Diffusion of H, C, and O Components in Silicate Melts

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INTRODUCTION

Silicate melts are complicated in structure and composition. Hence, diffusion in a melt (in this chapter, a melt includes both liquid and glass) can be very complicated due to the presence of many components, each of which can be present in different species, as well as various kinds of diffusion, such as self-diffusion, tracer diffusion, interdiffusion, effective binary diffusion and multi-component diffusion. In this chapter, the diffusion of H, C and O components is reviewed. H may be in the form of H₂O molecules (hereafter referred to as H₂Oₘ), OH groups (hereafter referred to as OH), H₂ molecules (hereafter referred to as H₂), and other species. H₂Oₘ and OH will be collectively referred to as the H₂O component, or the hydrous component. C may be present as CO₂ molecules (hereafter referred to as CO₂, molec), CO₃²⁻ groups (hereafter referred to as CO₃²⁻), and other species (such as CO and CH₄). CO₂, molecules and CO₃²⁻ groups will be collectively referred to as total CO₂ (CO₂, total) or the CO₂ component. O may be present in the form of network oxygen (such as bridging oxygen, non-bridging oxygen, and free O²⁻), H₂Oₘ, OH, CO₂, molec, CO₃²⁻, O₂ molecules (hereafter referred to as O₂), etc. H₂O and CO₂ are the major volatile components in melts and their diffusion plays a critical role in bubble growth (e.g., Proussevitch and Sahagian 1998; Gardner et al. 2000; Liu and Zhang 2000; Wang et al. 2009), magma degassing (e.g., Bottinga and Javoy 1990; Navon and Lyakhovsky 1998; Proussevitch and Sahagian 1998), magma fragmentation (Zhang 1999a), volcanic eruptions (e.g., Sparks et al. 1999). Hence, understanding H₂O and CO₂ diffusion is important in terms of volcanic hazard mitigation and global volatile budgets. Diffusion of H₂O may also play a role during diffusive and convective growth and dissolution of hydrous minerals (e.g., Chen and Zhang 2008, 2009; Zhang 2008). In glass industry, H₂O diffusion is important to glass stability and strength (e.g., Doremus 1973). On the other hand, oxygen is the most abundant element in silicate melts, and its diffusion controls many reactions and transport properties of melts and is related to the melt structure. The diffusion of H₂O, CO₂ and oxygen is assessed together because of the following: (1) The diffusion of these three components is all affected by the presence of multiple species. Hence, the diffusion belongs to the same category of multi-species diffusion. (2) To understand oxygen diffusion, it is often necessary to understand the diffusion of the individual oxygen species including especially H₂O (as well as other oxygen-bearing species such as bridging oxygen, non-bridging oxygen, free O²⁻, O₂ molecules, OH, CO₂ and CO₃²⁻). (3) As the major volatile components in silicate melts,
H$_2$O diffusion and CO$_2$ diffusion often must be considered together. For completeness of this review, molecular H$_2$ and O$_2$ diffusion is also included. Below, we first review H$_2$O (including OH) and molecular H$_2$ diffusion, then CO$_2$, and finally oxygen diffusion (including molecular O$_2$ diffusion). Other possible species of H, C, and O include CO and CH$_4$. However, in natural silicate melts, no data are available for the diffusion of these species, and the concentrations of these species are low, meaning that they are unlikely to play a major role in the transport of H, C and O in natural silicate melts.

**DIFFUSION OF THE H$_2$O COMPONENT**

A review covering H$_2$O diffusion was published recently (Zhang et al. 2007). Nonetheless, major progress has been made since then. As will be seen below, syntheses of experimental data to formulate more general models in several silicate melts have been carried out since 2007. Because H$_2$O speciation is the key in understanding the complicated behavior of H$_2$O diffusion, we first discuss both the equilibrium and kinetic aspects of H$_2$O speciation to prepare for the discussion of H$_2$O diffusion.

**H$_2$O speciation: equilibrium and kinetics**

In natural silicate melts, H is present in the oxidized form as the hydrous component. Dissolved H$_2$O in silicate melts is present in at least two species: one is H$_2$O$_m$, and the other is OH (Stolper 1982a,b). Total H$_2$O content will be referred as H$_2$O$_t$. Under highly reducing conditions, there may also be molecular hydrogen (H$_2$) that may transport the hydrogen component. In natural and experimental melts, the presence of H$_2$ has not been detected yet. H$_2$ diffusion will be discussed in a later section.

H$_2$O$_m$ and OH can interconvert through the following reaction in melts (Stolper 1982a,b):

\[
H_2O_m (\text{melt}) + O(\text{melt}) \rightleftharpoons 2OH(\text{melt})
\]

where O means an anhydrous oxygen ion, ionic charge is ignored, and the phase is indicated inside the parentheses. The two hydrous species, H$_2$O$_m$ and OH, can be detected easily by near-infrared (NIR) spectroscopy (Stolper 1982a; Cherniak et al. 2010, this volume). To convert IR peak heights or areas to H$_2$O$_m$ and OH concentrations requires independent calibration to determine molar absorptivities. The equilibrium constant of the above reaction can be written as:

\[
K = \frac{[OH]^2}{[H_2O_m][O]}
\]

where brackets mean activities approximated by mole fractions, and the subscript “e” means at stable or metastable equilibrium. The mole fractions are calculated as:

\[
[H_2O_m] = \frac{C_w}{18.015} \frac{C_w}{C_w + (100 - C_w)} \frac{1}{W}
\]

\[
[OH] = 2([H_2O_t] - [H_2O_m])
\]

\[
[O] = 1 - [H_2O_m] - [OH]
\]

where $C_w$ is wt% of H$_2$O$_t$ (at 2 wt%, $C_w = 2$), $C_1$ is wt% of H$_2$O$_m$, and $W$ is the molar mass of the dry melt on a single oxygen basis (Stolper 1982a; Zhang 1999b; see Table 1). The composition
Table 1. Chemical composition (wt%) of melts for H_2O diffusion studies.

