Abstract. Dissolved H$_2$O in silicate melts and glasses plays a crucial role in volcanic eruptions on terrestrial planets and affects glass properties and magma evolution. In this paper, major progress on several aspects of the H$_2$O-melt (or glass) system is reviewed, consistency among a variety of data is investigated, discrepancies are evaluated, and confusion is clarified. On the infrared measurement of total H$_2$O and species concentrations, calibration for a variety of glasses has been carried out at room temperature. The measurements for H$_2$O in rhyolitic glasses have undergone the most scrutiny, resulting in the realization that absorptivities for the near-infrared bands depend on total H$_2$O content. Although the variation of the absorptivities does not seem to significantly affect the determination of total H$_2$O, it does affect the determination of molecular H$_2$O and OH species concentrations. Calibration of the infrared technique for H$_2$O in rhyolitic glasses still needs much improvement, especially at high total H$_2$O. Furthermore, it is now almost certain that the molar absorptivities also depend on the measurement temperature in situ studies. Hence it will be necessary to carry out calibrations in situ at high temperatures. On H$_2$O speciation, results from two experimental approaches, the quench technique and the in situ technique, are very different, leading to controversy in our understanding of true speciation. A solution is presented to reconcile this controversy. It is almost certain that the quench technique does not suffer from a quench problem, but interpretation of in situ results suffered from ignoring the dependence of the molar absorptivities on measurement temperature. Accurate calibration at high temperatures is necessary for the quantitative application of the in situ technique to H$_2$O speciation in silicate melts and glasses. On H$_2$O solubility in silicate melts, recent experimental work has significantly expanded the $T$–$P$ range of solubility measurements, and recent solubility models fill a gap for predicting solubility for a wide range of melt compositions. I present a solubility model for rhyolitic and quasirhyolitic melts over a wide range of $T$ and $P$ (500°–1350°C, 0–8 kbar) by incorporating the role of speciation. The solubility model is able to recover the experimental solubility data and has extrapolative value, although the partial molar volume of H$_2$O derived from the solubility model differs from that derived from density measurements. On H$_2$O diffusion, recent studies on H$_2$O diffusion in a quasi-rhyolitic melt at 800°–1200°C, 0.5–5 kbar, and up to 7% total H$_2$O not only provide important new diffusion data, but are also challenging earlier understanding of H$_2$O diffusion based on data in rhyolitic glasses at 400°–550°C, 1 bar, and 0.2–1.8% total H$_2$O. A comparison between the earlier model and recent data is made. The recent high-temperature diffusivities at total H$_2$O $\approx$ 2% can be predicted by the earlier model. However, at higher total H$_2$O, the earlier model fails. New work is under way to understand the diffusion mechanisms at high H$_2$O contents.

1. INTRODUCTION AND OVERVIEW

As the most abundant volatile component in terrestrial magmas, dissolved H$_2$O in magmas controls the eruptive power of magma on terrestrial planets [e.g., Wilson, 1980; Wilson et al., 1980; Kiéffer, 1995]. The exsolution of dissolved H$_2$O from magmas most likely provided surface water on the terrestrial planets and hydrothermal fluids for ore formation. Dissolved H$_2$O in glasses affects glass properties. Dissolved H$_2$O in silicate melt affects its properties and evolution, such as viscosity [e.g., Shaw, 1963, 1972; Burnham, 1967; Stolper, 1982a, b; Schulze et al., 1996; Hess and Dingwell, 1996], density [e.g., Ochs and Lange, 1997, 1999], diffusivity [e.g., Watson, 1979], liquidus and solidus temperatures [e.g., Wassergurg, 1957; Tuttle and Bowen, 1958; Kushiro, 1969; Luth, 1976; Wyllie, 1979], crystallization sequence [e.g., Hamilton et al., 1964; Wyllie, 1979; Moore and Carmichael, 1998], and crystal nucleation and growth [Fenn, 1977]. The special volume published by the Mineralogical Society of America [Carroll and Holloway, 1994] reviewed water (and other volatiles) in silicate melts and glass. Chapters included contributions by Ihinger et al. [1994], Burnham [1994], McMillan [1994], Johnson et al. [1994], Lange [1994], and Watson [1994]. Many papers have been published on the subject since then. Although much progress has been made, controversies and confusion are abundant. In this paper I critically review work
in the last 5 years on the dissolved H₂O component in rhyolitic melt/glass (a rhyolite is a fine-grained silicic igneous rock; see Table 1 for composition) and a quasi-rhyolitic composition (sample name AOQ; see Table 1), concentrating on clarification of controversies, assessment of data, and consistency of models.

1.1. H₂O Concentration and Speciation

H₂O content (hereinafter H₂O refers to total H₂O contents and H₂O refers to H₂O as a chemical component) in glasses can be determined by several techniques, including manometry, Karl-Fischer titration, infrared spectroscopy, and ion microprobe. H₂O content in natural silicate melts spans a large range. It is typically 0.2–0.4 wt % (hereinafter % refers to weight percent unless otherwise specified such as % relative, or mol %) in mid-ocean ridge basaltic glasses [e.g., Dixon et al., 1988] and 0.2–0.7% in Hawaiian basaltic glasses [e.g., Dixon et al., 1991]. Rhyolitic glasses in lava domes and flows often contain 0.08–0.8% H₂O, and those in pyroclastic deposits contain 0.6–3.0% H₂O [e.g., Newman et al., 1986; Zhang et al., 1991a, 1997a, b]. Glass inclusions in crystals may contain up to 7% H₂O [Anderson et al., 1989; Skirius et al., 1990; Qin, 1994; Johnson et al., 1994; Wallace et al., 1995; Zhang et al., 1997a]. Tektite glasses contain 0.01–0.1% H₂O [Gilchrist et al., 1969]. The H₂O content in primitive lunar glasses is often below detection limit (<50 ppm H₂O) [Fogel and Rutherford, 1995]. Although the H₂O contents of volcanic rocks on Venus and Mars are not known, occurrences of caldera-like structures suggest that the preeruptive H₂O contents in volcanic rocks may reach a few weight percent [e.g., Kieffer, 1995].

Infrared spectroscopy can be used to distinguish H₂O species in silicate glasses. A dissolved H₂O component is present in silicate melts and glasses in at least two species with distinct infrared bands [Scholze, 1960; Stolper, 1982a]: H₂O molecules (hereinafter referred to as H₂Oₘ) characterized by the near-infrared combination band at 5230 cm⁻¹ (wavelength 1.91 μm; cm⁻¹ is used for wavenumber unit, both to follow convention and to distinguish it from the thickness unit mm), and OH groups (OH means XOH, where X may be Si, Al, Na, etc., but not H) characterized by the combination band at 4520 cm⁻¹ (2.21 μm) (Figure 1). The 5230 cm⁻¹ band is a combination band due to HOH bending + OH basic stretching, and the 4520 cm⁻¹ band is due to XOH bending/stretching + OH basic stretching [Scholze, 1960; Stolper, 1982a]. Davis and Tomozawa [1996] provided a comprehensive discussion of band assignment in hydrous silica glass. The reaction of dissolved H₂Oₘ with the network to form OH groups not only increases the solubility of H₂O, but also modifies the silicate network and depolymerizes the melt, accounting for the large effect of dissolved H₂O on melt properties.

1.2. Definitions of H₂O Mole Fractions

There are three definitions of H₂O mole fractions often encountered in literature, which may be somewhat confusing to nonspecialists. They are summarized below:

1. In the present work, mole fractions on a single-oxygen basis are used, following the work of Stolper [1982b]. The calculation of the mole fractions of H₂O, H₂Oₘ, OH, and O for hydrous rhyolitic melts/glasses is as follows:

\[
[H₂Oₘ] = (C/18.015)/(C/18.015 + (1 - C)/W),
\]

\[
[H₂O] = [H₂Oₘ][H₂Oₘ]/(H₂Oₘ),
\]

\[
[OH] = 2([H₂O] - [H₂Oₘ]),
\]

\[
[O] = 1 - [H₂Oₘ] - [OH],
\]

where parentheses indicate mass fraction, C is the mass fraction of H₂Oₘ, and W is the mass of dry rhyolite (Table 1) per mole of oxygen and is 32.49 g/mol. For AOQ (a quasi-rhyolitic glass; Table 1) composition, W = 32.6 g/mol. For albite (NaAlSi₃O₈), W = 32.778 g/mol.

2. In the H₂O-NaAlSi₃O₈ system, Burnham [1975] and other authors following him treated NaAlSi₃O₈ as one unit (whereas the definition on a single oxygen basis treats NaAlSi₃O₈ as eight units). In this definition,
$X_{H_2O_t} = \left(\frac{C}{18.015}\right) / \left\{\frac{C}{18.015} + (1 - C)/262.22\right\}$, where 262.22 is the molar mass of NaAlSi$_3$O$_8$.

3. Some authors [e.g., Moore et al., 1998] defined the H$_2$O oxide mole fraction by treating each oxide (e.g., SiO$_2$) as one unit (whereas the definition on a single-oxygen basis treats SiO$_2$ as two units and treats Al$_2$O$_3$ as three units). In this definition, $X_{H_2O_t} = \left(\frac{C}{18.015}\right) / \Sigma \left(\frac{C_i}{W_i}\right)$, where $C_i$ is the mass fraction of the oxide component $i$ (including H$_2$O) and $W_i$ is the molar mass of the oxide.

The above three different definitions result in very different mole fractions. For example, 5.0 wt % H$_2$O in albite melt translates into an H$_2$O$_t$ mole fraction of 0.0874 on a single-oxygen basis, to 0.161 using oxide moles, and to 0.434 using NaAlSi$_3$O$_8$ as one unit.

The definition of mass fraction (or weight percent) of OH may also cause confusion. It does not mean the actual mass fraction of OH per se, but rather the mass fraction of extracted H$_2$O that was present in the glass as OH (or in the form of OH). That is, it is the mass fraction of the species 2OH − O (two OH groups minus one oxygen). In this way, in terms of mass fraction or weight percent, $[H_2O_t] = [H_2O_m] + [OH]$. The definition of mole fraction of OH, however, is the mole fraction of OH per se, not the mole fraction of 2OH − O. In terms of mole fraction, $[H_2O_t] = [H_2O_m] + [OH]/2$.

1.3. Reactions of H$_2$O With Melt, Equilibrium, and Kinetics

For an understanding of H$_2$O solubility in and interaction with a silicate melt, the equilibrium of two reactions needs to be considered. The first is the heterogeneous reaction between the melt and vapor phases:

\[(R1)\quad H_2O (vapor) \Leftrightarrow H_2O_m (melt).\]

The equilibrium constant of the above reaction is

$$K_1 = \frac{[H_2O_m]}{[H_2O]},$$

where the brackets refer to mole fraction in the melt/glass phase on a single-oxygen basis. Since mole fraction instead of activity is used in the above equation, $K_1$ is not an equilibrium constant in the strict sense and may depend on H$_2$O$_t$. However, activities are difficult to determine. Zhang et al. [1997a] have found that dissolved H$_2$O$_m$ and OH behave roughly ideally at least up to 2.4% H$_2$O$_t$ based on species equilibrium data. Hence the mole fraction of H$_2$O$_m$, which is also the activity of the H$_2$O component in silicate melt, $K_1$ is hence used as the proxy for the equilibrium constant.

The second reaction is the homogeneous reaction in the silicate melt/glass phase for species interconversion:

\[(R2)\quad H_2O_m (melt) + O (melt) \Leftrightarrow 2OH (melt),\]

where O is an anhydrous oxygen. The equilibrium constant of the above reaction is

$$K_2 = \frac{[OH]^2}{[H_2O_m][O]}.$$  

Similar to $K_1$, $K_2$ is not an equilibrium constant in the strict sense but is used as a proxy. Note that (R2) implies that OH is the dominant species at low H$_2$O$_t$ and that the importance of H$_2$O$_m$ gradually increases with increasing H$_2$O$_t$ (Figure 2). This can be clearly shown from infrared spectra: The 5230 cm$^{-1}$ band is often not detectable when H$_2$O$_t$ is less than 0.2% and becomes more prominent with increasing H$_2$O$_t$ (Figure 1). The exact H$_2$O$_t$ concentration at which H$_2$O$_m$ becomes the dominant species depends on $K_2$ (Figure 2). The species equilibrium has been investigated experimentally both by the in situ method and by the study of quenched
The equilibrium constant \( K_2 \) increases with temperature [Ihinger, 1991; Zhang et al., 1991a, 1995, 1997a; Nowak and Behrens, 1995; Shen and Keppler, 1995]. Understanding the speciation reaction is critical to the understanding of many phenomena about dissolved \( \text{H}_2\text{O} \) in silicate melts and glasses. \( \text{H}_2\text{O} \) solubility in silicate melts and \( \text{H}_2\text{O} \) vapor [Newman et al., 1988; Dobson et al., 1989; Ihinger, 1991]. The data are consistent with a small D/H fractionation between dissolved \( \text{H}_2\text{O}_m \) in rhyolitic melt and \( \text{H}_2\text{O} \) in vapor and a large D/H fractionation between dissolved \( \text{OH} \) and \( \text{H}_2\text{O} \) in vapor. The speciation of \( \text{H}_2\text{O} \) also affects the thermodynamics of hydrous silicate liquids. In principle, speciation is also expected to affect viscosity and density.

