a) and are briefly summarized below. The synthesis of this Fe2⁺ sample was performed in a conventional type-K thermocouples at the top and bottom of the capsule differed by less than 1 °C, and for reaction-rate experiments, surface layers affected by diffusive loss of H2O are not expected to be significant (<3 vol%). Therefore, some doubly polished glass chips were not re-polished after each heating (see Table 2 for specifications). Unpolished glass chips were used only for equilibrium experiments and were polished after experiments to a thickness of 0.4–0.8 mm. Some samples cracked during quench.

Analyses of glass composition

Under the experimental conditions, dacitic liquid is metastable. Hence, there could be crystallization, oxidation, and bubbling in the sample during the experiment. All experimental charges were examined optically. No significant crystallization and bubbling were noticed. Some experimental charges (DC1sp2, DC2Asp2, DC2Bsp3, and DC55a1) were examined using back-scattered electron imaging with a scanning electron microscope (SEM Hitachi S3200N) but no crystals were found at the sub-micrometer scale. Glass compositions before and after experiments (Table 1) were determined using a Cameca MBX electron microprobe at University of Michigan. To minimize the problem of Na migration during the microprobe analyses, a broad beam (spot size ~12 μm in diameter) with a low beam current (3 nA) was used and Na was analyzed first. The intensity of Na X-rays was measured for six 5 s counting intervals and the “true” Na intensity was determined by extrapolation of the exponential decay curve of the intensity to the zero-time intercept. The oxide wt% on an anhydrous basis was calculated by dividing the microprobe measured oxide concentration by 1-C, where C is the weight fraction of H2O (obtained by infrared spectroscopy, see Table 2). No significant post-experiment compositional change was observed.

FTIR

Concentrations of H2O species in dacitic melt before and after experiments were determined by FTIR spectroscopy using the main chamber of a Perkin-Elmer FTIR GX spectrometer. During analyses, the main chamber was purged with dry N2. A round aperture with a diameter of 400 or 530 μm was used to limit the beam. Positions of analytical spots were chosen to be far away from edges and cracks. A typical infrared spectrum of hydrous dacitic glass is shown in Figure 1a. Absorption peaks at ~5230 cm⁻¹ and ~4520 cm⁻¹ are due to the stretching and bending vibrations of H2O and OH, respectively. The absorption peak at ~3900 cm⁻¹ is correlated to the H2O contents (Withers and Behrens 1999). The absorption peak at 5600 cm⁻¹ is related to Fe²⁺ in the glass sample. However, the coordination of Fe²⁺ in silicate glass and melt is still controversial (e.g., Keppler 1992; Brown et al. 1995; Wilke et al. 2002). The shape and intensity of this Fe²⁺ peak for samples before and after experiments are similar, indicating only minor structural change in samples. Concentrations of H2O species and H2O were calculated using the calibration of Ohlhorst et al. (2001).

Results

Eleven series of experiments were conducted for dacitic samples in a horizontal tube furnace at 480–590 °C and 1 bar (Table 2 and Fig. 2). Because spectrum fitting is not trivial, we first discuss the caveats in fitting IR spectra and in obtaining band intensities. Then we discuss the results on species concentrations and equilibrium constant.

IR band intensity data

To obtain species concentrations, the band intensity of the species in preparation. To minimize the baseline shape change after the experiment indicating structure changes such as changes in local environment and/or oxidation state of iron in the sample. This experiment was rejected as unsuccessful. Experimental procedures follow those of Zhang et al. (1991, 1995, 1997a) and are briefly summarized below. The synthesis of this Fe2⁺ sample was performed in a conventional type-K thermocouples at the top and bottom of the capsule differed by less than 1 °C, and for reaction-rate experiments, surface layers affected by diffusive loss of H2O are not expected to be significant (<3 vol%). Therefore, some doubly polished glass chips were not re-polished after each heating (see Table 2 for specifications). Unpolished glass chips were used only for equilibrium experiments and were polished after experiments to a thickness of 0.4–0.8 mm. Some samples cracked during quench.