<table>
<thead>
<tr>
<th>ID</th>
<th>Composition</th>
<th>SiO_2</th>
<th>TiO_2</th>
<th>Al_2O_3</th>
<th>FeO</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na_2O</th>
<th>K_2O</th>
<th>P_2O_5</th>
<th>W</th>
<th>Ref</th>
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<td>1.00</td>
<td>0.03</td>
<td>0.52</td>
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<td>4.88</td>
<td></td>
<td></td>
<td>32.55</td>
<td>a-c</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>32.60</td>
<td>d</td>
</tr>
<tr>
<td>3</td>
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<td>13.00</td>
<td>0.50</td>
<td>0.1</td>
<td>0.5</td>
<td>3.8</td>
<td>4.7</td>
<td></td>
<td></td>
<td>32.39</td>
<td>e</td>
</tr>
<tr>
<td>4</td>
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<td>0.04</td>
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<td>0.61</td>
<td>0.06</td>
<td>0.22</td>
<td>4.14</td>
<td>3.66</td>
<td></td>
<td></td>
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<td></td>
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<td>f</td>
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<td>CBS rhyolite</td>
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<tr>
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<td></td>
<td>33.84</td>
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<td>0.67</td>
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<td></td>
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<td>13.90</td>
<td>12.5</td>
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<td></td>
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</tr>
<tr>
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<td>Basalt 2</td>
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<td>1.50</td>
<td>16.11</td>
<td>10.84</td>
<td>0.20</td>
<td>7.60</td>
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<td>3.56</td>
<td></td>
<td></td>
<td>37.15</td>
<td>k</td>
</tr>
</tbody>
</table>

The compositions are listed on the anhydrous basis. W is weight of the dry melt per mole of oxygen (g/mol) assuming all Fe is ferrous. (Including ferric Fe would lower W values slightly.) For simplicity in treatment, small difference in W between similar compositions is ignored in literature. For example, for compositions 1–4, W = 32.49; for compositions 5 and 6, W = 33.24 (Wang et al. 2009 used a slightly different value of 33.14 by considering Fe_2O_3), etc. MAC is a peraluminous rhyolite; NSL and CBS rhyolite are peralkaline rhyolites.

and $W$ for some melts are listed in Table 1. The temperature dependence of $K$ takes the following form (e.g., Zhang et al. 1997a):

$$\ln K = A + B/T$$

(4)

where $A$ and $B$ are constants related to the standard state entropy and enthalpy of Reaction (1).

The equilibrium speciation of rhyolite, dacite and andesite melts has been investigated. Before an understanding of equilibrium speciation, it is necessary to understand (i) the kinetics on how long it would take to reach equilibrium (e.g., Zhang et al. 1991a, 1995, 1997b, 2000; Withers et al. 1999; Liu et al. 2004a; Hui et al. 2008), and (ii) the kinetic effect on the species concentrations during cooling (Dingwell and Webb 1990; Zhang 1994) so as to understand whether species concentrations can be preserved upon quench. These have been reviewed in Zhang (1999b), Zhang et al. (2007) and Hui et al. (2008) and only a brief summary is given below. Speciation data include both quench data and in situ data. Both the quench data and in situ data suffered from problems in the early stages as shown below. The experimental studies of H$_2$O speciation are probably the most debated experimental topics concerning H$_2$O in silicate melts, with two major issues (the quench effect on quench experiments, and the temperature dependence of molar absorptivities on in situ IR analyses) summarized below.

**Quench effect.** The equilibrium speciation data obtained by the quench technique before 1990 (e.g., Silver and Stolper 1989; Stolper 1989; Silver et al. 1990) at temperatures above ~1000 K suffered from the quench effect. The data obtained at significantly lower temperatures in these papers are generally acceptable. The time for Reaction (1) to reach equilibrium decreases as temperature and H$_2$O$_t$ increase. When the experimental temperature is high (typically ~1000 K, but depending on H$_2$O$_t$ and cooling rate), it often takes less than a second (shorter at higher H$_2$O$_t$) for Reaction (1) to reach equilibrium. That is, there is continuous reaction as the sample cools down. To facilitate discussion, we define quotient $Q$ as:

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

The expression of $Q$ is the same as that of $K$ except that $K$ is restricted to the case when equilibrium is reached. If $Q > K$, the reaction goes to the left to form H$_2$O$_m$. Otherwise, it goes to the right to form OH. For a sample cooled to room temperature, the measured species concentration can be used to calculate $Q$, which is the apparent equilibrium constant $K_{ae}$ of this sample (it is called “apparent equilibrium” since the sample did not exactly reach equilibrium at the corresponding temperature). This apparent equilibrium constant corresponds to an apparent equilibrium temperature ($T_{ae}$) as follows,

$$\ln Q = A + \frac{B}{T_{ae}}$$

(6)

That is, the apparent equilibrium temperature is the temperature calculated from the quotient $Q$ assuming $Q$ were the same as $K$ even though equilibrium is not reached at any temperature (comparing Eqns. 4 and 6). During cooling at various quench rates, the variation of $Q$ and $T_{ae}$ as a function of temperature is illustrated in Figure 1 (Zhang 1994, 2008; Zhang et al. 1997b, 2000).

Starting from a high temperature, if cooling rate is high, the resulting $T_{ae}$ after cooling down is also high, and vice versa. Even at a high cooling rate, species concentrations may change upon cooling. For a rhyolite melt containing 2.5 wt% H$_2$O$_t$ equilibrated at a temperature of 1000 K and cooled down at 70 K/s, the resulting $T_{ae}$ is only about 800 K (Zhang et al. 2000), rather than the experimental equilibrium temperature of 1000 K. Dingwell and Webb (1990) were the first to analyze this problem using the concept of cooling-rate-dependent glass transition temperature, and assumed that the apparent equilibrium temperature for Reaction (1) is similar to the glass transition temperature, which was verified later (e.g., Zhang et al.
Because the temperature was high for many early experiments using the quench method, equilibrium H$_2$O speciation was not fully quenchable even with the fastest achievable quench rate. That is, the reported data did not reflect true speciation at the experimental temperature; only $T_{ae}$ can be obtained. On the other hand, when the experimental temperature is low enough (usually below 900 K, but depending on H$_2$O t and quench rate), reaction during quench is negligible and $T_{ae}$ is roughly the same as the experimental temperature. However, the experimental temperature cannot be too low (such as < 600 K) either, otherwise it would require too long a duration to reach equilibrium. Based on the above considerations, the appropriate temperature range for quench method is typically 650-900 K (which are referred to as intermediate temperatures).

**Dependence of molar absorptivities on temperature.** The first *in situ* IR measurements indicated that the molar absorptivities depend on temperature (e.g., Keppler and Bagdassarov 1993). However, for some years afterwards, temperature effects were not considered in interpreting *in situ* IR speciation data (Nowak and Behrens 1995; Shen and Keppler 1995; Sowerby and Keppler 1999) and the results were inconsistent with speciation data quenched from intermediate temperatures (e.g., Zhang et al. 1991a, 1995; Ihinger et al. 1999). To resolve the inconsistency, two groups with different views collaborated (Zhang and Behrens 1998; Withers et al. 1999). They demonstrated that (i) molar absorptivities vary with temperature even below the glass transition, which led to an apparent change in species concentrations as well as inaccuracy of $K$ values in Nowak and Behrens (1995), Shen and Keppler (1995), and Sowerby and Keppler (1999); and (ii) after accounting for the temperature effect of the molar absorptivities, the speciation data from quench experiments from intermediate temperatures and those from *in situ* experiments are consistent, as also demonstrated by other studies (Zhang 1999b; Withers and Behrens 1999; Nowak and Behrens 2001; Behrens and Nowak 2003).
However, the two data sets cover different temperatures (with only small overlap) and seem to indicate a slightly different standard state enthalpy change for Reaction (1).