The kinetics of the interconversion reaction between the species can be used as a geospeedometer [Zhang et al., 1995, 1997b]. Because a natural or experimental hydrous glass underwent continuous cooling (or even a more complex thermal history), and because the reaction rate constant for (R2) decreases with decreasing temperature, the final \( \text{H}_2\text{O}_m \) and \( \text{OH} \) concentrations for a given reaction in the glass at room temperature reflect the continuous reaction during the cooling history and were not established when the reaction reached equilibrium at a specific temperature. Hence the symbol \( Q \) (quotient) is sometimes used to refer to the final speciation, where \( Q = \frac{[\text{OH}]}{[\text{H}_2\text{O}_m]} \) (the difference between \( Q \) and \( K_2 \) is that \( K_2 \) is the expression at equilibrium). A hypothetical equilibrium temperature can nonetheless be calculated from \( Q \), which is referred to as the apparent equilibrium temperature \( T_{ae} \) [Zhang, 1994]. For example, if a hydrous magma is cooled continuously from 850°C to a glass at room temperature, the \( \text{H}_2\text{O}_m \) and \( \text{OH} \) species concentrations may record a \( T_{ae} \) of 500°C. For a fixed \( \text{H}_2\text{O}_m \), slower cooling leads to smaller \( Q \) and lower \( T_{ae} \). Such relations can be used to infer cooling rates and the cooling environment: High cooling rates often indicate quench in water or air, and low cooling rates indicate cooling in the volcanic conduit, in a lava flow, or in a buried layer of pyroclastic deposits.

### 1.4. Outline of This Paper

In the following sections I review the large amount of information on recent progress on \( \text{H}_2\text{O} \) in rhyolitic and quasi-rhyolitic melt and glass (Table 1). I concentrate on \( \text{H}_2\text{O} \) in rhyolitic and quasi-rhyolitic glasses and melts because this system is best studied in many aspects. In section 2 I review the infrared measurement of dissolved \( \text{H}_2\text{O} \) and species concentrations in rhyolitic glasses at room temperatures. In section 3 I review the equilibrium speciation and the in situ versus quenched speciation controversy and how the controversy can be reconciled. In section 4 I review the \( \text{H}_2\text{O} \) solubility data and models and present a new solubility model applicable to 0–8000 bars and 500°C–1350°C. In section 5 I review \( \text{H}_2\text{O} \) diffusion, with a critical assessment of low versus high \( \text{H}_2\text{O} \) and low versus high \( T \) diffusion data. A simple expression for calculation of diffusivity of \( \text{H}_2\text{O} \) component is also presented. The review will clarify some confusion in literature and point to new directions for future research.
2. MEASUREMENT OF DISSOLVED H₂O IN RHYOLITIC GLASSES AT ROOM TEMPERATURE

All the advances in our understanding of the role of H₂O in silicate liquids and glasses require accurate measurement of H₂O and/or species concentrations of H₂Om and OH. Analytical methods for H₂O and species concentrations have been summarized by Ihinger et al. [1994]. There are two types of measurement techniques. In one type of technique, including manometry [e.g., Newman et al., 1986] and Karl-Fischer titration [e.g., De Jong et al., 1987; Behrens, 1995], dissolved H₂O is extracted from the solid material and then measured by either mass spectrometry or titration. The second technique is nondestructive microbeam techniques, including vibrational spectroscopy in the infrared (IR) and near-infrared (NIR) regions, ion microprobe (SIMS), nuclear magnetic resonance spectroscopy (NMR), nuclear reaction analysis (NRA), and Raman scattering spectroscopy [Mysen and Virgo, 1986a, b; McMillan et al., 1993; Holz et al., 1996]. In these techniques the dissolved H₂O component is not extracted (hence the sample is not destroyed) but is measured at spots (small areas) in the sample.

The different techniques are complementary, and each is useful in some aspects. The bulk extraction method determines the absolute amount of H₂O and are often used to calibrate other (spectroscopic) techniques. However, the bulk extraction methods are time-consuming, destructive to the sample, unable to measure species concentrations, and unable to measure H₂O precisely below 0.2%. The NRA technique does not require calibration and is not destructive and is therefore very useful in calibrating other techniques. However, its precision is not very high (±5% relative [Endisch et al., 1994]), and it cannot provide species information. Other microbeam techniques require calibration. The SIMS technique can analyze small spots and D/H ratios. In depth profiling, the SIMS technique has extremely high spatial resolution (≈0.01 μm). However, it cannot determine species concentrations and is not as sensitive as the IR technique at low H₂O [Ihinger et al., 1994]. The NMR technique has been used mostly to understand solubility mechanisms [Farnan et al., 1987; Kohn et al., 1989], but it has not been explored as a quantitative analytical tool. Even though Raman spectroscopy has the potential of determining the H₂Om and OH species concentrations, it has not been calibrated, and its calibration is more difficult than that for the IR technique because of problems in determining cross sections.

Infrared (IR, including near-infrared, NIR) spectroscopy provides a rapid, nondestructive microbeam technique for quantitative analysis of H₂O and species concentrations with high precision and sensitivity. The more recent IR studies all use Fourier transform infrared spectroscopy (FTIR). At present, IR spectroscopy is the only method that is capable of precisely determining H₂O at low concentrations and determining the H₂Om and OH species concentrations. In quantitative H₂Om and OH determinations, the two near-infrared bands at 4520 and 5230 cm⁻¹ are most often used because the band intensities for typical geological samples are neither too large nor too small. For example, although the 3550 cm⁻¹ band characterizes total H₂O, and is often used to investigate H₂O at low H₂O (e.g., in minerals), the band intensity is usually too strong for quantitative investigation of H₂O in hydrous rhyolitic glasses with 0.1–7% H₂O. The absorbance would be too high (that is, too few photons at ~3550 cm⁻¹ would reach the detector) unless H₂O is low or the sample thickness is made very thin (e.g., for a rhyolitic glass containing 5% H₂O, for the absorbance of the 3550 cm⁻¹ band to be less than 2, the thickness must be <40 μm). Thin samples are easy to break, have larger thickness measurement errors, and are more prone to interference fringes.

On the other hand, the 7100 cm⁻¹ band is typically too weak except for very thick samples or samples with very high H₂O. The discussion below concerns calibration for measurement at room temperature. In situ measurement at high temperature will be discussed in the next section since no calibration has been published yet.

The IR measurements provide only vibrational band intensities in the IR region. Converting IR band intensities into species concentrations is based on Beer’s law:

\[ C = \frac{wA}{\varepsilon d} \]

where \( w \) is the molar mass of the component or species; \( A = \log (I_0/I) \), with \( I_0 \) being the radiation transmitted without the species being measured and \( I \) being the radiation transmitted with the species present) is the absorbance; \( \varepsilon \) is the molar absorptivity; \( d \) is the thickness of the sample; and \( \rho \) is the density. Absorbance can be either in terms of the height of a peak or in terms of the total area under a peak. The molar absorptivity must be obtained through calibration because of the absence of a good theoretical understanding of the band intensities in glasses.

Because there are two H₂O species, the H₂O concentration can be expressed as [Stolper, 1982a; Newman et al., 1986]

\[ C = C_1 + C_2 = \frac{18.015A_{523}}{\rho \varepsilon_{523}} + \frac{18.015A_{452}}{\rho \varepsilon_{452}} \]

where \( C, C_1 \), and \( C_2 \) are mass fractions of H₂O, H₂Om, and OH, respectively, expressed as H₂O; \( A = A/d \); \( A_{523} \) and \( A_{452} \) are absorbances of the 5230 and 4520 cm⁻¹ bands per millimeter sample thickness; \( \rho \) is the density and depends on H₂O (about 2340 g/L for a typical dry rhyolitic glass); and \( \varepsilon_{523} \) and \( \varepsilon_{452} \) are the molar absorptivities for the 5230 and 4520 cm⁻¹ bands in L mol⁻¹ mm⁻¹ and depend on, among others, the anhydrous composition and how the baseline is fit (Figure 1) [Behrens et al., 1998]. With the estimation of peak height or...
peak area ($A_{523}$ and $A_{452}$) from infrared spectra the determination of $\varepsilon_{523}$ and $\varepsilon_{452}$ (i.e., calibration) is carried out by determining $C$ using an independent absolute method. The calibration is complicated because all absolute methods only determine $\text{H}_2\text{O}_i$, not $\text{H}_2\text{O}_m$ and OH. Other bands (including the 1630, 3550, and 7100 cm$^{-1}$ bands) can be calibrated similarly [Newman et al., 1986].

Fitting the baseline for the infrared spectra (Figure 1) is not trivial. Three bands (the broad band at 3550 cm$^{-1}$ and the 3900 and 4520 cm$^{-1}$ bands) are convoluted at 4200 cm$^{-1}$, elevating the base on the right-hand side of the 4520 cm$^{-1}$ band (Figure 1). The elevation at the 4200 cm$^{-1}$ region is more pronounced as $\text{H}_2\text{O}_i$ and/or measurement temperature increase. Owing to the elevation, there is still no objective way to obtain the true baseline. Two types of baselines (flexicurve and linear baselines) have been used in the literature (Figure 1). A third type of baseline is to use one tangential straight line for each peak and hence two straight lines (instead of a single straight line as shown in Figure 1) for two peaks. None of the baseline fits is entirely satisfactory in determining the true baseline and the true peak height (or peak area) of the 4520 cm$^{-1}$ band. The difficulty in determining the true peak height may contribute to some of the variability of the molar absorptivities discussed below.

2.1. Calibrations by Assuming Constant Molar Absorptivities, and Problems

Stolper [1982a] calibrated the IR technique for natural and synthetic aluminosilicate glasses but noted the potential error in the “known” $\text{H}_2\text{O}_i$ concentration values for his standard samples. Newman et al. [1986] recalibrated the IR technique by linear regression using a suite of rhyolitic glasses with $\pm 2.6\%$ $\text{H}_2\text{O}_i$ that were analyzed by manometry and IR, resulting in the widely used molar absorptivities $\varepsilon_{523} = 0.161$ and $\varepsilon_{452} = 0.173$ L mol$^{-1}$ mm$^{-1}$. Ihinger et al. [1994] reported a revised set of molar absorptivities ($\varepsilon_{523} = 0.186$ and $\varepsilon_{452} = 0.150$ L mol$^{-1}$ mm$^{-1}$) using additional manometry data at high $\text{H}_2\text{O}_i$ to improve the accuracy at high $\text{H}_2\text{O}_i$. In all of these calibrations each molar absorptivity value for a given anhydrous composition was assumed to be constant, independent of $\text{H}_2\text{O}_i$ and band intensities.

Possible problems with the calibrations of Newman et al. [1986] and Ihinger et al. [1994] were indicated by heating experiments. Because the equilibrium constant $K_2$ depends on temperature, the $\text{H}_2\text{O}_m$ and OH concentrations (and hence the band intensities) for a given $\text{H}_2\text{O}_i$ vary with the equilibrium temperature [e.g., Zhang et al., 1991a, 1997a] (Figure 3) and hence thermal history. (When some heating steps did not reach equilibrium, the apparent equilibrium temperature could be used as a proxy for the equilibrium temperature.) One basic requirement for an accurate calibration is that calculated $\text{H}_2\text{O}_i$ using the calibration should be constant for a piece of glass before and after heating if no $\text{H}_2\text{O}$ is lost or gained. Skirius et al. [1990], Zhang et al. [1991a], and Qin [1994] noted that by using the calibration of Newman et al. [1986], the same samples may have either greater or smaller calculated $\text{H}_2\text{O}_i$ after heating than before heating. These problems can be attributed to the inaccuracy of the calibration. Using data from kinetic experiments, Zhang et al. [1995] examined the molar absorptivity ratio ($\varepsilon_{523}/\varepsilon_{452}$) by rewriting (4) as

$$A_{523} = \frac{\rho C}{18.015} \varepsilon_{523} - \varepsilon_{523} A_{452} \varepsilon_{452}.$$  \hspace{1cm} (5)

Equation (5) suggests that by plotting $A_{523}$ versus $A_{452}$ for a single sample with fixed $C$ (and hence $\rho$) but heated to different $T$, the molar absorptivity ratio can be obtained from the slope. Zhang et al. [1995] heated the same piece of rhyolitic glass to different $T_{ae}$ so that $A_{523}$

Figure 3. (a) The intensity variations of the 4520 and 5230 cm$^{-1}$ bands upon heating. The horizontal axis is the apparent equilibrium temperature. The rhyolitic glass was heated to variable temperatures and quenched to room temperature for infrared measurement. (b) Calculated $\text{H}_2\text{O}_i$ using two calibrations. The calibration of Newman et al. [1986] does not return a constant $\text{H}_2\text{O}_i$, whereas that of Zhang et al. [1997a] returns roughly constant $\text{H}_2\text{O}_i$, satisfying a necessary condition for an accurate calibration. Figure 3b is from Zhang et al. [1997a]. Reprinted with permission from Elsevier Science.
and $\bar{A}_{452}$ vary at constant $\rho C$ (layers affected by significant diffusive loss of H$_2$O were polished away before IR analyses). They found that good straight lines were obtained in $A_{523}$ versus $A_{452}$ for a given sample with different thermal history and that $\varepsilon_{523}/\varepsilon_{452} \approx 1.6 \pm 0.3$, different from the ratio of 0.93 ($= 0.161/0.173$) of the calibration of Newman et al. [1986]. Hence the relative error in the calibration of Newman et al. [1986] for species concentrations is large.

### 2.2. Calibrations by Accounting for Variations of Molar Absorptivities

Zhang et al. [1997a] carried out a new calibration of the molar absorptivities by combining infrared/manometry measurements and a new FTIR study of hydrous rhyolitic glasses heated at different temperatures. Their heating experiments for constant H$_2$O$_m$ show that (1) $A_{523}$ versus $A_{452}$ for the same glass wafer with the same H$_2$O$_m$ but heated to different temperature is roughly a straight line, the slope of which gives the $\varepsilon_{523}/\varepsilon_{452}$ ratio for the sample; (2) the ratio $\varepsilon_{523}/\varepsilon_{452}$ varies with H$_2$O$_m$; and (3) the calculated H$_2$O$_m$ using the calibration of Newman et al. [1986] for a glass with the same H$_2$O is not constant but depends on $T_{\text{ce}}$ (Figure 3b). Therefore the earlier assumption of constant molar absorptivities is inaccurate. The accurate calibration must incorporate the variation of $\varepsilon_{523}$ and/or $\varepsilon_{452}$ with H$_2$O$_m$.