Table 1. Glass compositions

<table>
<thead>
<tr>
<th></th>
<th>DC55</th>
<th>DC55a1</th>
<th>DC1</th>
<th>DC1sp1</th>
<th>DC1sp2</th>
<th>DC2A</th>
<th>DC2B</th>
<th>DC2Bsp5</th>
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<tbody>
<tr>
<td>SiO2</td>
<td>65.18</td>
<td>65.03</td>
<td>65.7</td>
<td>65.2</td>
<td>0.32</td>
<td></td>
<td></td>
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<tr>
<td>TiO2</td>
<td>0.65</td>
<td>0.64</td>
<td>0.67</td>
<td>0.66</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al2O3</td>
<td>15.93</td>
<td>16.62</td>
<td>16.3</td>
<td>16.0</td>
<td>0.16</td>
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<tr>
<td>FeO</td>
<td>4.37</td>
<td>4.32</td>
<td>4.16</td>
<td>4.25</td>
<td>0.14</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>MgO</td>
<td>2.15</td>
<td>1.93</td>
<td>1.96</td>
<td>2.13</td>
<td>0.06</td>
<td></td>
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<td></td>
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<tr>
<td>CaO</td>
<td>5.05</td>
<td>5.13</td>
<td>5.10</td>
<td>4.77</td>
<td>0.92</td>
<td>0.11</td>
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<tr>
<td>Na2O</td>
<td>3.73</td>
<td>3.93</td>
<td>3.95</td>
<td>4.05</td>
<td>0.22</td>
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<tr>
<td>K2O</td>
<td>2.69</td>
<td>2.69</td>
<td>2.70</td>
<td>2.51</td>
<td>0.08</td>
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<tr>
<td>H2O</td>
<td>~1.5</td>
<td>~1.4</td>
<td>~2.5</td>
<td>~2.5</td>
<td>1.5</td>
<td>2.33</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The average uncertainty (1σ) in the microprobe analyses.
†N is the number of electron microprobe analyses using a defocused beam (~12 μm in radius) with a 3 nA current.
‡H2O contents were determined using FTIR (see Table 2).

Peak heights were determined after subtraction of the baseline (background) from the spectrum. Compared with the spectrum of rhyolitic glass with a nearly flat baseline due to a low Fe
concentration, the baseline of dacite spectrum is rather difficult to fit because of the Fe-related peak at 5600 cm\(^{-1}\) (Fig. 1a). Ohlhorst et al. (2001) used two methods to fit the baseline (referred to as TT and GG methods), and calibrated the relation between species concentration and band intensity for both methods. In the TT method, two straight lines are used for modeling the baseline. One line is tangential to both sides of the 4500 cm\(^{-1}\) peak, and the other is defined by drawing a tangent of the right-hand side (smaller wavenumber) of the 5200 cm\(^{-1}\) peak through the baseline point at 5400 cm\(^{-1}\) (Fig. 1a). In the GG method, two Gaussian curves are used to model the baseline. One Gaussian curve is fit to the 5600 cm\(^{-1}\) peak and the other to the 3930 cm\(^{-1}\) peak (Fig. 1a).

With the GG method to fit the spectrum, we found that, for consistency, it is best to normalize the spectrum to a fixed thickness and to shift the spectrum so that the minimum absorbance is roughly fixed. For all twelve samples in Ohlhorst et al. (2001), the majority (eight samples) has a thickness of 0.46–0.47 mm