**Summary of speciation data.** After two vigorous debates discussed above, one on the quench effect, and the other on the *in situ* measurements, it is now known that the quench method can be used to obtain reliable speciation data when the experimental temperature is low enough (usually below ~900 K, but the exact temperature depends on H$_2$O$_t$ and quench rate, and must be determined experimentally for a given system), and the *in situ* method can also be used to obtain reliable speciation data when the temperature dependence of the molar absorptivities is accounted for. In addition, the speciation constant as a function of temperature may be inferred by estimation of the glass transition temperature from viscosity models and assuming the glass transition temperature is the apparent equilibrium temperature (Dingwell and Webb 1990; Zhang et al. 2003); referred to as the fictive temperature method hereafter. Subsequently, speciation in the following melts have been investigated further: albite and some synthetic sodium-calcium aluminosilicate melts (Ohlhorst et al. 2000), AOQ (Q$_{28}$Ab$_{38}$Or$_{34}$ where Qz means quartz, Ab means albite and Or means orthoclase, and the values indicate wt%) melt (Nowak and Behrens 2001; Behrens and Nowak 2003), dacite melt (Liu et al. 2004a), andesite melt (Botcharnikov et al. 2006), NS4 (Na$_2$O-4SiO$_2$, or Na$_2$Si,O$_4$) and NS6 (Na$_2$O-6SiO$_2$, or Na$_2$Si$_6$O$_{13}$) melts (Behrens and Yamashita 2008), high-pressure rhyolite melts (Hui et al. 2008), and haploandesite melt (Ni et al. 2009a). The precision of the speciation data depends on the method (the $2\sigma$ precision in $\ln K$ is often about 0.025 for the quench method, 0.1 for the *in situ* method, and 0.1 to 0.5 for the fictive temperature method). The accuracy, on the other hand, depends on the accuracy of the infrared calibration for species concentrations, which is not well characterized. For example, even for rhyolite glass, which has been studied most extensively (Newman et al. 1986; Zhang et al. 1997a; Withers and Behrens 1999), the possible variation of molar absorptivities with H$_2$O$_t$ and quench rate is still not accurately known. Studies on hydrous speciation in Fe-rich melts such as dacite melt have another difficulty: the high iron concentration leads to significant and broad absorption bands that overlap with hydrous species bands in the NIR. What makes the problem worse is the variation of the shape and intensity of the iron-related bands before and after heating. Hence, many authors have opted to investigate iron-free analogs of natural silicate melts.

With the above preamble and precaution, some speciation data are shown and compared in Figure 2. The pressure effect on speciation is examined by Hui et al. (2008); $K$ may increase or decrease with pressure, but the effect is not very large and not included in Figure 2. From Figure 2, several observations can be made: (i) $K$ in sodium silicates (NS4 and NS6) is much greater than in natural aluminosilicate melts and their analogs (as well as albite melt), supporting the suggestion of formation of NaOH clusters (Kohn et al. 1989), especially in the absence of Al; (ii) $K$ in a natural rhyolite is similar to that in haplorhyolite (AOQ); the similarity also holds for natural andesite and haploandesite; (iii) $K$ increases with temperature (meaning Reaction (1) is an endothermic process); (iv) $K$ increases slightly from rhyolite to dacite to andesite melts, which means that $K$ values do not simply increase with Na$_2$O because the Na$_2$O (as well as the K$_2$O) content decreases from rhyolite to dacite to andesite melts. The speciation models (Zhang et al. 1997a; Liu et al. 2004a; Ni et al. 2009a) that are often used in diffusion studies (Zhang and Behrens 2000; Behrens et al. 2007; Ni and Zhang, 2008; Behrens and Zhang 2009; Wang et al. 2009; Ni et al. 2009a,b) are:

$$K_{\text{rhyolite}} = \exp\left(1.876 - \frac{3110}{T}\right)$$  \hspace{1cm} (7a)  

$$K_{\text{dacite}} = \exp\left(1.49 - \frac{2634}{T}\right)$$  \hspace{1cm} (7b)  

$$K_{\text{haploandesite}} = \exp\left(1.55 - \frac{2453}{T}\right)$$  \hspace{1cm} (7c)
Other expressions of equilibrium constants are available (e.g., Ihinger et al. 1999; Nowak and Behrens 2001; Hui et al. 2008), but they have not been much used in diffusion studies either because they are new, or because they are complicated, or because of the need to maintain internal consistency with other studies. Using different $K$ values would impact the retrieval of the diffusivities of individual $H_2O$ species but only negligibly the retrieval of $D_{H_2O_t}$ because the latter is essentially constrained by the length and shape of an $H_2O_t$ concentration profile.

More detailed studies of hydrous species reaction kinetics have been carried out through isothermal experiments or controlled cooling rate experiments (Zhang et al. 1995, 1997b, 2000; Liu et al. 2004a; Hui et al. 2008). However, in treating $H_2O$ diffusion, for simplicity, quasi-equilibrium is often assumed for the species reaction, and complicated kinetics are not incorporated. Hence, the kinetics is not discussed in detail here.