The variation of $\varepsilon_{523}$ and/or $\varepsilon_{452}$ could be explained in several ways. (1) Since $\varepsilon_{523}$ and $\varepsilon_{452}$ are expected to be constant only when H$_2$O$_m$ and OH concentrations are dilute, the interaction among the H-bearing clusters at high concentrations may cause the variation. (2) There may be several subspecies of OH (or H$_2$O$m$), such as Si-OH and AIOH or Q$_3$-OH and Q$_2$-(OH)$_2$. (Farman et al., 1987; Zotov and Keppler, 1998), whose concentrations depend on H$_2$O$_m$ and $T_{\text{ce}}$. The subspecies may have different molar absorptivities. The variation of their concentration ratios can lead to variable $\varepsilon_{523}$ and $\varepsilon_{452}$. (3) The inaccuracy in determining the true peak height may contribute to part of the variation of $\varepsilon_{452}$. Whatever the reasons, the variation of $\varepsilon_{523}$ and/or $\varepsilon_{452}$ needs to be accounted for empirically. Because the functional dependence of $\varepsilon_{523}$ and $\varepsilon_{452}$ on species concentrations is not known from first principles, the choice of the functional form introduces arbitrariness into the calibration and may cause difficulty in extrapolation. For simplicity, Zhang et al. [1997a] defined

$$\delta_{523} = 18.015 \rho \varepsilon_{523}, \quad \delta_{452} = 18.015 \rho \varepsilon_{452}, \quad (6)$$

so that (4) can be linearized to the following form:

$$\frac{\rho}{\rho_0} C = \delta_{523} A_{523} + \delta_{452} A_{452}, \quad (7)$$

where $\rho_0$ is the density of the anhydrous rhyolitic glass and $\rho$ is the density of the hydrous glass (a function of $C$) and $\rho/\rho_0 \approx 1 - C$. Then they assumed that each of $\delta_{523}$ and $\delta_{452}$ depends on both $A_{523}$ and $A_{452}$, where $A_{523}$ and $A_{452}$ are used as proxies for H$_2$O$_m$ and OH. That is,

$$\delta_{523} = a_0 + a_1 A_{523} + a_2 A_{452}, \quad (8a)$$

$$\delta_{452} = b_0 + b_1 A_{523} + b_2 A_{452}, \quad (8b)$$

where $a_0, a_1, a_2, b_0, b_1,$ and $b_2$ are fitting parameters. Preliminary fitting results show that $a_1$ and $a_2$ are close to zero. Hence they assumed that $a_1$ and $a_2$ are zero and refit the data to obtain the parameters (Table 2). Therefore the final expressions for calculating $C$ (mass fraction of H$_2$O$_m$), $C_1$ (H$_2$O$_m$), and $C_2$ (mass fraction of H$_2$O present as OH) are

$$C(1 - C) = a_0 A_{523} + (b_0 + b_1 A_{523} + b_2 A_{452}) A_{452}, \quad (9a)$$

$$C_1 = a_1 A_{523} / (1 - C), \quad (9b)$$

$$C_2 = (b_0 + b_1 A_{523} + b_2 A_{452}) A_{452} / (1 - C). \quad (9c)$$

From an IR spectrum the right-hand side of (9a) can be calculated, and hence $C$ can be solved from the quadratic equation. $C_1$ and $C_2$ can then be obtained from (9b) and (9c).

### 2.3. Discussion

Comparison of the calibration of Zhang et al. [1997a] with that of Newman et al. [1986] shows that the calibration of Newman et al. [1986] is still good in retrieving H$_2$O$_m$ within 5% relative precision, but not species concentrations. As shown in Figure 3, the calibration of Zhang et al. [1997a] has a high internal reproducibility in calculating H$_2$O$_m$ for a sample heated to different temperatures (Figure 3) with a precision of about 0.7% relative, about a factor of 6 better (smaller) than that of Newman et al. [1986]. Owing to the input data range and the arbitrary choice of the functional dependence of molar absorptivities on band intensities, Zhang et al. [1997a] concluded that their calibration is most accurate for H$_2$O$_m$ and species concentrations at $\leq 2.7\%$ H$_2$O$_m$.

One important contribution of this new calibration is to reveal that $K_2$ is independent of H$_2$O$_m$ at least up to 2.4% H$_2$O$_m$. This is contrary to the H$_2$O$_m$ dependence of $K_2$ (modeled using a regular solution model [Zhang et al. [1997a]]).
The work of Zhang et al. [1997a] is not the last word on the calibration of the IR measurement of H$_2$O in rhyolitic glasses. In terms of species concentrations their calibration may not be very accurate at H$_2$O$_i$ > 2.7%. Despite improvement in reproducibility, the accuracy in H$_2$O$_i$ of their calibration is not significantly better than that of Newman et al. [1986], owing to uncertainties in manometry data. Recent work (Y. Zhang and H. Behrens, H$_2$O diffusion in silicate glasses and melts, submitted to Chemical Geology, 1999; hereinafter referred to as submitted manuscript, 1999) indicates that at H$_2$O$_i$ > 5.5%, the accuracy of the calibration of Zhang et al. [1997a] deteriorates rapidly, implying that the complicated formulation in (9) cannot be extrapolated. For example, calculated H$_2$O$_i$ for a sample that contains 7.6% H$_2$O$_i$ (by Karl-Fischer titration) is only 6.6% using Zhang et al. [1997a], 7.5% using Newman et al. [1986], and 6.9% using Ihinger et al. [1994]. Note that the calibration of Newman et al. [1986], although using samples containing only ≤2.3% H$_2$O$_i$, agrees best with the Karl-Fischer-titrated result at very high H$_2$O$_i$. Since Ihinger et al. [1994] used higher H$_2$O$_i$ samples for calibration and assumed ε$_{523}$ and ε$_{452}$, the discrepancy between the calibration of Ihinger et al. [1994] and Karl-Fischer titration may mean a discrepancy between the manometry method and Karl-Fischer titration for obtaining bulk H$_2$O$_i$.

At low H$_2$O$_i$ (<0.2%) the 5230 and 4520 cm$^{-1}$ band intensities are weak. For example, for a sample containing 0.1% H$_2$O$_i$ and with a thickness of 1 mm, the absorbance of the 4520 cm$^{-1}$ band is ~0.024 absorbance unit and that of the 5230 cm$^{-1}$ band is typically too small to resolve. Hence it is best to use the 3550 cm$^{-1}$ band for determination of low H$_2$O$_i$. Newman et al. [1986], Dobson et al. [1989], and Ihinger et al. [1994] reported calibration of this band. However, the discrepancy is still large owing to the uncertainty in measuring H$_2$O$_i$ by manometry at such low H$_2$O$_i$. For example, Baghdassarov et al. [1996] applied two different calibrations to obtain H$_2$O$_i$ with a range of 0.12–0.16%.

In conclusion, much improvement in the calibration is still necessary for both high and low H$_2$O$_i$. It is also necessary to carry out an interlaboratory comparison of manometry and Karl-Fischer titration measurements. Some workers may think that we have reached a point of diminished returns. However, in my opinion, improving the calibration remains one of the high priorities in future work on water in silicate melts and glasses, because reliable calibration is a prerequisite for studies on H$_2$O speciation (such as how $K_2$ depends on H$_2$O$_i$), solubility, and diffusion.

### 2.4. Calibrations of the IR Technique for H$_2$O in Other Glasses

The infrared measurement of H$_2$O$_i$ and species concentrations in other silicate glasses has also been calibrated [Dixon et al., 1988, 1995; Silver and Stolper, 1989; Silver et al., 1990; Pandya et al., 1992; Danyushevsky et al., 1993; Behrens, 1995; Behrens et al., 1996; Nowak and Behrens, 1997]. Published linear molar absorptivities and densities required for the calculation of species and H$_2$O$_i$ concentrations using (4) (or a similar equation for other IR bands) for other glasses are listed in Table 3. All these other calibrations assumed H$_2$O$_i$-independent molar absorptivities, and none of them has been subjected to the same kind of scrutiny as the calibration for rhyolitic glasses. Therefore they may have potential problems similar to those of the calibration of Newman et al. [1986], although this has not been demonstrated yet. Some calibrations are based on a curve fit to the baseline using a flexicurve (solid curves in Figure 1), and some are based on a straight-line fit to the baseline (dashed lines in Figure 1). For self-consistency the baseline fitting procedure must follow that used in the calibration for calculation of H$_2$O$_i$, H$_2$O$_{m}$, and OH concentrations. Note that density determination is for glasses prepared and quenched at high pressures, and hence the densities are somewhat greater than those at 1-bar pressures.

### 3. EQUILIBRIUM SPECIATION OF H$_2$O IN SILICATE GLASSES AND MELTS

Understanding the equilibrium speciation of H$_2$O in silicate glasses and melts is critical to modeling the thermodynamic properties of silicate melts, understanding solubility, diffusion, and H isotopic fractionation, inferring apparent equilibrium temperature of a glass, and setting the stage for kinetic studies. There are two experimental approaches for studying the equilibrium speciation of H$_2$O as a function of temperature (and pressure) and H$_2$O$_i$ content. One method is to hold the silicate glass at high temperature to reach equilibrium and then rapidly quench it to room temperature [Silver and Stolper, 1989; Silver et al., 1990; Stolper, 1989; Ihinger, 1991; Zhang et al., 1991a, 1995, 1997a]. The species concentrations in the quenched glass are then measured at room temperature by IR. This approach will be referred to as the quench technique hereinafter. The other method of characterizing high-temperature speciation is the in situ method, in which the species concentrations are measured in situ as the sample is held at high temperature and pressure [Nowak and Behrens, 1995; Shen and Keppler, 1995]. The disagreements between earlier and more recent speciation data using the quench technique [Silver and Stolper, 1989; Silver et al., 1990; Stolper, 1989; Ihinger, 1991; Zhang et al., 1991a, 1997a, b; Ihinger et al., 1999], the changes in calibration, and the disagreement between data using the quench and the in situ techniques [e.g., Zhang et al., 1991a, 1995, 1997a, b; Nowak and Behrens, 1995; Shen and Keppler, 1995] have caused much confusion in understanding the true speciation in silicate glasses and melts. Different


### Experimental Data Obtained From the Quench Technique

The quench technique used in the earlier IR studies [Silver and Stolper, 1989; Silver et al., 1990] should be clearly distinguished from that used in more recent studies [Ihinger, 1991; Zhang et al., 1991a, 1995, 1997a, b; Ihinger et al., 1999]. Reaction (R2) is a homogeneous reaction and does not require mass transfer over micrometer distance. Hence the reaction can continue and can significantly alter the speciation even in the short timescale of quenching. If the species concentrations vary significantly during a quench, measured concentrations do not represent those at the experimental temperature, a problem typically referred to as the quench problem. Silver and Stolper [1989] and Silver et al. [1990] carried out extensive experimental work on the equilibrium of (R2). They held natural rhyolitic and other silicic samples at 800°–1400°C and quenched the samples to room temperature for infrared analyses. All workers in this field, including the authors of these studies [Silver and Stolper, 1989; Silver et al., 1990], now agree that these data suffered from a significant quench problem, as first pointed out by Dingwell and Webb [1990] on the basis of glass relaxation theory and later demonstrated by Zhang et al. [1995] using experimental data on the kinetics of the reaction. The quench problem arises because reaction rates at ≥700°C are extremely high and reaction continues during quench. Although most data of Stolper [1989] using the quench technique were at T ≤ 600°C and were hence not affected by this quenching problem, Stolper used other quench data from 600°C in formulating an expression for X2. The numeric models for the dependence of X2 on H2O on T and X [Silver and Stolper, 1989; Stolper, 1989; Silver et al., 1990] are invalid because of the use of the data with significant quench problems. These data and models are excluded from the following discussion.

Experimental data using the rapid quench technique discussed below are obtained at relatively low experi-

---

### Table 3: Linear Molar Extinction Coefficients for H2O Species in Glasses

<table>
<thead>
<tr>
<th>Species</th>
<th>1.91 μm, 5230 cm⁻¹</th>
<th>2.21 μm, 4520 cm⁻¹</th>
<th>2.82 μm, 3550 cm⁻¹</th>
<th>6.13 μm, 1630 cm⁻¹</th>
<th>H2O Range, wt %</th>
<th>Density, g L⁻¹</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhyolite see text</td>
<td>0.161</td>
<td>0.173</td>
<td>5.5 ± 0.2</td>
<td>0.1–5.3%</td>
<td>not needed</td>
<td>2350/(1 + 0.31X)</td>
<td>1</td>
</tr>
<tr>
<td>Rhyolite</td>
<td>8.8 ± 0.2</td>
<td>0–0.4%</td>
<td>2350/(1 + 0.31X)</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rhyolite</td>
<td>8.0 ± 0.4</td>
<td>0–0.4%</td>
<td>2350/(1 + 0.31X)</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basalt</td>
<td>0.062</td>
<td>0.067</td>
<td>6.3</td>
<td>2.5</td>
<td>0.1–5.3%</td>
<td>2363/(1–0.61)</td>
<td>5, 6</td>
</tr>
<tr>
<td>Basalt</td>
<td>6.1</td>
<td>1.6</td>
<td>measured</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basalt</td>
<td>6.06</td>
<td>measured</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basanite</td>
<td>0.056</td>
<td>0.058</td>
<td>7.0 ± 0.2</td>
<td>0.1–5.3%</td>
<td>measured</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>NaAlSi2O6(Ab)</td>
<td>0.113</td>
<td>0.112</td>
<td>1.2–10.2%</td>
<td>2384/(1–0.58)</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaAlSi2O6</td>
<td>0.149</td>
<td>0.128</td>
<td>1.6–5.3%</td>
<td>2395/(1–0.67)</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAlSi3O8(Or)</td>
<td>0.165</td>
<td>0.158</td>
<td>2.2–13.3%</td>
<td>2382/(1–0.84)</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiAlSi3O8</td>
<td>0.112</td>
<td>0.133</td>
<td>0.9–7.4%</td>
<td>2373/(1–0.48)</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaAlSi3O8(Ab)</td>
<td>0.147</td>
<td>0.126</td>
<td>2.4–7.3%</td>
<td>2389/(1–0.59)</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAlSi3O8(Or)</td>
<td>0.187</td>
<td>0.143</td>
<td>1.7–6.9%</td>
<td>2386/(1–0.62)</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaAl2Si2O8</td>
<td>0.150</td>
<td>0.120</td>
<td>1.0–8.7%</td>
<td>2363/(1–0.61)</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AOQ</td>
<td>0.179</td>
<td>0.156</td>
<td>1.0–8.7%</td>
<td>2363/(1–0.61)</td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaAlSi2O6(Ab)</td>
<td>0.149</td>
<td>0.128</td>
<td>1.2–10.2%</td>
<td>2384/(1–0.58)</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ab900Or10</td>
<td>0.147</td>
<td>0.126</td>
<td>2.4–7.3%</td>
<td>2389/(1–0.59)</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ab700Or30</td>
<td>0.143</td>
<td>0.148</td>
<td>1.7–6.9%</td>
<td>2386/(1–0.62)</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ab500Or50</td>
<td>0.149</td>
<td>0.157</td>
<td>1.6–7.1%</td>
<td>2390/(1–0.5C)</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ab300Or70</td>
<td>0.151</td>
<td>0.158</td>
<td>2.1–5.7%</td>
<td>2373/(1–0.5C)</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ab100Or90</td>
<td>0.156</td>
<td>0.159</td>
<td>1.6–5.3%</td>
<td>2395/(1–0.67C)</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAlSi3O8(Or)</td>
<td>0.165</td>
<td>0.158</td>
<td>2.2–13.3%</td>
<td>2382/(1–0.84C)</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiAlSi3O8</td>
<td>0.112</td>
<td>0.123</td>
<td>1.0–7.2%</td>
<td>2379/(1–0.5C)</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li2K2AlSi3O8</td>
<td>0.136</td>
<td>0.124</td>
<td>0.9–7.4%</td>
<td>2373/(1–0.48C)</td>
<td>13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li2Na2AlSi3O8</td>
<td>0.133</td>
<td>0.119</td>
<td>1.0–7.2%</td>
<td>2379/(1–0.5C)</td>
<td>13</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