**TABLE 2.** The speciation of H\(_2\)O in dacitic melt at 1 bar

<table>
<thead>
<tr>
<th>Sample</th>
<th>(T) (°C)</th>
<th>Time (s)</th>
<th>Thickness* (mm)</th>
<th>A5230</th>
<th>A4520</th>
<th>H(_2)O(_m) (wt%)</th>
<th>H(_2)O(_s) (wt%)</th>
<th>OH (wt%)</th>
<th>InK</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC1</td>
<td>500</td>
<td>278</td>
<td>0.709</td>
<td>0.0466</td>
<td>0.0940</td>
<td>0.419</td>
<td>0.995</td>
<td>1.414</td>
<td>-1.70</td>
</tr>
<tr>
<td>DC1sp4</td>
<td>3602</td>
<td>4202</td>
<td>0.567</td>
<td>0.0437</td>
<td>0.0726</td>
<td>0.491</td>
<td>0.962</td>
<td>1.453</td>
<td>-1.92</td>
</tr>
<tr>
<td>DC1sp1</td>
<td>519</td>
<td>540</td>
<td>0.536*</td>
<td>0.0394</td>
<td>0.0709</td>
<td>0.469</td>
<td>0.994</td>
<td>1.463</td>
<td>-1.81</td>
</tr>
<tr>
<td>DC1sp2</td>
<td>560</td>
<td>2100</td>
<td>0.518</td>
<td>0.0238</td>
<td>0.0413</td>
<td>0.477</td>
<td>0.976</td>
<td>1.453</td>
<td>-1.86</td>
</tr>
<tr>
<td>DC1sp3</td>
<td>590</td>
<td>0.720</td>
<td>0.1469</td>
<td>0.1827</td>
<td>0.0918</td>
<td>0.388</td>
<td>1.023</td>
<td>1.411</td>
<td>-1.56</td>
</tr>
<tr>
<td>DC2A</td>
<td>1.000</td>
<td>0.1469</td>
<td>0.1827</td>
<td>0.041</td>
<td>1.377</td>
<td>2.318</td>
<td>-1.84</td>
<td></td>
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</tr>
<tr>
<td>DC2b</td>
<td>0.899</td>
<td>0.1470</td>
<td>0.1677</td>
<td>1.049</td>
<td>1.409</td>
<td>2.458</td>
<td>-1.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DC2Bsp3</td>
<td>480</td>
<td>120</td>
<td>0.904*</td>
<td>0.1499</td>
<td>0.1691</td>
<td>1.063</td>
<td>1.411</td>
<td>2.475</td>
<td>-1.91</td>
</tr>
<tr>
<td>DC2Bsp4</td>
<td>500</td>
<td>360</td>
<td>0.905*</td>
<td>0.1536</td>
<td>0.1663</td>
<td>1.102</td>
<td>1.386</td>
<td>2.489</td>
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</tr>
<tr>
<td>DC2Asp2</td>
<td>518</td>
<td>270</td>
<td>0.109*</td>
<td>0.1574</td>
<td>0.1657</td>
<td>1.114</td>
<td>1.380</td>
<td>2.494</td>
<td>-2.00</td>
</tr>
<tr>
<td>DC2Asp1</td>
<td>537</td>
<td>119</td>
<td>0.107*</td>
<td>0.1581</td>
<td>0.1664</td>
<td>1.130</td>
<td>1.387</td>
<td>2.517</td>
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</tr>
<tr>
<td>DC5a1</td>
<td>464</td>
<td>0.108*</td>
<td>0.1409</td>
<td>0.1895</td>
<td>0.0896</td>
<td>1.418</td>
<td>2.314</td>
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</tr>
<tr>
<td>DC5a2</td>
<td>572</td>
<td>0.180</td>
<td>0.0590</td>
<td>0.1329</td>
<td>0.416</td>
<td>1.102</td>
<td>1.518</td>
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<tr>
<td></td>
<td>0.274</td>
<td>0.0179</td>
<td>0.0405</td>
<td>0.160</td>
<td>1.109</td>
<td>1.525</td>
<td>-1.47</td>
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</table>

Notes: Absorbance of each peak is reproducible within 1% relative error. The molar absorptivities used for 5230 and 4520 bands are 1.13 and 0.96 L/mol/cm for the TT method, and 1.21 and 1.07 L/mol/cm for the GG method, respectively (Ohlhorst et al. 2001). Density of the glass was calculated using the equation (2) in Ohlhorst et al. (2001).

* The sample was doubly polished before the experiment and not re-polished afterward.
† This sample was cut from sample DC1sp4.