The variations of $H_2O_m$ and OH concentrations with $H_2O_t$ for a fixed equilibrium constant $K$ are shown in Figure 3. It can be seen that $H_2O_m$ is not proportional to $H_2O_t$ (that is, the $X_m/X$ curve in Fig. 3 is not a horizontal line). Instead, at low $H_2O_t$, $H_2O_m$ is roughly proportional to the square of $H_2O_t$ (in other words, $H_2O_m/H_2O_t$ ratio is proportional to $H_2O_t$), meaning a more rapid increase of $H_2O_m$ concentration as $H_2O_t$ increases. Below about 0.2 wt% $H_2O$, almost all $H_2O_t$ is OH (which does not mean that OH would play a main role in $H_2O$ diffusion, as will be clear later in this chapter). This behavior arises from the stoichiometric coefficient 2 for OH in Reaction (1), which means the square of OH concentration is proportional to $H_2O_m$ concentration, leading to the complicated relation between $H_2O_m$ and $H_2O_t$ concentrations as well as the complicated behavior of $H_2O_t$ diffusion.
Technological improvements and theoretical modeling were the keys in the development of H$_2$O diffusion studies. Most H$_2$O diffusion experiments can be characterized as follows: hydration of an originally homogeneous and almost water-free sample by exposure to water vapor or fluid, dehydration of an initially homogeneous hydrous glass by exposure to dry N$_2$ or Ar, and diffusion couple (two samples with different water contents juxtaposed against each other). In the early years of H$_2$O diffusion studies in silicate melts, diffusion profiles could not be measured, so either the bulk H$_2$O mass loss from dehydration or mass gain from hydration was determined by weight change or mass spectrometry or infrared spectroscopy, from which the diffusivity was inferred (e.g., Shaw 1974). Later, advancements in ion microprobe analyses (Coles and Long 1974; Hofmann 1974) allowed the microanalytical determination of H$_2$O diffusion profiles (Delaney and Karsten 1981), but species concentrations could not be determined. Afterwards, advancement in infrared spectroscopy (Stolper 1982a,b; Acocella et al. 1984) led to the measurement of concentration profiles of both H$_2$O$_m$ and OH species (Zhang et al. 1991a). Coupled speciation and diffusion studies (Zhang et al. 1991a) helped establish the basic mechanism of H$_2$O diffusion. Later studies, especially those at high temperatures, used only H$_2$O$_t$ concentration profiles from micro-IR to model H$_2$O diffusion because species concentrations cannot be quenched from high temperatures.

In the glass and materials science literature, H$_2$O diffusion studies began in the 1960’s. The studies were limited to low H$_2$O concentrations, with H$_2$O$_t$ typically no more than 0.1 wt% (e.g., Drury and Roberts 1963; Cockram et al. 1969; Burn and Roberts 1970; Lanford et al. 1979; Houser et al. 1980; Tsong et al. 1980; Nogami and Tomozawa 1984a,b; and the recent review by Shelby 2008). The average OH concentration (proportional to H$_2$O$_t$) in a thin wafer upon heat treatment is monitored by IR and the diffusivity is obtained from the diffusive mass loss equation for a thin wafer (Crank 1975):

$$F = \frac{4\sqrt{D}}{\sqrt{\pi L}} \sqrt{t}$$

(8)
where $F$ is the fractional mass loss ($\text{H}_2\text{O}_t$ loss divided by initial $\text{H}_2\text{O}_t$), $L$ is the thickness of the wafer, $t$ is time, and $D$ is apparent diffusivity (more specifically, $D$ is diffusion-out diffusivity of $\text{H}_2\text{O}_t$, denoted as $D_{\text{out}}$, see below). It is often observed that $D_{\text{out}}$ is proportional to $\text{H}_2\text{O}_t$, from which it was suggested that the diffusing species is $\text{H}_2\text{O}_m$ (because the $\text{H}_2\text{O}_m$ concentration is proportional to the square of the $\text{H}_2\text{O}_t$ concentration; a rigorous explanation can be found below in Eqn. 11) (Doremus 1969, 1973; Ernsberger 1980; Smets and Lommen 1983; Nogami and Tomozawa 1984a,b), but other explanations included the interdiffusion of hydronium $\text{H}_3\text{O}^+$ and cations (e.g., Cockram et al. 1969; Doremus 1975; Lanford et al. 1979; Houser et al. 1980; Tsong et al. 1980), or the depolymerization of the silicate network (e.g., Haller 1963; Roberts and Roberts 1966; Delaney and Karsten 1981). These other explanations gradually become less cited as later direct measurements of species concentration profiles and modeling showed that assuming $\text{H}_2\text{O}_m$ as the diffusing species can model the detailed diffusion profiles almost perfectly.

Shaw (1974) was the first to investigate $\text{H}_2\text{O}$ diffusion in a geologically relevant silicate melt. He determined total mass gain due to hydration, and inferred that $\text{H}_2\text{O}_t$ diffusivity depends strongly on $\text{H}_2\text{O}_t$ content. Jambon (1979) carried out dehydration experiments and measured the mass loss from the sample. This study was later corrected by Jambon et al. (1992): because of an error in the estimated initial $\text{H}_2\text{O}_t$ in the sample (0.38 wt% in Jambon 1979 versus the correct 0.114 wt% in Jambon et al. 1992), the diffusion-out $\text{H}_2\text{O}_t$ diffusivity was corrected upward by a factor of 11.

Delaney and Karsten (1981) and Karsten et al. (1982) were the first to measure $\text{H}_2\text{O}$ concentration profiles using the ion microprobe after hydration experiments. The profiles were fit by numerical solutions assuming some dependence of $D_{\text{H}_2\text{O}_t}$ on $\text{H}_2\text{O}_t$. Good fits were obtained for $D_{\text{H}_2\text{O}_t} = D_0 \exp(bC_w)$ where $C_w$ is the $\text{H}_2\text{O}_t$ concentration and $D_0$ and $b$ are two fitting parameters. Hence, it was assumed that $D_{\text{H}_2\text{O}_t}$ depends exponentially on $\text{H}_2\text{O}_t$. However, the expression does not work at low $\text{H}_2\text{O}_t$ (such as below 0.5 wt%) because it implies that $D_{\text{H}_2\text{O}_t}$ approaches a constant as $C_w$ approaches zero, but prior experimental data in the glass science literature showed that $D_{\text{H}_2\text{O}_t}$ is proportional to $C_w$ even down to very low $C_w$. Lapham et al. (1984) used a similar technique and compared diffusion of $^1\text{H}_2\text{O}$ and $^3\text{H}_2\text{O}$ (or $\text{D}_2\text{O}$) in rhyolite melts using ion microprobe measurements. Their data apparently showed that the $^1\text{H}_2\text{O}$ diffusivity was 2 times the $^3\text{H}_2\text{O}$ diffusivity. However, a later publication from the same laboratory (Stanton et al. 1985) retracted this claim and found no measurable difference between $^1\text{H}_2\text{O}$ and $^3\text{H}_2\text{O}$ diffusivities.