**Notes:**
- Unit of molar absorptivities is L mol⁻¹ mm⁻¹. References are 1, Zhang et al. [1997a]; 2, Newman et al. [1986]; 3, Dobson et al. [1989]; 4, Ihinger et al. [1994] (these values were listed without giving details); 5, Dixon et al. [1998]; 6, Dixon et al. [1995]; 7, Pandya et al. [1992]; 8, Danyushevsky et al. [1993]; 9, Silver and Stolper [1989]; 10, Silver et al. [1990]; 11, Nowak and Behrens [1997]; 12, Behrens [1995]; 13, Behrens et al. [1996]; and 14, Yamashita et al. [1997].
- In the density expression, C is mass fraction of H2O, and X is mole fraction of H2O on a single-oxygen basis.
- Obtained by interpolation.
mental temperatures, 400°–600°C [Ihinger, 1991; Zhang et al., 1991a, 1995, 1997a; Ihinger et al., 1999]. At these temperatures the reaction timescale is minutes to hours depending on H₂O₂ and T [Zhang et al., 1995], much longer than the quench timescale (a few seconds) for rapid quench. Furthermore, Zhang et al. [1991a, 1995, 1997a, b], Ihinger [1991] and Ihinger et al. [1999] compared the reaction timescale and quench timescale case by case and excluded data that might have been affected by quench (such as ≈2.5% H₂O₂ at 600°C). Therefore these data do not suffer from the above obvious quench effect. These authors also tested possible quench effects in several ways. One of the tests is to examine directly whether speciation may change when the experimental temperature is sufficiently low. Zhang et al. [1995] heated a hydrous glass to 400°, 350°, 300°, 250°, and 200°C for 5–10 min. The quenched speciation does not vary (Figure 4), implying that reaction rates at these temperatures are negligible. A second test is to see if the final speciation changes with quench rate if the initial temperature is sufficiently low. Zhang et al. [1997b] cooled a sample from 300°C slowly at 1°C min⁻¹ and rapidly in liquid nitrogen and found no difference in the final speciation. They concluded that the quench effect is negligible in these quench data unless there is a portion of the reaction that is unquenchable (i.e., a portion of the reaction would continue to reach equilibrium at room temperature). The presence of such a portion of the reaction would not affect the inference of the apparent equilibrium temperature [Zhang et al., 1991a, 1995, 1997a] and cooling rate [Zhang et al., 1995, 1997b] but would affect the understanding of the true species concentrations at high T, the modeling of solubility data, and the values of molecular H₂O₂m diffusivity.

Although the experimental IR data at 400°–600°C remain the same [Zhang et al., 1991a, 1995], the expression for K₂ from the speciation data using the quench technique has evolved with time [Zhang et al., 1991a, 1997a], owing to the improvement in calibration. Using the calibration of Zhang et al. [1997a], the equilibrium coefficient K₂ (see equation (2)) in a rhyolitic glass and melt at H₂O₂ ≤ 2.4% and 400°–600°C is independent of H₂O₂ content and can be expressed as

$$K_2 = 6.53e^{-3100T/7}.$$  

The pressure dependence of K₂ is small at 550°C and P ≈ 10 kbar [Zhang, 1993; Ochs and Lange, 1997]. At higher H₂O₂, up to 6% [Ihinger et al., 1999], the experimental data can be modeled either by an ideal mixing model if uncertainty in infrared calibration is allowed or by a regular solution model.

One disadvantage of the quench technique compared with the in situ technique is that only a small temperature range (400°–600°C) can be investigated, because the reaction rate is too slow at lower temperatures and too high (and hence the speciation is unquenchable) at higher temperatures. One advantage of the quench technique is that the IR technique is extensively calibrated only at room temperature (see previous section), and measurement at room temperature is simple and hence less prone to technical complications.

### 3.2. Experimental Data Obtained From the in Situ Technique

Nowak and Behrens [1995] and Shen and Keppler [1995] developed the in situ technique for determining equilibrium speciation under high T and high P. Compared with the simple quench technique, the in situ technique is more sophisticated and appealing. Since the sample is measured in situ at the high T and high P experimental conditions, an obvious advantage is that there is no quench effect and so the method provides actual band intensities at high temperatures and pressures (although one must still be careful to ensure that equilibrium is attained). Furthermore, it can be used to study speciation over a wide temperature range. The technique hence has great potential if molar absorptivities do not vary with measurement temperature and pressure. However, the technique also suffers from several disadvantages, including the following: (1) Technical difficulties for the in situ measurements mean that the precision is usually not as good as the room temperature measurements. (2) The possible variation of the molar absorptivities with temperature must be quantified. Nowak and Behrens [1995] and Shen and Keppler [1995] assumed that the molar absorptivities are independent of measurement T, but this is by no means proven. (3) Even if data from this method indicate actual speciation at high temperatures, if they are different from the quenched speciation, they are not directly applicable to estimation of the temperature or cooling rate recorded by the reaction in naturally or experimentally quenched glasses.

The in situ infrared spectra have been taken for two
hydrous glasses: a hydrous AOQ melt/glass (Table 1) containing 4.14% H$_2$O$_t$ [Nowak and Behrens, 1995] and a hydrous potassic aluminosilicate melt/glass (composition 3 in Table 1) containing 8.1% H$_2$O$_t$ [Shen and Keppler, 1995]. The AOQ composition used by Nowak and Behrens [1995] is similar to a rhyolitic composition and will be referred to as quasi-rhyolitic. Because Shen and Keppler [1995] used a glass with composition very different from that of rhyolite and did not report the original band intensities, their data are not included in the following discussion. However, owing to the similarity of the data between the two in situ studies, the conclusions based on the work of Nowak and Behrens [1995] are expected to be equally applicable to the work of Shen and Keppler [1995]. The available in situ data do not yet allow the examination of the dependence of K$_2$ on H$_2$O$_t$.

Nowak and Behrens [1995] showed that the intensities of the 5230 and 4520 cm$^{-1}$ bands vary in the glass state at $\leq$400°C. The variations can be caused by either the true variation of speciation concentrations with temperature, which is unexpected, or the temperature dependence of molar absorptivities. The authors assumed that the molar absorptivities are constant and suggested that the variations imply that a portion of the speciation reaction is unquenchable. At higher temperatures the band intensities vary more rapidly with temperature. Again by assuming constant molar absorptivities, they calculated K$_2$ values as a function of T, shown in Figure 5. When compared with quenched speciation data, not only do the K$_2$ values differ, but the slopes in ln K$_2$ versus 1/T (i.e., the inferred enthalpy of reaction (2)) also differ significantly. Nowak and Behrens [1995] and Shen and Keppler [1995] concluded that the quench technique cannot be used to investigate equilibrium speciation for (R2). The validity of this claim is discussed below.

Figure 5. A comparison of equilibrium coefficient K$_2$ from two studies [Zhang et al., 1997a; Nowak and Behrens, 1995]. The data are as reported by the authors without any reinterpretation.

3.3. Discussion

There is a large difference between the in situ data (assuming constant molar absorptivities) and the quenched data (Figure 5). I present the following reinterpretation of the in situ data [Zhang, 1999], which reconciles the difference between the two experimental techniques. Assuming that the band intensity variation with temperature at 0°–400°C [Nowak and Behrens, 1995] is caused by the temperature dependence of the molar absorptivities, this dependence can be obtained using original band intensity data (Figure 6a). A simple linear extrapolation of ln ($\varepsilon/\varepsilon_{25°C}$) versus T is used to extrapolate absorptivities at high T. Using these absorptivities, the “actual” species concentrations are calculated (although the accuracy may not be high). When the resulting K$_2$ values are compared with the data of Zhang...
et al. [1997a], the agreement is very good (Figure 6b). More recent experimental data show that (1) IR molar absorptivities do vary with measurement temperature [Behrens et al., 1998; Grezchik and McMillan, 1998; Zhang and Behrens, 1998a; A. C. Withers et al., Reconciliation of experimental results on H$_2$O speciation in rhyolitic glass using in situ and quenching techniques, submitted to Earth and Planetary Science Letters, 1999] and (2) Raman band shapes also change with temperature [Holz et al., 1996] and hence support the above reinterpretation. How rapidly the molar absorptivities vary with temperature depends on whether the baseline is fit by a straight line or by a curve (Figure 1). There is no theoretical basis for the prediction of molar-absorptivity variation with temperature. Hence, although the in situ technique has many advantages and may represent the future of infrared study of H$_2$O in silicate melts and glasses, quantitative application of the technique must await the determination of the dependence of molar absorptivities on measurement temperature.

In conclusion, speciation data obtained from the quench technique do not suffer from a quench problem as long as the experimental temperature is not too high. On the other hand, quantification of in situ data requires calibration of the IR technique at the measurement temperatures. At present, (10) is the best representation of the dependence of $K_2$ with temperature at $H_2O \leq 2.4\%$ and $P \leq 5$ kbar.

4. **H$_2$O SOLUBILITY IN RHYOLITIC MELT**

A quantitative understanding of H$_2$O solubility (dissolved H$_2$O content in equilibrium with an H$_2$O pressure) in silicate melts is necessary for understanding the conditions under which H$_2$O exsolves in volcanic eruptions and the exsolution of a hydrothermal fluid that is important to the formation of ore deposits. Solubility of H$_2$O is expected to increase with $P_{H_2O}$, but not proportionally to $P_{H_2O}$ because of the species reaction (R2). The dependence of H$_2$O solubility on temperature at a given pressure is more complicated because $H_2O_m$ is expected to decrease with temperature ($K_1$ decreases with temperature) and OH is expected to increase with temperature ($K_2$ increases with temperature).

Early experimental work [e.g., Goranson, 1938; Tuttle and Bowen, 1958; Shaw, 1963; Kadik et al., 1972] demonstrated the high solubility of H$_2$O compared with other volatile components such as CO$_2$ and noble gases. Although H$_2$O solubility increases with pressure, it is not proportional to $P_{H_2O}$ (or $f_{H_2O}$). The solubility coefficient (the concentration of H$_2$O in the melt divided by that of H$_2$O in the equilibrium vapor phase, or mole fraction of $H_2O_1$ in the melt divided by $f_{H_2O}$) depends on $f_{H_2O}$. The nonconstancy of the solubility coefficient is largely caused by the formation of OH groups by the reaction of H$_2$O with the network oxygen. OH is the dominant species at low $H_2O_1$ [Burnham and Davis, 1974] and becomes less dominant (but still significant) at high $H_2O_1$ [Solper, 1982b]. Our current understanding is that H$_2$O solubility is roughly proportional to $(P_{H_2O})^{1/2}$ at low $P_{H_2O}$ ($\leq$2 kbar) because OH is the dominant species, but it increases more rapidly with further increase of $P_{H_2O}$ because $H_2O_m$ becomes an important species. McMillan [1994] reviewed H$_2$O solubility models. Papale [1997] and Moore et al. [1998] summarized H$_2$O solubility data and modeled the compositional dependence of H$_2$O solubility in a wide range of natural melt compositions. Other workers also investigated the compositional dependence of H$_2$O solubility in synthetic silicate melts [e.g., Holz et al., 1992, 1995; Behrens, 1995]. The following discussion, however, concentrates on rhyolitic and quasi-rhyolitic melts.

4.1. **Solubility Data**

Various workers have reported experimental data on H$_2$O solubility in rhyolitic and quasi-rhyolitic melts [Kadik et al., 1972; Khitarov and Kadik, 1973; Shaw, 1974; Dingwell et al., 1984; Silver et al., 1990; Ihinger, 1991; Holz et al., 1992, 1995; Blank et al., 1993; Moore et al., 1995, 1998]. In spite of these efforts, the data for H$_2$O solubility in rhyolitic melts as a function of temperature and pressure are still limited for the following reasons:

1. In the earlier studies the measurement of dissolved H$_2$O was not as accurate as in more recent work, especially at low H$_2$O$_m$. For example, Jambon et al. [1992] showed that the H$_2$O$_1$ is 0.114% for a glass for which Shaw [1974] reported 0.38% H$_2$O$_m$. Hence there may be a discrepancy in the earlier and more recent data. There may also be other experimental problems in the earlier studies. Even in more recent studies, the slow-quench data of Silver et al. [1990] show more scatter than their rapid-quench data, and the solubility data of Ihinger [1991] also show considerable scatter (e.g., Figure 7a).