**FIGURE 1.** IR spectra of dacitic samples. All spectra were scaled to a thickness of 0.46 mm and then shifted down so that the minimum absorbance is at 0.1. (a) An IR spectrum of sample DC2Asp1 after experiment (solid curve) and one for an anhydrous dacitic glass (200 ppm H\(_2\)O\(_m\), dotted curve). The peak at \~5600 cm\(^{-1}\) is related to Fe in the sample. Both GG-fitting (dashed curve) and TT-fitting (thin solid lines) baselines are shown. (b) FTIR spectrum of sample DC2Bsp5 (solid curve), showing a change in the shape of the baseline.
LIU ET AL.: THE SPECIATION OF DISSOLVED H₂O IN DACITIC MELT

whereas two samples are 0.28 mm thick, one sample is 0.45 mm, and one is 0.49 mm. The median thickness, 0.46 mm, was used to normalize our samples. The normalization was conducted by dividing the spectra by the thickness of the sample and then multiplying by 0.46 mm. The spectrum was then shifted down so that the minimum absorbance of the spectrum is 0.1. The GG fitting procedure was conducted by fixing the positions of two Gaussian peaks and obtaining a least-squares fit in three data ranges: ~4000–4150 cm⁻¹, ~4700–4800 cm⁻¹, and ~5500–5800 cm⁻¹. Ohlhorst et al. (2001) suggested 5770 cm⁻¹ for the second peak. This difference in peak positions for both Gaussian peaks (5600 or 5650 cm⁻¹ for the first peak and 3937 or 3950 cm⁻¹ for the second peak). This difference in the peak position may be related to the difference in the shape of spectra between our samples and those of Ohlhorst et al. (2001). Compared with the spectrum in Ohlhorst et al. (2001), the shape of spectra of our samples have a more pronounced Fe peak (shown by the tilted baseline of the OH peak in Fig. 1a).

Another complexity is the change of baseline shapes for sample DC2Bsp5 after one heating step (Fig. 1b, this sample is not included in Table 2). For samples DC55a1 and DC55a2, the shape of the baseline changed upon further heating (these results are not shown in Table 2). Deviations in the shape of the Fe-related peaks indicate differences in the structure of the glass (at least in the neighborhood of Fe atoms) and/or changes in composition (by changing Fe²⁺/Fe³⁺). These changes may influence not only the baseline correction but also the absorption coefficients (note the strong compositional dependence of the absorption coefficients in Silver et al. 1990; Behrens et al. 1996; Ohlhorst et al. 2001). Hence we cannot use the calibration of Ohlhorst et al. (2001) for samples with changed baseline. To ensure consistency, sample DC2Bsp5 is excluded from quantitative modeling of the data.

With the above procedures, the precision (reproducibility, as judged from several analyses of the same sample) in measured IR band intensities is about 1% relative (or better) for both the TT and GG methods. However, the accuracy in obtaining species concentrations is probably significantly worse than the precision due to uncertainties in the calibration. Band intensity data are reported in Table 2 so that with future improvement of the calibration, species concentrations, and K values can be recalculated. Band intensity data with the GG method recalculated to the sample thickness. Due to uncertainty in fitting the spectra, we have included the original digital spectra in the online database for future use.

Species concentrations and equilibrium constants

From band intensity data of both fitting methods, the species concentrations are calculated and presented in Table 2. Of the two baseline fitting methods (GG and TT), Ohlhorst et al. (2001) recommend the GG method for speciation study because it models the baseline of spectrum more closely than the TT method. In the present study, speciation data are presented using both GG and TT fitting methods, but the speciation model based on the GG method is recommended. Species concentrations are presented for both methods in Table 2. The equilibrium constant K based on the TT method is always smaller than that based on the GG method, by 0.13 to 0.35 in terms of lnK (13 to 35% relative difference in terms of K).

Attainment and retention of equilibrium

Kinetic experiments have been carried out to ascertain that our experimental results reflect attainment of equilibrium. The TT method and the corresponding calibration from Ohlhorst et al. (2001) were used to obtain the species concentrations. The approach of Reaction 1 to equilibrium is shown by plotting the parameter,

\[ Q = \frac{X_{\text{OH}}}{X_{\text{H}_2\text{O}}X_{\text{O}}^2} \]

where \( X_i \) is the mole fraction of species \( i \) in melt on a single oxygen basis, with time (Zhang et al. 1995). A molecular weight of anhydrous dacite on a single oxygen basis of 33.82 g/mol is used for calculating \( X_i \). For an ideal solution, the above equation expresses the equilibrium constant, \( K \), when Reaction 1 reaches equilibrium. Figure 3a shows an experimental reversal:

1For a copy of the spectra spreadsheet, document item AM-03-061, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site at http://www.minsocam.org.
the equilibrium $K$ value is reached from both above and below. For this case with 1.5 wt% H$_2$O$_t$ at 519 °C, about 20 minutes are necessary to reach equilibrium. Reaction kinetics are faster in glasses with a higher water content. A sample with 2.5 wt% H$_2$O$_t$ at 480 °C only needs about 10 minutes to reach equilibrium (Fig. 3b). The designed experimental duration of the equilibrium experiments depends on the temperature and H$_2$O$_t$, and each run is estimated to be sufficient to reach equilibrium.