Wasserburg (1988) analyzed the role of $\text{H}_2\text{O}$ speciation in $\text{H}_2\text{O}$ diffusion. Zhang et al. (1991a) were the first to utilize FTIR to measure concentration profiles of both $\text{H}_2\text{O}_m$ and OH species in dehydration studies of natural obsidian, at 676-823 K, 0.1 MPa, and ≤ 1.7 wt% $\text{H}_2\text{O}_t$. By considering the interconversion reaction between $\text{H}_2\text{O}_m$ and OH and the diffusion of both $\text{H}_2\text{O}_m$ and OH in concert, they concluded that OH diffusivity is negligible compared to $\text{H}_2\text{O}_m$ diffusivity (i.e., $\text{H}_2\text{O}_m$ is the diffusing species), and $\text{H}_2\text{O}_m$ diffusivity is roughly independent of $\text{H}_2\text{O}_t$ in the samples studied. At low $\text{H}_2\text{O}_t$, a constant $\text{H}_2\text{O}_m$ diffusivity leads to proportionality between the $\text{H}_2\text{O}_m$ diffusivity and $\text{H}_2\text{O}_t$ content, consistent with the glass science literature. The much higher diffusivity of $\text{H}_2\text{O}_m$ than OH is understandable because $\text{H}_2\text{O}_m$ is a neutral molecule hence its diffusion does not require breaking strong bonds, whereas OH is bonded to other cations ($\text{Si}^{4+}$, $\text{Al}^{3+}$, $\text{Na}^+$, etc) and its motion requires breaking strong bonds in the silicate structure. In terms of particle size, $\text{H}_2\text{O}_m$ is similar or slightly smaller than OH (Shannon 1976; Zhang and Xu 1995). Zhang et al. (1991a) also distinguished $\text{H}_2\text{O}_t$ diffusivities during diffusion-out (dehydration) versus diffusion-in (hydration) experiments (Moulson and Roberts 1961). Because of the dependence of $D_{\text{H}_2\text{O}_t}$ on $\text{H}_2\text{O}_t$ content, the diffusion-in diffusivity is 1.78 times the diffusion-out diffusivity when $D_{\text{H}_2\text{O}_t}$ is proportional to $\text{H}_2\text{O}_t$ under otherwise identical conditions (see also Wang et al. 1996). Zhang and Stolper (1991) investigated $\text{H}_2\text{O}$ diffusion in basalt melt at 1573-1773 K, 1.0 GPa, and ≤ 0.42 wt% $\text{H}_2\text{O}_t$, and found that the $\text{H}_2\text{O}_t$
diffusivity is roughly proportional to $H_2O_t$, consistent with $H_2O_m$ being the diffusing species and the $H_2O_m$ diffusivity being independent of $H_2O$. Jambon et al. (1992) re-interpreted their earlier dehydration data and found that (i) the data are consistent with Zhang et al. (1991a) and (ii) disequilibrium in Reaction (1) can significantly affect $D_{H_2O}$.

Nowak and Behrens (1997) carried out diffusion couple experiments and investigated $H_2O$ diffusion in a synthetic rhyolite melt (AOQ) at 1073-1473 K, 0.05-0.5 GPa, and ≤ 9.0 wt% $H_2O_t$. They demonstrated that the $H_2O_t$ diffusivity at $H_2O_t > 3$ wt% increases exponentially with $H_2O_t$, implying that the $H_2O_m$ diffusivity cannot be constant but must increase with $H_2O_t$ content at $H_2O_t > 3$ wt%. They fit $\log D_{H_2O_t}$ as a polynomial function of $H_2O_t$. Zhang and Behrens (2000) studied $H_2O$ diffusion in rhyolite melts at 673-1473 K, 0.0001-0.81 GPa, and ≤ 7.7 wt% $H_2O_t$. They confirmed the observations of Nowak and Behrens (1997) and found that the diffusion profiles can be accurately modeled by assuming $H_2O_m$ is the diffusing species and $D_{H_2O_m}$ increases exponentially with $H_2O_t$, $D_{H_2O_m} = D_0 e^{aX}$, where $X$ is mole fraction of $H_2O_t$, $D_0$ is the $D_{H_2O_m}$ value as $X$ approaches zero, and $a$ is a parameter characterizing how rapidly $D_{H_2O_m}$ increases with $H_2O_t$. The exponential increase means that at low $H_2O_t$, $D_{H_2O_m}$ increases only slowly with $H_2O_t$ and can be treated roughly as a constant (e.g., for $a = 25$ and from 0 to 1 wt% $H_2O_t$, $e^{aX}$ varies from 1 to 1.56, only slightly outside the experimental uncertainty of diffusivity determinations at high temperatures), consistent with the observations of Zhang et al. (1991a). The exponential increase is also consistent with the diffusivities of neutral molecular species such as Ar (Behrens and Zhang 2001) and $CO_2$ (Watson et al. 1982; Watson 1991).

Later experimental studies in general followed the framework established in Zhang et al. (1991a), Zhang and Stolper (1991), and Zhang and Behrens (2000). Freda et al. (2003) investigated $H_2O$ diffusion in a trachyte melt at 1334-1601 K, 1 GPa, and ≤ 2.0 wt% $H_2O_t$. Okumura and Nakashima (2004, 2006) developed the in situ FTIR measurements of $H_2O$ loss due to dehydration to obtain diffusivities, and reported results on rhyolite melts at ≤ 4.1 wt% $H_2O_t$ and on dacite, andesite and basalt melts at ≤ 1.1 wt% $H_2O_t$. Their method works well for rapidly obtaining diffusion data but cannot resolve how $D_{H_2O_t}$ depends on $H_2O_t$. Liu et al. (2004b) explored $H_2O$ diffusion in dacite melts by dehydration experiments at 824-910 K, ≤ 0.15 GPa, and ≤ 2.5 wt% $H_2O_t$. Behrens et al. (2004) studied $H_2O$ diffusion in dacite and andesite melts at 1458-1858 K, 0.5-1.5 GPa, and ≤ 6.3 wt% $H_2O_t$; some of their data are consistent with concentration-independent $D_{H_2O_t}$. Behrens et al. (2007) obtained some $H_2O$ diffusion data in rhyolite melts in a study comparing oxygen and $H_2O$ diffusion. Ni and Zhang (2008) further resolved the pressure effect on $H_2O$ diffusion in rhyolite melts and constructed a general $H_2O$ diffusivity model over a large range of $T$, $P$ and $H_2O_t$. Behrens and Zhang (2009) and Wang et al. (2009) quantified $H_2O$ diffusion in peralkaline rhyolite melts. Ni et al. (2009a,b) examined $H_2O$ diffusion in dacite and haploandesite melts. All the melt compositions that have been studied for $H_2O$ diffusion are listed in Table 1.

**H_2O diffusion, theory and data summary**

Strictly speaking, silicate melts are multicomponent systems, and $H_2O$ diffusion should fall into the category of multicomponent diffusion. However, the anhydrous melt composition generally does not vary along a diffusion profile in the typical design of the experiments, and addition of $H_2O$ mainly causes a dilution effect. Therefore, $H_2O$ diffusion in the literature is treated as effective binary diffusion, or the first kind of effective binary diffusion defined by Zhang (2010, this volume) and Zhang et al. (2010, this volume).