2. Few studies examined the temperature dependence of the H$_2$O solubility in rhyolitic melts. The earlier experimental data were at 1200°C [Kadik et al., 1972; Khitarov and Kadik, 1973]. Most recent experimental data on rhyolitic melts were at 850°C. Only Holz et al. [1992, 1995] examined the temperature dependence systematically for an AOQ (Qz28Ab38Or34) melt (composition 2 in Table 1). Ihinger [1991] reported two data points at 750°C in addition to data at 850°C for rhyolitic melts (composition 1 in Table 1).

3. The investigated pressure range of the H$_2$O solubility in silicate melts is still limited, mostly from 100 to 2000 bars. Most of the solubility data in rhyolitic and quasi-rhyolitic melts at pressures greater than 2 kbar were reported by Holz et al. [1995] for the AOQ melt (Table 1). (Interestingly, the H$_2$O solubility in this melt was most extensively studied covering the widest range of $T$ and $P$.) Besides their study, there are only five data points at higher pressures and two data points at lower pressures. Low-pressure solubility data are important, not only because they constrain solubility models and exsolution enthalpy, but also because H$_2$O exsolution at
low pressures is important for understanding explosive volcanic eruptions. There is hence a need for H₂O solubilities at both lower pressures (1–100 bars) and higher pressures (>2 kbar). At pressures greater than 5 kbar, because of bubble formation in melts containing very high H₂O during quench [Holtz et al., 1995], it may be necessary to use the in situ technique to determine H₂O solubility [Shen and Keppler, 1997].

Figure 7a compares reported experimental solubility data in rhyolitic melt at 850°C [Shaw, 1974; Silver et al., 1990; Ihinger, 1991; Blank et al., 1993]. H₂O from IR spectra are all recalculated using the new calibration [Zhang et al., 1997a]. Data from manometry or Karl-Fischer titration are directly used. The consistency between different laboratories is good. However, there is still considerable scatter, much greater than the analytical uncertainty. Such scatter leads to difficulties in using solubility data to test solubility models and to extract thermodynamic properties.

4.2. Modeling the Solubility Data

Burnham [1975], Silver and Stolper [1985], Ihinger [1991], Blank et al. [1993], Holtz et al. [1995], and Moore et al. [1998] modeled H₂O solubility in silicate melts. These models can be classified into three types: (1) assuming all dissolved H₂O dissociates to OH groups [Burnham, 1975, 1994]; (2) ignoring the role of speciation in H₂O solubility [Moore et al., 1995, 1998; Papale, 1997]; and (3) accounting for the role of two dissolved H₂O species [Silver and Stolper, 1985; Ihinger, 1991; Blank et al., 1993; Holtz et al., 1995].

The model of Burnham [1975] was developed before establishment of H₂O speciation in silicate melts. The model assumes that the activity of H₂O is proportional to the square of H₂O mole fraction (i.e., it implicitly assumes that all dissolved H₂O dissociates to OH groups) at H₂O₁ ≥ 6.4% and a complicated empirical function at greater H₂O. The equilibrium constant for the solubility coefficient is a polynomial function of T and ln P calibrated from measured solubility and partial molar volume of H₂O. The model works well at low pressures but less satisfactorily at high pressures. For example, at 1100°C and 5 kbar for the AOQ melt, using the adjustable parameter of 5.13 [Burnham, 1994] to account for 28% SiO₂ component in the melt, the calculated solubility using the Burnham model is 8.4%, lower than the experimental 10.8% of Holtz et al. [1995].

In two recent papers, Moore et al. [1995, 1998] obtained H₂O solubility data for a wide range of natural melt compositions. They fit the experimental solubility data using the following equation:

\[ 2 \ln X_{H_2O}^{melt} = \frac{2565}{T} - 14.21 + 1.171 \ln f_{H_2O} + \frac{P}{T} (2.736X_{NaO} - 1.997X_{AlO} - 0.9275X_{FeO}) \]

![Figure 7. Comparison of experimental solubility data on rhyolitic and AOQ melts and solubility models.](image)

(a) Experimental solubility data on natural rhyolitic melt. The calculated curve 1 uses K₁ from equation (14) and K₂ from equation (10). Curves 2 and 3 are produced using K₁ from equation (17) with the H₂O molar volume of Ochs and Lange [1997] and K₂ of either the present work or Nowak and Behrens [1995]. (b) Comparison of experimental and calculated solubility for the quasi-rhyolitic AOQ (Qz28Ab38Or34) melt at 800°C using K₁ from equation (14) and K₂ from equation (10). (c) Comparison of all experimental solubility data for the AOQ melt with calculation using K₁ from equation (14) and K₂ from equation (10). The solid line is the 1:1 line.
where \( X_{\text{H}_{2}\text{O}^\text{melt}}, X_{\text{Al}_{2}\text{O}_3}, X_{\text{Fe}_{2}\text{O}_3}, \) and \( X_{\text{Na}_{2}\text{O}} \) are the mole fractions on an oxide molar basis, \( P \) is in bars, and \( T \) is in kelvins. Papale [1997] constructed a regular solution model to account for the effect of anhydrous melt composition on \( \text{H}_2\text{O} \) solubility. The models of Papale [1997] and Moore et al. [1998] fill a gap for prediction of solubility over a wide range of compositions, but both ignored the role of speciation in \( \text{H}_2\text{O} \) solubility. The model of Papale [1997] lacks details for calculation, is difficult to use, and hence will not be discussed further. The model of Moore et al. [1998] can predict solubility data in the intermediate pressure range (100–3000 bars) very well. However, owing to its empirical nature (especially the 1.71 \( \ln f_{\text{H}_2\text{O}} \) term, implying that the activity of \( \text{H}_2\text{O} \) is proportional to the 1.7th power of \( \text{H}_2\text{O} \) mole fraction), the formulation does not account for the effect of \( \text{H}_2\text{Om} \) and \( \text{OH} \) species and has large relative errors at \( P > 3 \) kbar (as cautioned by the authors themselves).

The models of Silver and Stolper [1985], Ihinger [1991], Blank et al. [1993], and Holtz et al. [1995] account for the role of two species and hence have more potential for accurately predicting \( \text{H}_2\text{O} \) solubilities in a wide range of \( T \) and \( P \). The solubility is the summation of two terms: dissolved \( \text{H}_2\text{O} \) m, whose concentration is related to the \( \text{H}_2\text{O} \) fugacity through (R1), and \( \text{OH} \) groups, whose concentration is related to the \( \text{H}_2\text{O} \) m concentration through (R2). Following these workers, I present an updated model for \( \text{H}_2\text{O} \) solubility in rhyolitic and quasi-rhyolitic melts using the new speciation model (equation (10)). From the model results, the thermodynamic consistency of solubility, speciation, and other available data is evaluated.

Because species concentrations depend on \( \text{H}_2\text{O} \) that depends on \( P_{\text{H}_2\text{O}} \), the \( \text{H}_2\text{O} \) fluid pressure affects solubility in two ways: (1) pressure effect on equilibrium constants of (R1) and (R2), reflected in partial molar volumes, and (2) pressure effect on \( \text{H}_2\text{O} \) m concentration that affects the relative species concentrations (Figure 2). Temperature affects the equilibrium constants of both (R1) and (R2) and hence the solubility. Total solubility of \( \text{H}_2\text{O} \) can be expressed as

\[
[H_{\text{2}O}] = [H_{\text{2}O}^\text{m}] + 0.5[\text{OH}]
= K_1f + 0.5(K_1K_2f[O])^{1/2},
\]

where \( f \) is the fugacity of \( \text{H}_2\text{O} \), \( K_1 \) depends on both \( T \) and \( P \), and \( K_2 \) depends only on \( T \) at pressures below 10 kbar. In calculating \( f \), the vapor phase in equilibrium with the melt at high \( T \) and \( P \) is assumed to be pure \( \text{H}_2\text{O} \). Because the anhydrous components (\( \text{Na}_2\text{O}, \text{K}_2\text{O}, \text{SiO}_2 \), etc.) can dissolve in the vapor phase, especially at high \( T \) and high \( P \), it is expected that the error of this assumption increases with both temperature and pressure, but the effect cannot be quantitatively estimated at this time. Knowing \( K_2 \) and \( [H_{\text{2}O}^\text{m}] \) (equal to \( K_1f \)), \( [\text{OH}] \) in (11) can be solved from (2) and \( [H_{\text{2}O}^\text{m}] + [\text{OH}] + [O] = 1 \), leading to

\[
[H_{\text{2}O}] = K_1f
+ K_1K_2f(1 - K_1f)
+ K_1K_2f[(K_1K_2f)^2 + 4K_1K_2f(1 - K_1f)]^{1/2}.
\]

Holtz et al. [1992, 1995] experimentally examined the temperature and pressure dependence of \( \text{H}_2\text{O} \) solubility in a quasi-rhyolitic melt (composition 2 in Table 1) that is similar to natural rhyolitic melts in composition (Table 1). \( \text{H}_2\text{O} \) solubility in this melt is similar to that in rhyolitic melt of composition 1 in Table 1 (H. Behrens, personal communications, 1998) (Figure 7a). The model for \( \text{H}_2\text{O} \) solubility in this melt is derived as follows. It is assumed that \( K_2 \) in this melt is the same as that in rhyolitic melt (equation (10)) and is independent of \( \text{H}_2\text{O} \) to 14 wt \% \( \text{H}_2\text{O} \). That is, mixing of \( \text{H}_2\text{O}^\text{m}-\text{OH-O} \) species is assumed to be ideal for up to 14\% \( \text{H}_2\text{O} \). Although speciation is not well understood at such high \( \text{H}_2\text{O} \), it is judged that using an approximate speciation model is better than simply assuming all dissolved \( \text{H}_2\text{O} \) dissociates into \( \text{OH} \) groups or ignoring speciation as in some previous models. For a given \( T \) and \( P \) (\( = P_{\text{H}_2\text{O}} \)), \( \text{H}_2\text{O} \) fugacity is calculated from the equation of state for \( \text{H}_2\text{O} \) [Pitzer and Sterner, 1994]. From every measured \( \text{H}_2\text{O} \) solubility, \( \text{H}_2\text{O} \) m concentration can be calculated from \( K_2 \) and \( \text{H}_2\text{O} \) m by combining (2), \( [\text{H}_2\text{O}^\text{m}] + 0.5[\text{OH}] = [\text{H}_2\text{O}^\text{m}], \) and \( [\text{H}_2\text{O}^\text{m}] + [\text{OH}] + [O] = 1 \), leading to

\[
[H_{\text{2}O}^\text{m}] = 
- \frac{8X^2}{8X + K_2(1 - 2X) + [(K_1(1 - 2X))^2 + 16K_2X(1 - X)]^{1/2}},
\]

where \( X = [H_{\text{2}O}] \). Then \( K_1 = [H_{\text{2}O}^\text{m}]/f_{\text{H}_2\text{O}} \) can be obtained for every solubility datum given by Holtz et al. [1992, 1995]. Table 4 lists how \( K_1 \) depends on \( T \) and \( P \) (\( = P_{\text{H}_2\text{O}} \)) for the AOO melt. These data are used to calibrate the following equation by linear regression:

\[
\ln K_1 = (-13.869 + 0.0002474P)
+ (3890.3 - 0.3948P)/T,
\]

where \( P \) (total \( P \), not necessarily \( P_{\text{H}_2\text{O}} \)) is in bars and \( T \) is in kelvins. Using (14) for \( K_1 \) and (10) for \( K_2 \), \( \text{H}_2\text{O} \) solubility can be calculated using (12) to an average 1σ accuracy of 0.19\% \( \text{H}_2\text{O} \) in the range of 300–8000 bars and 700°–1350°C (Figures 7b and 7c) and a maximum error of 0.68\% (at 700°C and 5000 bars).

To investigate whether the approach using the above formulation has extrapolative value, the model was also calibrated using only data with \( P \leq 3 \) kbar [Holtz et al., 1992, 1995], resulting in slightly different parameters from those in (14). The error in extrapolating such a model to 5 and 8 kbar is relatively small: At 5 kbar and 800°C the experimental solubility is 9.97\% versus calculated 10.22\% (12.72\% if the Moore et al. [1998] model is used); at 8 kbar and 800°C the experimental solubility is 13.82\% versus calculated 14.51\% (23.15\% using the
model of Moore et al. [1998]). This exercise shows that the solubility model incorporating speciation has extrapolative value.