The experimental data shown in Figure 3 can also be used to estimate the quench effect. Because it took only about 2 s in air to cool a 0.9 mm thick sample to less than 350 °C (Xu and Zhang 2002), reaction during quench is negligible. Other samples were quenched in water with an even shorter cooling time scale. Hence at 480–590 °C, species concentrations can be quenched within 14 K. If the TT method is used, ln$K$ values are within 0.04 for the two H$_2$O$_t$ contents and ln$K$ = (1.49 ± 0.20) − (2634 ± 158)/$T$ (Fig. 2b). In this case, the standard state enthalpy is smaller (21.9 ± 1.31 kJ/mol).

Owing to uncertainties in the calibration, we recast our speciation data directly in terms of IR band intensities (Ihinger et al. 1999). For a given baseline fitting method, such a geothermometer will not be changed with future improvement of absorption coefficients. We define $K' = A'_{4520}^2/A'_{5230}$ as a proxy for the equilibrium constant, where $A'$ is the absorbance normalized by the thickness of the sample (in mm). Using the GG method, the ln$K'$ values of all samples (except for outliers discussed earlier) follow a single straight line:

$$\text{ln}K' = 3.54 - 3675/T.$$

The above equation reproduces experimental temperature to within 14 K. If the TT method is used, ln$K' = 1.98 - 2737/T$, which reproduces experimental temperature to within 7 K. However, we emphasize that this method can be applied only to dacitic glasses displaying a similar shape of the Fe-related bands as the glasses used in this study.

**DISCUSSION**

**Speciation in dacitic melt**

No previous research has investigated the equilibrium speciation in dacitic melt directly as a function of temperature. Ohlhorst et al. (2001) reported speciation data on hydrous dacitic glasses quenched from high temperatures (>1200 °C). The measured species concentrations in glass quenched from high temperature experiments reflect equilibrium at $T_{eq}$. Assuming equivalence between $T_{eq}$ and the glass transition temperature for dacitic melt (Dingwell and Webb 1990; Zhang et al. 1997a; Behrens and Nowak 2003), the equilibrium speciation data may be extracted and compared with our data. The $T_{eq}$ is inferred using log$\eta$ (at $T_{eq}$) = 11.45 − log$[\eta]$, where the viscosity (η) is in Pa s and $q$ is the quench rate in °C/s (Zhang et al. 2003). A slightly different equation, log$\eta$ (at $T_{eq}$) = 11.3 − log$[\eta]$ [after Scherer (1984)], was applied by Dingwell and Webb (1990) and Behrens and
Nowak (2003) to estimate apparent equilibrium temperatures for water speciation in silicic glasses. The $T_{eq}$ values calculated by both equations differ only by a few Kelvin, much less than the estimated total error of $T_{eq}$. A viscosity model for hydrous dacitic melt is not available. Thus, the viscosity of dacitic melt is estimated by averaging log $\eta$ values of hydrous andesitic melts (Richet et al. 1996) and rhyolitic melts (Zhang et al. 2003). Using a quench rate of 150 °C/s, the estimated $T_{eq}$ for dacitic samples from Ohlhorst et al. (2001) is between 531 and 646 °C. The difference (0.7 log unit) between the model of Richet et al. (1996) for Fe-free andesite and the viscosity datum for a hydrous Fe-bearing andesitic melt from Liebske et al. (2003) is taken as the uncertainty of the viscosity of andesitic melts. Considering a $2\sigma$ error of 0.36 for the viscosity model of rhyolitic melt (Zhang et al. 2003), the uncertainty in estimated viscosity of dacitic melt is about 0.4. Because the quench rate depends on sample size (Xu and Zhang 2002), the estimated quench rate may have an error of a factor of 2. Hence, these uncertainties translate to a $2\sigma$ uncertainty of 31 °C in the estimated $T_{eq}$ (0.04 in 1000/$T_{eq}$). These speciation data for quenched dacite using the apparent equilibrium temperature form a parallel line below our equilibrium data (Fig. 4). The data are not far off when the large uncertainty in calculated $T_{eq}$ is considered.