Because $D_{H_2O_t}$ depends on $H_2O_t$ concentration, the general equation for one-dimensional diffusion is as follows:

$$\frac{\partial X}{\partial t} = \frac{\partial}{\partial x} \left( D_{H_2O_t} \frac{\partial X}{\partial x} \right)$$ (9)
where $t$ is time, $x$ is distance, $D_{\text{H}_2\text{O}_t}$ is the diffusivity (effective binary diffusivity) of $\text{H}_2\text{O}_t$, and $X = [\text{H}_2\text{O}_t]$ (see Eqn. 3a). The above diffusion equation can be solved given how $D_{\text{H}_2\text{O}_t}$ varies with $\text{H}_2\text{O}_t$, and boundary and initial conditions. For hydration and dehydration experiments, the equilibrium surface concentration and the initial concentration (usually uniform) are the boundary and initial conditions, respectively. For diffusion couple experiments, no boundary condition is needed and the initial concentrations in the two starting halves are the initial condition. If $D_{\text{H}_2\text{O}_t}$ were independent of $\text{H}_2\text{O}_t$ (or $X$), then the diffusion profile could be fit by an error function solution. However, this is rarely the case: the variation of $D_{\text{H}_2\text{O}_t}$ with $\text{H}_2\text{O}_t$ turns out to be complicated.

Experimental results in the glass and geological literature show that when $\text{H}_2\text{O}_t$ is sufficiently low ($\leq 2$ wt%, but depending on temperature), $D_{\text{H}_2\text{O}_t}$ is proportional to $\text{H}_2\text{O}_t$ (or proportional to $X$ in Eqn. 9). Such an equation can be solved numerically (e.g., Crank 1975) and the solution has been applied to fit diffusion profiles. If a profile can be fit within experimental uncertainty (e.g., Fig. 4), then the proportionality relation is assumed to describe how $D_{\text{H}_2\text{O}_t}$ varies with $\text{H}_2\text{O}_t$.

![Figure 4](image-url) **Figure 4.** Experimental $\text{H}_2\text{O}_t$ diffusion profile (points) in a peraluminous rhyolite melt and two fits. The dashed curve is an error function fit (assuming $D_{\text{H}_2\text{O}_t}$ is independent of $\text{H}_2\text{O}_t$). The solid curve is a fit assuming $D_{\text{H}_2\text{O}_t}$ is proportional to $\text{H}_2\text{O}_t$. The solid curve agrees well with experimental data. From Behrens and Zhang (2009).

At high $\text{H}_2\text{O}_t$ (such as >3 wt%, especially at relatively low temperatures such as 800 K), the proportionality relation often does not work well (Nowak and Behrens 1997; Zhang and Behrens 2000; Liu et al. 2004b; Ni and Zhang 2008; Ni et al. 2009a,b; Wang et al. 2009). One example is given in Figure 5. Hence, more complicated relations are proposed to describe how $D_{\text{H}_2\text{O}_t}$ varies with $\text{H}_2\text{O}_t$. Based on our knowledge of $\text{H}_2\text{O}$ speciation, the general and mechanistic approach is to consider the diffusion of both species:

$$\frac{\partial X}{\partial t} = \frac{\partial}{\partial x} \left( D_{\text{H}_2\text{O}_m} \frac{\partial X_m}{\partial x} + \frac{1}{2} D_{\text{OH}} \frac{\partial X_{\text{OH}}}{\partial x} \right)$$  \hspace{1cm} (10)

where $X_m$ is the mole fraction of $\text{H}_2\text{O}_m$, $X_{\text{OH}}$ is the mole fraction of OH, and $D_{\text{H}_2\text{O}_m}$ and $D_{\text{OH}}$ are the diffusivities of $\text{H}_2\text{O}_m$ and OH. The factor 1/2 is due to the fact that one mole of $\text{H}_2\text{O}_m$ reacts to form two moles of OH (Reaction 1).

Experimental data show $D_{\text{OH}} \ll D_{\text{H}_2\text{O}_m}$ in rhyolite melt so that diffusive flux due to OH diffusion can be ignored (Zhang et al. 1991a). (The small diffusivity of OH does not mean that OH profile is flat, because interconversion between OH and $\text{H}_2\text{O}_m$ can change OH concentration.) Therefore, Equation (10) can be simplified as:
The above equation means that $D_{H_2O} = D_{H_2O_m} dX_m/dX$ if equilibrium for Reaction (1) is reached at every point along a profile ($dX_m/dX$ for $K = 0.5$ is shown in Fig. 3). (Equilibrium for Reaction (1) is necessary because without equilibrium the partial differential $\partial X_m/\partial X$ would depend on time and cannot be simplified to $dX_m/dX$.) At low $H_2O$ (e.g., below 2 wt% but depending on the temperature), $D_{H_2O_m}$ is roughly independent of $H_2O$, and $dX_m/dX$ is proportional to $H_2O$ (Fig. 3), leading to $D_{H_2O}$ proportional to $H_2O$. However, at high $H_2O$, $D_{H_2O_m}$ must increase with $H_2O$ (Nowak and Behrens 1997) and has been shown to increase exponentially with $H_2O$ (Zhang and Behrens 2000; Liu et al. 2004b; Ni and Zhang 2008; Ni et al. 2009a,b; Wang et al. 2009):

$$D_{H_2O_m} = D_0 e^{aX}$$ (Eqn. 12)

where $a$ is a fitting parameter that may vary with $T$ and $P$. Numerous studies have found that $a$ increases with decreasing temperature, indicating a stronger dependence of $D_{H_2O_m}$ on $H_2O$ at lower temperatures. This finding is not surprising since at low $T$ the presence of $H_2O$ has a larger impact on melt properties such as viscosity (e.g., Zhang et al. 2003), which is not simply related to the formation of the number of OH but is also related to the larger effect of each OH and $H_2O_m$ on the melt viscosity at low temperatures. The above approach can fit all $H_2O$ profiles within experimental uncertainty (as well as species concentration profiles if the species concentrations can be preserved during quench), including those profiles that cannot be fit by assuming $D_{H_2O}$ is proportional to $H_2O$ (Fig. 5). Furthermore, experiments using samples with different $H_2O$ generally yield the same set of parameters $D_0$ and $a$, which further supports the validity of Equation (12). The exponential dependence of the diffusivity of $H_2O_m$ as well as other neutral molecules (Watson 1991; Behrens and Zhang 2001) on $H_2O$ concentration might be related to the dramatic change of melt structure, as evidenced by the significantly reduced melt viscosity caused by the addition of $H_2O$ (e.g., Shaw 1974; Zhang et al. 2003).