The formulation in (14) also reproduces very well the H₂O solubility in rhyolitic melt (calculated curve 1 in Figure 7a), demonstrating its applicability to natural rhyolitic melts. Furthermore, the formulation also repro-

<table>
<thead>
<tr>
<th>T, °C</th>
<th>P, bars</th>
<th>H₂O, wt %</th>
<th>fH₂O, bars</th>
<th>XH₂O</th>
<th>ln K₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>5000</td>
<td>10.07</td>
<td>3837</td>
<td>0.0979</td>
<td>−10.576</td>
</tr>
<tr>
<td>750</td>
<td>2000</td>
<td>6.00</td>
<td>1481</td>
<td>0.0476</td>
<td>−10.345</td>
</tr>
<tr>
<td>800</td>
<td>300</td>
<td>2.13</td>
<td>285.5</td>
<td>0.0096</td>
<td>−10.305</td>
</tr>
<tr>
<td>800</td>
<td>500</td>
<td>2.79</td>
<td>461.2</td>
<td>0.0146</td>
<td>−10.358</td>
</tr>
<tr>
<td>800</td>
<td>500</td>
<td>2.71</td>
<td>461.2</td>
<td>0.014</td>
<td>−10.403</td>
</tr>
<tr>
<td>800</td>
<td>500</td>
<td>2.91</td>
<td>461.2</td>
<td>0.0156</td>
<td>−10.293</td>
</tr>
<tr>
<td>800</td>
<td>700</td>
<td>3.77</td>
<td>626.2</td>
<td>0.0231</td>
<td>−10.206</td>
</tr>
<tr>
<td>800</td>
<td>700</td>
<td>3.74</td>
<td>626.2</td>
<td>0.0229</td>
<td>−10.218</td>
</tr>
<tr>
<td>800</td>
<td>1000</td>
<td>4.11</td>
<td>857.5</td>
<td>0.0263</td>
<td>−10.392</td>
</tr>
<tr>
<td>800</td>
<td>1000</td>
<td>4.07</td>
<td>857.5</td>
<td>0.0259</td>
<td>−10.407</td>
</tr>
<tr>
<td>800</td>
<td>1000</td>
<td>4.10</td>
<td>857.5</td>
<td>0.0262</td>
<td>−10.396</td>
</tr>
<tr>
<td>800</td>
<td>1300</td>
<td>5.02</td>
<td>1078</td>
<td>0.0351</td>
<td>−10.331</td>
</tr>
<tr>
<td>800</td>
<td>1400</td>
<td>5.16</td>
<td>1150</td>
<td>0.0365</td>
<td>−10.357</td>
</tr>
<tr>
<td>800</td>
<td>2000</td>
<td>5.86</td>
<td>1592</td>
<td>0.0437</td>
<td>−10.503</td>
</tr>
<tr>
<td>800</td>
<td>2000</td>
<td>5.84</td>
<td>1592</td>
<td>0.0435</td>
<td>−10.507</td>
</tr>
<tr>
<td>800</td>
<td>2000</td>
<td>5.77</td>
<td>1592</td>
<td>0.0428</td>
<td>−10.524</td>
</tr>
<tr>
<td>800</td>
<td>3000</td>
<td>7.45</td>
<td>2407</td>
<td>0.0608</td>
<td>−10.587</td>
</tr>
<tr>
<td>800</td>
<td>3000</td>
<td>7.45</td>
<td>2407</td>
<td>0.0608</td>
<td>−10.587</td>
</tr>
<tr>
<td>800</td>
<td>4000</td>
<td>8.94</td>
<td>3387</td>
<td>0.0774</td>
<td>−10.687</td>
</tr>
<tr>
<td>800</td>
<td>4800</td>
<td>9.38</td>
<td>4330</td>
<td>0.0824</td>
<td>−10.87</td>
</tr>
<tr>
<td>800</td>
<td>5000</td>
<td>9.90</td>
<td>4591</td>
<td>0.0883</td>
<td>−10.859</td>
</tr>
<tr>
<td>800</td>
<td>5000</td>
<td>10.07</td>
<td>4591</td>
<td>0.0903</td>
<td>−10.837</td>
</tr>
<tr>
<td>800</td>
<td>5000</td>
<td>9.86</td>
<td>4591</td>
<td>0.0879</td>
<td>−10.864</td>
</tr>
<tr>
<td>800</td>
<td>5000</td>
<td>10.02</td>
<td>4591</td>
<td>0.0897</td>
<td>−10.843</td>
</tr>
<tr>
<td>800</td>
<td>5000</td>
<td>10.04</td>
<td>4591</td>
<td>0.0899</td>
<td>−10.841</td>
</tr>
<tr>
<td>800</td>
<td>5000</td>
<td>9.94</td>
<td>4591</td>
<td>0.0888</td>
<td>−10.853</td>
</tr>
<tr>
<td>800</td>
<td>8000</td>
<td>13.95</td>
<td>10175</td>
<td>0.1356</td>
<td>−11.226</td>
</tr>
<tr>
<td>800</td>
<td>8000</td>
<td>13.70</td>
<td>10175</td>
<td>0.1327</td>
<td>−11.248</td>
</tr>
<tr>
<td>850</td>
<td>1000</td>
<td>4.00</td>
<td>899.4</td>
<td>0.0238</td>
<td>−10.53</td>
</tr>
<tr>
<td>850</td>
<td>2000</td>
<td>5.73</td>
<td>1687</td>
<td>0.0402</td>
<td>−10.644</td>
</tr>
<tr>
<td>850</td>
<td>5000</td>
<td>10.48</td>
<td>4919</td>
<td>0.0915</td>
<td>−10.893</td>
</tr>
<tr>
<td>900</td>
<td>500</td>
<td>2.72</td>
<td>476.7</td>
<td>0.0122</td>
<td>−10.57</td>
</tr>
<tr>
<td>900</td>
<td>500</td>
<td>2.48</td>
<td>476.7</td>
<td>0.0105</td>
<td>−10.72</td>
</tr>
<tr>
<td>900</td>
<td>2000</td>
<td>5.80</td>
<td>1769</td>
<td>0.0389</td>
<td>−10.724</td>
</tr>
<tr>
<td>950</td>
<td>2000</td>
<td>5.48</td>
<td>1838</td>
<td>0.0341</td>
<td>−10.894</td>
</tr>
<tr>
<td>1000</td>
<td>500</td>
<td>2.28</td>
<td>487.1</td>
<td>0.008</td>
<td>−11.014</td>
</tr>
<tr>
<td>1000</td>
<td>500</td>
<td>10.65</td>
<td>5706</td>
<td>0.0841</td>
<td>−11.125</td>
</tr>
<tr>
<td>1050</td>
<td>2000</td>
<td>5.57</td>
<td>1947</td>
<td>0.0319</td>
<td>−11.019</td>
</tr>
<tr>
<td>1100</td>
<td>500</td>
<td>2.44</td>
<td>494.2</td>
<td>0.008</td>
<td>−11.033</td>
</tr>
<tr>
<td>1150</td>
<td>2000</td>
<td>5.31</td>
<td>1989</td>
<td>0.0284</td>
<td>−11.157</td>
</tr>
<tr>
<td>1150</td>
<td>500</td>
<td>10.94</td>
<td>6080</td>
<td>0.082</td>
<td>−11.214</td>
</tr>
<tr>
<td>1150</td>
<td>500</td>
<td>10.69</td>
<td>6080</td>
<td>0.0794</td>
<td>−11.246</td>
</tr>
<tr>
<td>1150</td>
<td>2000</td>
<td>5.47</td>
<td>2024</td>
<td>0.0285</td>
<td>−11.17</td>
</tr>
<tr>
<td>1150</td>
<td>2000</td>
<td>5.35</td>
<td>2024</td>
<td>0.0276</td>
<td>−11.205</td>
</tr>
<tr>
<td>1200</td>
<td>500</td>
<td>3.23</td>
<td>499.2</td>
<td>0.0066</td>
<td>−11.238</td>
</tr>
<tr>
<td>1200</td>
<td>1000</td>
<td>3.54</td>
<td>1000</td>
<td>0.0135</td>
<td>−11.211</td>
</tr>
<tr>
<td>1200</td>
<td>3000</td>
<td>7.25</td>
<td>3258</td>
<td>0.0424</td>
<td>−11.25</td>
</tr>
<tr>
<td>1200</td>
<td>4000</td>
<td>8.73</td>
<td>4676</td>
<td>0.0559</td>
<td>−11.335</td>
</tr>
<tr>
<td>1200</td>
<td>5000</td>
<td>10.85</td>
<td>6356</td>
<td>0.0765</td>
<td>−11.328</td>
</tr>
<tr>
<td>1350</td>
<td>1000</td>
<td>3.88</td>
<td>1019</td>
<td>0.011</td>
<td>−11.437</td>
</tr>
</tbody>
</table>

Three leftmost columns are from Holtz et al. [1992, 1995]; fH₂O is calculated from Pitzer and Sterner [1994]; XH₂O is calculated using equation (13) and K₂ is calculated from equation (10), K₁ = XH₂O fH₂O. This exercise shows that the solubility model incorporating speciation has extrapolative value.

The formulation in (14) also reproduces very well the H₂O solubility in rhyolitic melt (calculated curve 1 in Figure 7a), demonstrating its applicability to natural rhyolitic melts. Furthermore, the formulation also reproduces a datum for metastable H₂O solubility at 490°C and 250 bars in a rhyolitic glass (calculated 3.21% versus experimental ~3.1%, hydration data of Zhang et al. [1991a]), suggesting it can be extrapolated to low temperatures. Hence I recommend (10), (12), and (14) for the calculation of H₂O solubility from 0 to 8 kbar and from 500° to 1350°C (despite thermodynamic inconsistencies among the data discussed below). Figure 8 shows the calculated H₂O solubility as a function of P (= P₁H₂O) at several temperatures and can be used for estimating H₂O solubility. Although accurate extension of this approach to examine the compositional dependence of H₂O solubility requires a knowledge of the speciation equilibrium in other melts, a rough estimate of speciation using (10) is better than simply ignoring the role of speciation.

Incorporation of more terms (such as terms linear to ln T, T, P²/T, and 1/T² to account for heat capacity, compressibility, etc.) into the expression of ln K₁ improves the quality of the fit only slightly, and the coefficients have large uncertainties. That is, incorporation of more terms can fit the data better at 700°–1350°C and...
The partial molar volume of H$_2$Om is.

The absolute value of the slope at each given plot at several fixed points is proportional to the partial molar volume of H$_2$Om.

The partial molar volume of H$_2$Om, V$_{H2Om}^{\text{melt}}$, may be obtained as

$$V_{H2Om}^{\text{melt}} = -RT \frac{\partial \ln K_1}{\partial P} = 32.8 - 0.02057T, \quad (15)$$

where $T$ is in kelvins and $V_{H2Om}^{\text{melt}}$ is in cm$^3$ mol$^{-1}$. The simplicity of the right-hand side of (15) (e.g., there is no pressure term) clearly suggests that it is not possible yet to obtain accurate $V_{H2Om}^{\text{melt}}$ from solubility data. Furthermore, $V_{H2Om}^{\text{melt}}$ in (15) decreases with increasing $T$, an unreasonable result. $V_{H2Om}^{\text{melt}}$ calculated from the above equation would be 15.9 cm$^3$ mol$^{-1}$ at 550°C and 0 at 1321°C. The apparent decrease of $V_{H2Om}$ with $T$, although unexpected, is consistent with the ln $K_1$ versus $P$ plot at several fixed $T$ (Figure 9). The absolute values of the slope in ln $K_1$ versus $P$ (which is proportional to $V_{H2Om}^{\text{melt}}$) clearly decrease as $T$ increases.

The term $V_{H2Om}^{\text{melt}}$ has been determined from density measurements of silicate melts and glasses [Ochs and Lange, 1997, 1999]. For the purpose of comparison, $V_{H2Om}^{\text{melt}}$ and $V_{H2O}^{\text{melt}}$ can be related as follows [Zhang, 1999]:

$$V_{H2O}^{\text{melt}} = \frac{X_{H2O}^{\text{melt}}}{X_{H2O}} V_{H2Om}^{\text{melt}} + \frac{X_{(OH)2-O}^{\text{melt}}}{X_{H2O}} V_{(OH)2-O}^{\text{melt}}, \quad (16)$$

where the subscript (OH)$_2$O means one cluster of two OH groups minus one oxygen, that is, H$_2$O dissolved in the form of OH groups. Because Zhang [1993] inferred from the speciation data that the partial molar volume of (OH)$_2$O is only 0.7 cm$^3$ mol$^{-1}$ greater than $V_{H2Om}^{\text{melt}}$ at $P < 10$ kbar, $T = 550^\circ$C and H$_2$O = 0.8%, $V_{H2Om}^{\text{melt}}$ is expected to be roughly the same as $V_{H2Om}^{\text{melt}}$. However, the $V_{H2Om}^{\text{melt}}$ values determined from solubility and speciation data are clearly different from $V_{H2Om}^{\text{melt}}$ determined by Ochs and Lange [1997, 1999]. For example, at 850°C and ±3 kbar, Ochs and Lange [1997, 1999] obtained $V_{H2Om}^{\text{melt}} = 21$ cm$^3$ mol$^{-1}$, whereas (15) gives $V_{H2Om}^{\text{melt}} = 9.7$ cm$^3$ mol$^{-1}$.

The inconsistency between solubility, speciation, and partial molar volume data can also be examined from a different approach. At a constant temperature, $K_1$ depends on pressure as follows:

$$K_1 = A_1 \exp \left[ -\int_1^P \frac{V_{H2Om}^{\text{melt}} dP}{(RT)} \right], \quad (17)$$

where $P$ is in bars. Using $V_{H2Om}^{\text{melt}} \approx V_{H2O}^{\text{melt}} = 21$ cm$^3$ mol$^{-1}$ in albite melt at 850°C below 3 kbar [Ochs and Lange, 1997, 1999] and $K_2 = 0.410$ at 850°C in rhyolitic melt (equation (10)), H$_2$O solubility can be calculated from (12) given $T$ and $P$ if $A_1$ is specified. In other words, the above formulation can be used to fit the solubility data to obtain $A_1$. Such a best fit solubility curve at 850°C is shown as curve 2 in Figure 7a. Though the agreement is not bad, the shape of the calculated curve does not match the data in detail so that either the high-pressure or low-pressure data cannot be well fit. (If $K_2$ is chosen to be 0.99 from Nowak and Behrens [1995], the fit, shown as curve 3 in Figure 7a, is slightly worse.) The imperfect fit indicates that there is some inconsistency between the speciation model, the solubility, and partial molar volume data. The examination also shows high precision and accuracy is necessary if $V_{H2Om}^{\text{melt}}$ is to be derived from solubility data.

The inconsistency between solubility, speciation, and partial molar volume data may be explained in several different ways. (1) $V_{H2Om}^{\text{melt}}$, determined from density data by linear regression may be in error. Although density measurements have very high accuracy, obtaining the partial molar volume by assuming all $V$ are constant may generate errors. (2) The inability to accurately constrain higher-order terms using the solubility data means that $V_{H2Om}^{\text{melt}}$ (and similarly $\Delta H_{298}$) may not be well-constrained at present. (3) The most likely explanation is as follows: The H$_2$O solubility in AOQ melt is determined at 700–1350°C and has its best precision at high H$_2$O (and hence high $P$) because Karl-Fischer titration is used to obtain H$_2$O, whereas the H$_2$O speciation in rhyolitic glasses is determined at 400–600°C and the speciation model is calibrated only at ±2.4% H$_2$O. Combination of the two data sets to model solubility requires the extrapolation of the speciation model to much higher $T$ and much higher H$_2$O, which may be problematic and result in inaccuracy of $V_{H2Om}^{\text{melt}}$. Whatever the explanations, more work is necessary to maintain data consistency. With future improvement on these experimental data, an op-
timization method can be used to reconcile and constrain all the input data.