**Comparison with speciation data in other melts**

In addition to an extensive database of H$_2$O speciation in rhyolitic melts, speciation data have been reported on basaltic melts (Dixon et al. 1995; Ohlhorst et al. 2001) and andesitic glasses (Ohlhorst et al. 2000, 2001; Mandeville et al. 2002) by quenching from temperatures above 1000 °C. There are no reliable viscosity models for hydrous basalt, and $T_{eq}$ for quenched melt cannot be calculated from the quench rate. For hydrous andesite, using a quench rate of 100 °C/s for rapid quench and 2 °C/s for normal quench (Mandeville 2002 personal communication), the $T_{eq}$ values of samples from Mandeville et al. (2002) are 535–658 °C. Because Mandeville et al. (2002) used the TT method, results from TT method are included in the comparison (Fig. 5a).

The $\ln K$ values in hydrous dacitic melt are larger than those in hydrous rhyolitic melt by ~0.2 with the TT fitting method and by ~0.5 with the GG fitting method (Fig. 5). The increase of $\ln K$ from hydrous rhyolitic to dacitic melt indicates that a greater proportion of dissolved H$_2$O exists as OH in dacitic melts at the same temperature and H$_2$Ot content (Fig. 6). Data of andesitic melt from Ohlhorst et al. (2000) and Mandeville et al. (2002) are similar to those in dacitic samples (Fig. 5). With the TT fitting method, $\ln K$ values from Fe-free andesitic melt are greater than those in others by ~0.4 (Fig. 5a). More accurate speciation data on hydrous andesitic and basaltic melts are needed.

**Application to natural dacitic samples**

Equation 3 can be applied to infer the apparent equilibrium temperature. The apparent equilibrium temperature can be applied to infer cooling rate of natural dacitic glasses, or applied to investigate viscosity of hydrous dacitic melt (Zhang et al. 2003).

Natural dacitic glasses are found in submarine volcanoes in island arc environments. Newman and Van der Laan (1992)
reported an FTIR study of natural dacitic glasses from the Izu-Bonin forearc. Compared with our samples, these dacitic glasses contain a low K$_2$O content (0.59–0.74 wt%). This possible compositional effect is deemed small and ignored. We obtained the samples from Newman and reanalyzed them by FTIR. The shape of baselines of the spectra of both natural samples is different from our samples (Fig. 7a). After subtracting a straight line, each spectrum was roughly fit with the GG method (Fig. 7b). Both samples show low $T_{ae}$ values (340–360 ºC) (Fig. 8), implying extremely slow cooling rates (<0.003 °C/yr). This slow cooling rate is difficult to reconcile with the glassy nature of dacite. Hence, these samples most likely were hydrated after eruption, which preferentially added H$_2$Om into the glass (Newman and Van der Laan 1992). Because the shape of the baseline for the natural glass samples is different from that of our experimental samples (Fig. 7), the uncertainty in the estimated $T_{ae}$ is large and is estimated to be 50 K based on our experience on experiments with altered baseline shapes.

**Future improvement**

There is still considerable uncertainty in H$_2$O speciation in dacitic melt. To improve the understanding of hydrous species equilibrium in dacite, it is necessary to improve the calibration of molar absorptivities and their possible dependence on Fe$^{3+}$/Fe$^{2+}$ ratio. Given the dependence of the shape of the IR spectrum on the Fe absorption peaks, different calibrations may well be needed for different glasses. Alternatively, the spectrum may be fit by subtracting the spectrum of an anhydrous dacite from that of a hydrous one. The variation of Fe$^{2+}$ absorption peaks can be accounted for by preparing a series of anhydrous glasses at different conditions (temperature, pressure, oxygen fugacity).

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