If equilibrium for Reaction (1) is reached at every point along a profile, the general relation between $D_{H_2O}$ and $D_{H_2O_m}$ is (Wang et al. 2009):

$$D_{H_2O} = D_{H_2O_m} \frac{dX_m}{dX} = D_{H_2O_m} \left[ 1 - \frac{(0.5 - X)}{[X(1-X)((4/K) - 1) + 0.25]^{1/2}} \right]$$ (13)
where $K$ is the equilibrium constant of Reaction (1) and depends on temperature (to a lesser extent, on pressure or $H_2O$), and $X$ and $X_m$ are mole fractions of $H_2O$ and $H_2O_m$ on a single oxygen basis. Hence, if $K$ is known or fixed, $D_{H_2O}$ can be calculated from $D_{H_2O_m}$ using the above equation. Figure 6 illustrates how $D_{H_2O_m}$ and $D_{H_2O}$ vary with $H_2O_t$ concentration at given $K$ and $a$. At low $H_2O$, $D_{H_2O}$ is approximately proportional to $H_2O_t$; while at higher $H_2O$, the relation transitions to exponential. For rhyolite, dacite and haploandesite melts, $K$ is given by Equations (7a) to (7c). Diffusion data in various melts are summarized below.

If equilibrium for Reaction (1) is not reached (at relatively low temperatures and low $H_2O$), one would have to consider the kinetics of Reaction (1) and couple the kinetic equation with the diffusion equation 11 to solve the concentration profiles. Such full treatment has not been carried out yet, but experimental data have been noted where these conditions exist (Jambon et al. 1992; Zhang et al. 2007).

**Metaluminous and peraluminous rhyolite melts.** “Normal” metaluminous rhyolite melts including haplorhyolite melts (compositions 1-3 in Table 1) have been studied most extensively (Shaw 1974; Delaney and Karsten 1981; Karsten et al. 1982; Zhang et al. 1991a; Nowak and Behrens 1997; Zhang and Behrens 2000; Okumura and Nakashima 2004; Behrens et al. 2007; Ni and Zhang 2008). Figure 7 compares $D_{H_2O}$ in rhyolite melts at 1 wt% $H_2O$ from various laboratories. It can be seen that the original diffusivity data from different laboratories are largely consistent at this $H_2O$ when cast in the same way. Furthermore, there is a significant pressure effect on $D_{H_2O}$, especially at low temperature.

Ni and Zhang (2008) combined their new experimental data and literature data at 676-1900 K, 0-1.9 GPa, 0-8 wt% $H_2O$ (reflecting the coverage of conditions by the experimental data), using $K$ from Equation (7a), and obtained $D_{H_2O_m}$ (m$^2$/s) as follows:

$$D_{H_2O_{rhyolite}} = \exp \left( -14.26 + 1.888P - 37.26X - \frac{12939 + 3626P - 75884X}{T} \right)$$  \hspace{1cm} (14)$$

where $T$ is in K, $P$ is in GPa, and $X$ is mole fraction of $H_2O$ on a single oxygen basis. The $H_2O$ diffusivity in peraluminous rhyolite melts (composition 4 in Table 1) at ≤ 0.5 GPa is indistinguishable from that in “normal” rhyolite melts and can be described by the above expression as well (Behrens and Zhang 2009). Hence, $D_{H_2O}$ for metaluminous and peraluminous rhyolite melts can be calculated from the above $D_{H_2O_m}$ using Equation (13) with $K$ from Equation (7a). The 2σ uncertainty in $\ln D_{H_2O}$ is about 0.5 for this and other melts discussed below.

The above equation implies that $D_{H_2O_m}$ increases rapidly with $H_2O$, at low temperatures but slowly at higher temperatures. Therefore, at higher temperatures, $D_{H_2O}$ is proportional to $H_2O$ from zero to higher concentrations of $H_2O$. Because the proportionality equation is easy to apply and works well at low $H_2O$ (which means ≤ 1 wt% at 773 K and ≤ 3 wt% at 1473 K), it is given below (Ni and Zhang 2008):
where $T$ is in K, $P$ is in GPa, and $C_w$ is wt\% of H$_2$O$_t$ ($C_w = 1$ for 1 wt\% H$_2$O$_t$).

Peralkaline rhyolite melts. Behrens and Zhang (2009) and Wang et al. (2009) investigated H$_2$O diffusion in peralkaline (PA) rhyolite melts (compositions 5 and 6 in Table 1) covering 789-1516 K, 0-1.4 GPa, 0-4.6 wt\% H$_2$O$_t$. Behrens and Zhang (2009) investigated diffusion at low H$_2$O$_t$, and Wang et al. (2009) expanded the studied range of H$_2$O$_t$ and pressure. Even though these studies are not numerous, the effort was coordinated and systematic so that the data are sufficient to allow the construction of a general model for $D_{H_2O_m}$ (and hence $D_{H_2O_t}$). Figure 8 compares the H$_2$O$_t$ diffusivities in peralkaline rhyolite melts to metaluminous rhyolite melts. On average, $D_{H_2O}$ at 0.5 GPa and 1 wt\% H$_2$O$_t$ in peralkaline rhyolite melt is ~2 times that in metaluminous rhyolite melt. The effect of pressure on $D_{H_2O_t}$ in peralkaline rhyolite melts is smaller than that in metaluminous rhyolite melts. For example, ln$D_{H_2O_t}$ decreases by ~1.6 as pressure increases from 0.0001 to 0.5 GPa for metaluminous rhyolite melts; but by only ~0.3 for peralkaline rhyolite melts. At various $P$-$T$ conditions, the difference between $D_{H_2O}$ in peralkaline rhyolite melts and that in metaluminous rhyolite melts is often a factor of 2 or smaller.