An alternative approach to model H\textsubscript{2}O solubility and to extract \( K_2 \) at high H\textsubscript{2}Ot is to assume that the partial molar volume data [Ochs and Lange, 1997, 1999] are accurate and applicable. If low-pressure solubilities are well known, then \( K_1 \) at low pressures can be calculated from the solubility data and \( K_2 \) (since \( K_2 \) is well known at \( \pm 2.4\% \) H\textsubscript{2}Ot). \( K_1 \) as a function of pressure can then be obtained from (17). From high-pressure solubility data, \( K_2 \) at high pressures, i.e., at high H\textsubscript{2}Ot, can be obtained. Using the dependence of \( K_2 \) on H\textsubscript{2}Ot, an expression for calculation of solubility can be obtained. This approach requires accurate solubility data at low pressures and various \( T \), which are not available at present.

5. DIFFUSION OF H\textsubscript{2}O IN RHYOLITIC GLASSES AND MELTS

Diffusion of H\textsubscript{2}O in rhyolitic and other melt plays a critical role in bubble growth. Diffusion is caused by random motion of molecules, atoms, and ions in a phase. Although such random motion is always present with or without a concentration gradient, only when there is a concentration (more accurately a chemical potential) gradient does diffusion lead to a net mass flux. For one-dimensional binary diffusion the mass flux \( J \) can be written as [e.g., Crank, 1975]

\[
J = -D \frac{\partial C}{\partial x}, \tag{18}
\]

where \( D \) is the binary diffusivity, \( C \) is the concentration of the diffusing component, \( x \) is distance, and \( \partial C/\partial x \) is the concentration gradient. The concentration variation with time can be written as

\[
\frac{\partial C}{\partial t} = - \frac{\partial J}{\partial x} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right). \tag{19}
\]

H\textsubscript{2}O diffusion in commercial glasses has been investigated extensively (see Doremus [1994] for a review). I concentrate on H\textsubscript{2}O diffusion in rhyolitic and quasi-rhyolitic glasses and melts.

Shaw [1974] carried out the first study of H\textsubscript{2}O diffusion in a rhyolitic melt. He showed that the diffusivity of the H\textsubscript{2}O component is high compared with that of other components and increases with its concentration. Subsequent reports [Friedman and Long, 1976; Jambon, 1979; Delaney and Karsten, 1981; Karsten et al., 1982; Lapham et al., 1984] confirmed the conclusions and also showed that the activation energy for H\textsubscript{2}O diffusion is low. These workers used (19) or a variation of it to obtain the diffusivity of the H\textsubscript{2}O component.

5.1. Role of Speciation During H\textsubscript{2}O Diffusion at Low H\textsubscript{2}Ot

Because the dissolved H\textsubscript{2}O component is present in silicate melts and glasses as at least two species, H\textsubscript{2}O\textsubscript{m} molecules and OH groups, and because H\textsubscript{2}O\textsubscript{m} and OH are expected to have different diffusivities, it is natural to consider the role of speciation in diffusion. This approach started from glass scientists for treating H\textsubscript{2}O diffusion at low H\textsubscript{2}Ot [e.g., Doremus, 1969, 1994]. Wasseburg [1988] presented a formal analysis on how to treat the diffusion of the H\textsubscript{2}O component at low to high H\textsubscript{2}Ot if H\textsubscript{2}O\textsubscript{m} is the diffusing species. Zhang et al. [1991a] carried out experiments and examined the role of speciation in the diffusion of the H\textsubscript{2}O component in a rhyolitic glass/melt containing 0.4–1.8% H\textsubscript{2}O at 1 bar and 400°–550°C. They treat the one-dimensional diffusion of the H\textsubscript{2}O component by explicitly considering the role of speciation:

\[
\frac{\partial [\text{H}_2\text{O}]}{\partial t} = \frac{\partial}{\partial x} \left( D_{\text{H}_2\text{O}m} \frac{\partial [\text{H}_2\text{O}]}{\partial x} - D_{\text{OH}} \frac{\partial [\text{OH}]/2}{\partial x} \right), \tag{20}
\]

where \( D_{\text{H}_2\text{O}m} \) is the diffusivity of molecular H\textsubscript{2}O and \( D_{\text{OH}} \) is the diffusivity of OH groups. From diffusion experiments, H\textsubscript{2}O\textsubscript{m}, H\textsubscript{2}O\textsubscript{m}, and OH profiles are measured. Hence both \( D_{\text{H}_2\text{O}m} \) and \( D_{\text{OH}} \) can be obtained by fitting the profiles to the above equation if the diffusivities are assumed to be constant. Whether they are indeed constant can be determined from the quality of the fit. Using this approach, Zhang et al. [1991a] found that their H\textsubscript{2}O diffusion data can be almost perfectly modeled if (1) the \( D_{\text{OH}}/D_{\text{H}_2\text{O}m} \) ratio is much smaller than 1, and (2) \( D_{\text{H}_2\text{O}m} \) is roughly constant over the H\textsubscript{2}Ot range of each experiment (<2%). That is, of the two species of the dissolved H\textsubscript{2}O component, only molecular H\textsubscript{2}O\textsubscript{m} is mobile, whereas OH is immobile. The OH profile is not due to diffusion of OH, but due to the local interconversion between H\textsubscript{2}O\textsubscript{m} and OH. Zhang et al. [1991a] obtained \( D_{\text{H}_2\text{O}m} \) values from diffusion profiles, in which the species concentrations were calculated using the calibration of Newman et al. [1986].

There are other systems in which mobile and immobile “species” are inferred but cannot be directly measured. Therefore a detailed understanding of the role of H\textsubscript{2}O\textsubscript{m} and OH in H\textsubscript{2}O diffusion, where both can be measured (even with the complexities discussed earlier), may be instructive for these systems in which mobile and immobile species are not directly measurable [e.g., Wang et al., 1996]. Zhang and Stolper [1991] investigated diffusion of the H\textsubscript{2}O component in basaltic melt with 0.04–0.4% H\textsubscript{2}Ot at 10 kbar and 1300°–1500°C. They found that \( D_{\text{H}_2\text{O}m} \) in a basaltic melt is significantly higher than in a rhyolitic melt at similar temperatures. Although the H\textsubscript{2}O\textsubscript{m} concentration cannot be directly measured, the observed proportionality between \( D_{\text{H}_2\text{O}m} \) and H\textsubscript{2}Ot led them to suggest that molecular H\textsubscript{2}O\textsubscript{m} is also the diffusing species.
5.2. Distinguishing Different Diffusivities of H₂O Diffusion

Because of the presence of two species, the diffusion of the H₂O component is complicated. Zhang et al. [1991b] examined the general role of speciation in diffusion and the particular case of how H₂O diffusion affects the hydrothermal oxygen “self-diffusion.” The strong dependence of H₂O diffusivity on H₂O₂ also leads to differences in several definitions of diffusivities that are typically identical. For example, diffusion-out and diffusion-in diffusivities obtained from mass loss and gain methods assuming constant D are typically the same. However, for H₂O diffusion, diffusion-out (dehydration) and diffusion-in (hydration) diffusivities are different. In this section the different diffusivities and how they are related are summarized [Zhang et al., 1991a, b; Wang et al., 1996].

1. Diffusivity of molecular H₂O₉₉ (D_{H₂O₉₉}) is defined in (20) and obtainable by fitting diffusion profiles to the equation. Its dependence on H₂O₂ is weak at H₂O₂ ≤ 2.0% [Zhang et al. [1991a] and the present work]. However, at >2% H₂O₂, D_{H₂O₉₉} increases rapidly (exponentially) with H₂O₂ [Zhang and Behrens, 1998b, submitted manuscript, 1999].

2. Diffusivity of OH groups (D_{OH}) is defined in (20) and is much smaller than D_{H₂O₉₉} at H₂O₂ < 2.0% [Zhang et al., 1991a].

3. Diffusivity of the H₂O component (D_{H₂O}) is defined in (19). The diffusivity of each species reflects the intrinsic mobility of the species, but D_{H₂O₉₉} does not. Hence D_{H₂O₉₉} is also called the effective or apparent diffusivity of total H₂O, or simply the diffusivity of H₂O₂. Because it depends strongly on H₂O₂, it is often obtained using the Boltzmann-Matano method [Nowak and Behrens, 1997; Behrens and Nowak, 1997], or by fitting concentration profiles assuming D_{H₂O₉₉} = [H₂O₂] at low H₂O₂ or by assuming a function for D_{H₂O₉₉} [Zhang and Behrens, 1998b, submitted manuscript, 1999]. D_{H₂O₉₉} is equal to the sum of diffusivities using

\[
D_{H₂O₉₉} = D_{H₂O₉₉} \left[ \frac{d[H₂O₂]}{d[H₂O]} \right] + D_{OH} \left[ \frac{d[OH]}{d[H₂O₂]} \right].
\]

If H₂O₉₉ is the diffusing species, then

\[
D_{H₂O₉₉} = D_{H₂O₉₉} \left[ \frac{d[H₂O₉₉]}{d[H₂O₂]} \right].
\]

The above equation allows the calculation of D_{H₂O₉₉} if D_{H₂O₉₉} is known and the differential d[H₂O₉₉]/d[H₂O₂] can be calculated. If equilibrium is reached, the differential can be calculated from a speciation model. Different diffusivities (such as D_{H₂O₉₉} and D_{H₂O₉₉}) may have different temperature dependence [Zhang et al., 1991a].

4. Diffusion-out diffusivity (D_{out}) is defined by [e.g., Crank, 1975; Wang et al., 1996]

\[
M_1 = M_0 - M_0 \sqrt{\frac{16D_{H₂O₉₉}}{\pi L^2}} \chi_i.
\]

where M₁ is the total H₂O mass still remaining in a slab after partial dehydration (desorption), M₀ is the initial mass, and L is the thickness of the slab. The above equation is valid when M₁/M₀ is greater than 0.5 and when the surface concentration of H₂O₂ is zero. The D_{out} is some kind of average of D_{H₂O₉₉} across the whole diffusion profile. At low H₂O₂ (≤2%), D_{H₂O₉₉} ∝ [H₂O₂], leading to

\[
D_{H₂O₉₉} = 0.347D_{H₂O₉₉,0}
\]

for zero surface H₂O₂, where D_{H₂O₉₉,0} is D_{H₂O₉₉} at the initial H₂O₂.

5. Diffusion-in diffusivity (D_{in}) is defined by [e.g., Crank, 1975]

\[
M_i = M_0 + M_1 \sqrt{\frac{16D_{H₂O₉₉}}{\pi L^2}} \chi_i,
\]

where L is the thickness of the slab, Mᵢ is the total H₂O mass that is now in the slab after partial hydration (soption), M₀ is the initial mass, and M₁ is the total mass that would enter the slab after infinite time. The above equation is valid when (M₁ - M₀)/M₀ is less than 0.5. The D_{in} is another average of D_{H₂O₉₉} across the whole diffusion profile. If D is independent of concentration, D_{in} = D_{out} = D. However, for H₂O diffusion, D_{in} ≠ D_{out} ≠ D_{H₂O₉₉}. At low H₂O₂ (≤2%), D_{H₂O₉₉} ∝ [H₂O₂], leading to

\[
D_{in} = 0.619D_{H₂O₉₉,0}
\]

for zero initial H₂O₂ where D_{H₂O₉₉,0} is D_{H₂O₉₉} at the surface H₂O₂.

6. The D-H interdiffusion coefficient (D_{D-H}) is obtained from (19) by allowing D₂O to diffuse in (or out) of a hydrous glass/melt by maintaining constant mole fractions (not weight percent) of D₂O + H₂O₂. Since the total D₂O + H₂O₂ is constant, the D_{D-H} is constant in an experiment and can be obtained by fitting an error function to the diffusion profile. However, D_{D-H} depends on [D₂O] + [H₂O₂]. If molecular D₂O and H₂O₂ are the diffusing species, then

\[
D_{D-H} = 0.5D_{H₂O₉₉}.
\]

If OH and OD are the diffusing species, then

\[
D_{D-H} = D_{H₂O₉₉}.
\]

Equations (27) and (28) show that accurate determination of D_{D-H} and D_{H₂O₉₉} can be used to distinguish the diffusing species. Equation (27) also shows that isotopic exchange can be slower than chemical diffusion of a component. This result is interesting because Lesher [1990, 1994] and van der Laan et al. [1994] showed that homogenization of isotopic ratio gradients of K, Ca, Sr, and Nd is typically more rapid than or at about the same rate as that of chemical concentration gradients.
5.3. $H_2O$ Diffusion at High $H_2O_2$: Controversy and Discussion

In light of recent progress, the calibration and speciation used by Zhang et al. [1991a] in extracting $D_{H_2O_m}$ are not accurate anymore. Hence $D_{H_2O_m}$ values are inaccurate. Nevertheless, because the total $H_2O$ diffusivity ($D^{*}_{H_2O}$) is constrained from experimental diffusion profiles, it is independent of the specific speciation model and $D_{H_2O}$. Therefore $D^{*}_{H_2O}$ can still be retrieved accurately from (22) from both $D_{H_2O}$ and the speciation model of Zhang et al. [1991a] as long as self-consistency is maintained. However, one cannot combine $D_{H_2O_m}$ of Zhang et al. [1991a] and a new, even a more accurate, speciation model (such as equation (10) above) to calculate $D^{*}_{H_2O}$ unless $H_2O_m$ and OH concentrations and $D_{H_2O_m}$ are recalculated using the new calibration.

Recently, Nowak and Behrens [1997] and Behrens and Nowak [1997] reported important new diffusion data in the AOQ (Table 1) melt with 0–9% $H_2O_2$ at 0.5–5 kbar and 800–1200°C. Nowak and Behrens [1997] found a very strong dependence of $D^{*}_{H_2O}$ on $H_2O_2$, especially at $H_2O_2 > 3\%$, which differs from the model of Zhang et al. [1991a]. Furthermore, they found that $D^{*}_{H_2O}$ decreases with increasing pressure. They fit their experimental diffusivity data as a linear function of $T$, $P/T$, and a polynomial function of $H_2O_2$. Behrens and Nowak [1997] examined the dependence of $H_2O_2$ diffusivity on the anhydrous composition of polymerized melts and found that $H_2O_2$ diffusivity does not change significantly from albitic to rhyolitic melt.

In order to examine whether the formulation of Zhang et al. [1991a] applies to high $T$ and low $H_2O_2$, Behrens and Nowak [1997] compared $D^{*}_{H_2O}$ values from their experiments with those calculated (and extrapolated) from Zhang et al. [1991a]. They calculated $D^{*}_{H_2O}$ by adopting the formulation for $D_{H_2O}$ of Zhang et al. [1991a] but using their own in situ speciation model [Nowak and Behrens, 1995]. They found disagreement in this comparison. Further, they calculated $D^{*}_{H_2O}$ at low 490°C and 0.5% $H_2O_2$ using their own equation [Nowak and Behrens, 1997] and found that the value is significantly different from the experimental value of Zhang et al. [1991a]. From these disagreements they concluded that the formulation of Zhang et al. [1991a] cannot be extrapolated to high temperature and that their own expression cannot be extrapolated to low temperature, possibly owing to the effect of glass transition. When they compared the shape of the $D^{*}_{H_2O}$ versus $H_2O_2$ curve, they found that the calculated curve using Zhang et al. [1991a] does not increase rapidly enough as $H_2O_2$ increases, especially at $H_2O_2 > 3\%$. From this disagreement they concluded that the formulation of Zhang et al. [1991a] cannot predict their experimental $D^{*}_{H_2O}$ at high $H_2O_2$.

Because Behrens and Nowak [1997] combined the speciation model of Nowak and Behrens [1995] and the $D_{H_2O}$ expression of Zhang et al. [1991a], their calculation of $D^{*}_{H_2O}$ using the formulation of Zhang et al. is not self-consistent. In Figure 10 I compare experimental $D^{*}_{H_2O}$ values of Nowak and Behrens [1997] and Behrens and Nowak [1997] with those calculated from Zhang et al. [1991a]. In Figure 10a, all the experimental data of Nowak and Behrens [1997] and Behrens and Nowak [1997] on AOQ melt and albitic melt at $H_2O_2 < 2\%$, $P = 1$ kbar are compared with calculated $D^{*}_{H_2O}$ using the formulation of Zhang et al. [1991a]. The agreement is excellent, demonstrating that the formulation of Zhang et al. [1991a] can be used to predict diffusivities at high $T$ and that the effect of glass transition is small. That is, one of the conclusions by Behrens and Nowak...
Figure 11. The value of ln \( D_{H_2O}^* \) versus 1/T, where \( C \) is the mass fraction (or weight percent) of \( H_2O \) and \( C_0 \) is the reference concentration chosen to be the mass fraction of 0.01 (i.e., 1 wt %). That is, \( D_{H_2O}^* C_0/C \) is \( D_{H_2O}^* \) at 1% \( H_2O \). Data are from Lapham et al. [1984], Zhang et al. [1991a], Wang et al. [1996], and Nowak and Behrens [1997]. The solid line is a straight-line fit through the data.

The mechanism for the rapid increase of \( D_{H_2O}^* \) with \( H_2O \) at high \( H_2O \) is not clear. It may result from an increase of \( D_{H_2O}^* \) with \( H_2O \) [Zhang and Behrens, 1998b, submitted manuscript, 1999] or from a significant contribution of OH to the diffusivity, or some other mechanisms (such as the formation of OH pairs proposed by Behrens and Nowak [1997]). Because preeruptive melts of explosive volcanic eruptions often contain 6% or more \( H_2O \), it is crucial to quantify the diffusivity of \( H_2O \) at both low and high \( H_2O \) for the quantitative modeling of bubble growth. Zhang and Behrens [1998b, submitted manuscript, 1999] are carrying out a comprehensive investigation of \( H_2O \) diffusion as a function of \( H_2O, T, \) and \( P \).

5.4. A Simple Formula for \( H_2O \) Diffusion at Low \( H_2O \) and 400°C–1100°C

Because the formulation of Zhang et al. [1991a] is difficult to use and because calibration of the infrared technique is still improving, I present a simple equation below for calculating \( D_{H_2O}^* \) at \( H_2O \) ≤ 2% for ease of use. The formulation of Zhang et al. [1991a] implies that at low \( H_2O \), \( D_{H_2O}^* \) is proportional to \( H_2O \) if local species equilibrium is maintained. Nowak and Behrens [1997] also showed that \( D_{H_2O}^* \) is proportional to \( H_2O \) at \( H_2O \) ≤ 2% at high \( T \). Hence diffusivity data are used to fit

\[
D_{H_2O}^* = \frac{C_0}{C} \exp \left( \frac{A - E_a}{RT} \right),
\]

where \( A \) is a constant, \( C \) is mass fraction of \( H_2O \), \( C_0 \) is the reference mass fraction of \( H_2O \), \( E_a \) is the effective activation energy (in J mol\(^{-1}\) K\(^{-1}\)) for \( H_2O \) diffusion. Figure 11 shows \( D_{H_2O}^* \) data at \( H_2O \) ≤ 2%; \( D_{H_2O}^* \) at 400°C–550°C calculated from \( D_{H_2O}^* \) data of Zhang et al. [1991a] assuming local species equilibrium, \( D_{H_2O}^* \) at 697°C of Wang et al. [1996], \( D_{H_2O}^* \) at 850°C from Lapham et al. [1984] with refit of Zhang et al. [1991a], and 0.5- to 1-kbar data of Nowak and Behrens [1997]. A small adjustment was made to the \( D_{H_2O}^* \) at 0.5–1 kbar using an activation volume of 9 cm\(^3\) mol\(^{-1}\) [Nowak and Behrens, 1997]. All these 1-bar \( D_{H_2O}^* \) values (400°C–1100°C) are shown in Figure 11. Although the data seem to show a small curvature in ln \( D_{H_2O}^* \) versus 1/T, the curvature is small and only slightly outside the experimental uncertainties. Therefore the effect of glass transition on the \( H_2O \) diffusion behavior is negligible [Zhang et al., 1991a; Watson, 1994]. A simple straight line is used to fit the data, yielding

\[
D_{H_2O}^* = (C/C_0) \exp \left[ -16.83 - \frac{10992}{T} \right],
\]

where \( T \) is in kelvins and \( D_{H_2O}^* \) is in m\(^2\) s\(^{-1}\). The above equation is applicable to 400°C–1200°C, 0–2% \( H_2O \), and 1 bar. The average (1σ) and maximum error in using the above equation to predict ln \( D_{H_2O}^* \) is 0.24 and 0.60. \( D_{H_2O}^* \) at higher \( H_2O \) and 800°C–1200°C can be calculated using the formulation of Nowak and Behrens [1997]. Work is under way on a general equation to predict \( D_{H_2O}^* \) at both low and high \( H_2O \) [see Zhang and Behrens, 1998b, submitted manuscript, 1999]. The main advantage of the above simple equation is its ease of use. However, it does not have the generality of the formulation of Zhang et al. [1991a] in that it cannot handle local disequilibrium, which may be important at low \( T \) (<550°C) and low \( H_2O \) (<0.3%).

6. CONCLUSIONS AND FUTURE DIRECTIONS

Major progress has been made on \( H_2O \) in silicate melts and glasses in the last 5 years, although there has
been confusion. I hope that the above review clarifies some of the confusion and controversies. There are still many unsolved issues. The following is a summary of our present understanding on several issues concerning H₂O in rhyolitic glasses and melts.

1. Despite extensive research, more work is still necessary for accurate calibration of the infrared technique for room temperature measurement of H₂O. The calibration is complicated because molar absorptivities depend on both H₂O content and the measurement temperature. Specifically, improvement is necessary for measurement of species concentrations at H₂O > 2.7% and for H₂O determination both below 0.2% and above 5%. Furthermore, interlaboratory comparison of bulk H₂O analyses between manometry and Karl-Fischer titration will be helpful. Besides room temperature calibrations, calibration for in situ high-temperature measurements is also much needed.

2. In studying the equilibrium of the homogeneous reaction H₂Oₘ + O ⇌ 2OH in rhyolitic melt and glass, experimental data using the quench technique are almost certainly valid as long as the experimental temperature is low enough (typically 400°–600°C) for the species to be quenched. The interpretation of the in situ speciation data, on the other hand, must await the quantification of the temperature effect on molar absorptivities. On the basis of quenched speciation data up to 2.4% H₂O, and using the most recent calibration, the equilibrium constant for the species reaction in rhyolitic melt and glass is independent of H₂O, and can be expressed as [Zhang et al., 1997a]

\[ K_2 = \frac{[\text{OH}]^2}{[[\text{H}_2\text{O}_\text{m}]][\text{O}]} = 6.53e^{-3110/T}. \]

Better room temperature calibration at higher H₂O in situ high-temperature calibration and in situ investigation of species equilibrium will allow improvement of the above speciation model.

3. Many previous solubility models (including the recent model of Moore et al. [1998]) do not account for H₂O speciation in silicate melts. They are therefore very useful for interpolation but not useful for extrapolation. Using the recent speciation model, an updated solubility model has been developed using the solubility data of Holtz et al. [1992, 1995], leading to the following expression for the equilibrium constant for the heterogeneous reaction H₂O (vapor) ⇌ H₂Oₘ (melt):

\[ K_1 = \frac{[\text{H}_2\text{O}_\text{m}]^{f_{\text{H}_2\text{O}}}}{[\text{H}_2\text{O}]^{f_{\text{H}_2\text{O}}} + \exp[(-13.869 + 0.0002474P) + (3890.3 - 0.3948P)/T]]. \]

The solubility of the H₂O component at 800°–1350°C and 0–8000 bars can be calculated using

\[ [\text{H}_2\text{O}] = [\text{H}_2\text{O}_\text{m}] + 0.5[\text{OH}] = K_1f \]

\[ + \frac{K_1K_2f(1 - K_1f)}{K_1K_2f + [(K_1K_2f)^2 + 4K_1K_2f(1 - K_1f)]^{1/2}}, \]

where \( f \) is the fugacity of H₂O and \( K_1 \) and \( K_2 \) are given above. The accuracy of the above equation approaches the analytical accuracy (1σ accuracy of 0.19 wt % H₂O). The above expressions may be extrapolated to 500°C. Future experimental investigation of H₂O solubility at both high pressure (>3 kbar) and low pressure (<100 bars) and as a function of temperature will be important to further constrain the solubility model and mechanism.

4. At H₂O \( \approx 2\% \) the H₂O diffusion model of Zhang et al. [1991a] can be used to accurately (meaning with an average accuracy of 30% relative) calculate \( D^*_\text{H}_2\text{O} \) in rhyolitic melt from 400°C to 1200°C. Glass transition does not significantly affect the diffusion behavior. A simple equation for the calculation of H₂O diffusivity (in m² s⁻¹) is

\[ D^*_\text{H}_2\text{O} = \frac{(C/C_0) \exp[-16.83 - 10992/T]}{[\text{H}_2\text{O}]^{f_{\text{H}_2\text{O}}} + \exp[(-13.869 + 0.0002474P) + (3890.3 - 0.3948P)/T]}. \]

where \( T \) is in kelvins, \( C \) is H₂O content, \( C_0 \) is the reference concentration of 1 wt % H₂O, and \( D^*_\text{H}_2\text{O} \) is in m² s⁻¹. The above expression is applicable to 400°–1200°C, 1 bar, and \( \leq 2\% \) H₂O. At H₂O > 2%, neither the formulation of Zhang et al. [1991a] nor the above equation is applicable. The work of Nowak and Behrens [1997] and Behrens and Nowak [1997] significantly expanded the database on H₂O diffusion. Their H₂O diffusivity expressions are applicable at H₂O > 1% and \( \geq 800°C \). Because Nowak and Behrens [1997] used a polynomial to fit their experimental diffusivity data, their expression may not extrapolate well. Future experimental study is necessary for formulating a general model to encompass H₂O diffusion at both low and high H₂O and as a function of \( T \) and \( P \) and for understanding the diffusion mechanism of the H₂O component at higher H₂O.

Improvement on the above issues will not only constrain the above issues, but also will impact on our understanding of volcanic eruptions, the thermodynamics, transport, and other physical and chemical properties of hydrous magma, and glass durability.

ACKNOWLEDGMENTS. The first draft of this paper (presented at the Geological Conference for the Centennial Celebration of Peking University) was started in 1997 and finished in early 1998 while I was visiting the Institut für Mineralogie, Universität Hannover, Germany. I thank H. Behrens for his hospitality during my visit. Many thanks to H. Behrens, E. J. Essene, F. Holtz, R. A. Lange, M. Nowak, A. Withers, and Z. Xu for informal reviews and stimulating discussion and to my students and coworkers over the last 10 years. Detailed and constructive reviews by B. de Jong, M. C. Wilding, and P. deMenocal are appreciated. This work is partially supported by NSF grants EAR-9458368 and EAR-9706107.

Roel Snieder was the Editor responsible for this paper. He thanks Bernard de Jong and Martin C. Wilding for the technical reviews and Peter B. deMenocal for the cross-disciplinary review.
REFERENCES


Behrens, H., C. Romano, M. Nowak, F. Holtz, and D. B. Dingwell, Near-infrared spectroscopic determination of water species in glasses of the system MAI₅O₈ (M = Li, Na, K); An interlaboratory study, Chem. Geol., 128, 41–63, 1996.
Behrens, H., A. Withers, and Y. Zhang, In situ IR spectroscopy on hydrous albite and rhyolitic glasses and its implications for water speciation and water reactions in silicate glasses and melts, Mineral Mag., 624, 139–140, 1998.