Using results from both Behrens and Zhang (2009) and Wang et al. (2009), and $K$ from Equation (7a), Wang et al. (2009) constructed the following expression for $D_{H_2O_m}$ (m$^2$/s):

$$D_{H_2O_m}^{PA\ rhyolite} = C_w \exp \left(-18.10 + 1.888P - \frac{9699 + 3626P}{T}\right)$$  \hspace{1cm} (15) $D_{H_2O_t}$ for peralkaline rhyolite melts can be calculated from the above $D_{H_2O_m}$ using Equation (13) with $K$ from Equation (7a). The resulting $D_{H_2O_m}$ and $D_{H_2O_t}$ are slightly larger than that in “normal” rhyolite melts, but no more than a factor of 2. By combining the data in both Behrens and Zhang (2009) and Wang et al. (2009), a simple equation to calculate directly $D_{H_2O_t}$ at low H$_2$O$_t$ (which means ≤ 1 wt\% at 773 K and ≤ 3 wt\% at 1473 K) is as follows:
**Figure 8.** Comparison between $\text{H}_2\text{O}_\text{t}$ diffusivities in peralkaline rhyolite melt at 0.5 GPa (filled circles) and those in metaluminous (or “normal”) rhyolite melts at 0.0001 and 0.5 GPa (open circles and squares). Data sources for peralkaline rhyolite: Behrens and Zhang (2009) and Wang et al. (2009). See Figure 7 for data sources for metaluminous rhyolite.

\[
D_{H_2O_\text{t}, \text{PA rhyolite}} = C_w \exp \left( -16.55 - \frac{10870 + 1101P}{T} \right)
\]

where $T$ is in K, $P$ is in GPa, and $C_w$ is wt% of H$_2$O$_t$.

**Dacite melts.** Liu et al. (2004b), Behrens et al. (2004), Okumura and Nakashima (2006), and Ni et al. (2009b) quantified H$_2$O diffusion in dacite melts (compositions 7 and 8 in Table 1), covering 786-1800 K, 0-1 GPa, 0-8 wt% H$_2$O$_t$. Liu et al. (2004b) and Okumura and Nakashima (2006) conducted dehydration experiments at intermediate temperature and low pressure; Behrens et al. (2004) carried out diffusion couple experiments at high temperature and high pressure; and Ni et al. (2009b) investigated H$_2$O diffusion at intermediate temperature and high pressure. All data have been combined to evaluate the effect of temperature, pressure and H$_2$O$_t$ on H$_2$O diffusion. Figure 9 shows some experimental diffusion data and compares these with data in rhyolite melts. At 1 wt% H$_2$O$_t$, $D_{H_2O_\text{t}}$ in dacite melts is lower than that in rhyolite melts at $< 1470$ K. Furthermore, for both rhyolite and dacite melts, $D_{H_2O_\text{t}}$ decreases as pressure increases. As pressure increases from 0.0001 to 0.5 GPa, ln$D_{H_2O_\text{t}}$ decreases by ~1.6 for rhyolite melt; but only by ~1.0 for dacite melts. That is, the pressure effect becomes smaller from rhyolite melt to dacite melt.

Using results from Liu et al. (2004b), Behrens et al. (2004) and Ni et al. (2009b), and $K$ from Equation (7b), $D_{H_2O_\text{t}}$ at 786-1800 K, 0-1 GPa, and 0-8 wt% H$_2$O$_t$ (reflecting conditions covered by the experimental data) can be expressed as (Ni et al. 2009b):

\[
D_{H_2O_\text{t}, \text{dacite}} = \exp \left( -9.42 - 62.38X - \frac{19064 + 1477P - 108882X}{T} \right)
\]

where $T$ is in K, $P$ is in GPa, and $X$ is the mole fraction of H$_2$O$_t$ on a single oxygen basis. $D_{H_2O_\text{t}}$ for dacite melts can be calculated from the above $D_{H_2O_\text{t}, \text{PA rhyolite}}$ using Equation (13) with $K$ from Equation (7b). At $\leq 0.7$ wt% H$_2$O$_t$ at 773 K, and $\leq 6.2$ wt% H$_2$O$_t$ at 1673 K, $D_{H_2O_\text{t}}$ is proportional to H$_2$O$_t$ and can be expressed as follows:
where \( T \) is in K, \( P \) is in GPa, and \( C_w \) is wt\% of H\(_2\)O. Note that the proportionality relation holds for a smaller H\(_2\)O\(_t\) range (\( \leq 0.7 \) wt\%) in dacite than in rhyolite at intermediate temperatures such as 773 K, but for a larger H\(_2\)O\(_t\) range (\( \leq 5 \) wt\%) in dacite than in rhyolite (\( \leq 3 \) wt\%) at high temperatures such as 1473 K.

**Andesite melts.** There have been three studies (Behrens et al. 2004; Okumura and Nakashima 2006; Ni et al. 2009a) on andesite melts (compositions 9-11 in Table 1). However, the data are insufficient for the construction of a general model for \( D_{H_2O_t} \) or \( D_{H_2O_m} \). There is also a significant compositional difference (e.g., 5 wt\% difference in SiO\(_2\), 7 wt\% difference in FeO) between the three andesites used in these studies. H\(_2\)O diffusion data are summarized in Figure 10.

Examining Figure 10, the pressure dependence of \( D_{H_2O_t} \) at 1 wt\% H\(_2\)O in andesite melts is small, at least at high temperature. For example, from 0.5 to 1.5 GPa at high temperature (triangular points), the variation of \( D_{H_2O_t} \) is within uncertainty. Furthermore, the difference in \( D_{H_2O_t} \) between haploandesite melt and normal andesite melt is small. Hence, we ignore the pressure dependence and compositional difference and fit all \( D_{H_2O_t} \) data at low H\(_2\)O\(_t\) in three andesite melts to obtain the following equation:

\[
D_{H_2O_t}^{\text{andesite}} = C_w \exp\left(-11.80 - \frac{18340}{T}\right)
\]

where \( T \) is in K, \( D \) is in m\(^2\)/s, and \( C_w \) is wt\% of H\(_2\)O. The above proportionality relation is applicable to \( \leq 0.7 \) wt\% H\(_2\)O, at 773 K and \( \leq 3.5 \) wt\% H\(_2\)O, at 1473 K. At temperatures \( \geq 1573 \) K, there is ambiguity regarding how \( D_{H_2O_t} \) depends on H\(_2\)O\(_t\): whether \( D_{H_2O_t} \) is proportional to H\(_2\)O\(_t\) or independent of H\(_2\)O\(_t\) (Behrens et al. 2004).

**Figure 9.** Comparison of \( D_{H_2O_t} \) in dacite melts (solid circles, triangles and squares) and rhyolite melts (open circles and squares) at 1 wt\% H\(_2\)O. Data sources for dacite melts: \( <0.15 \) GPa: Liu et al. (2004b); 0.5 GPa and 1 GPa: Behrens et al. (2004) and Ni et al. (2009b). Data sources for rhyolite melt: see Figure 7. The data of Okumura and Nakashima (2006) are not shown because there is a small systematic difference between their data and other data (Ni et al. 2009b).
Diffusion of H, C, O Components in Silicate Melts

At intermediate temperatures and high H$_2$O$_t$, $D_{H_2O_t}$ increases strongly with H$_2$O$_t$ and calculation of $D_{H_2O_t}$ is best through $D_{H_2O_m}$. For haploandesite melts (composition 11 in Table 1) at 743-873 K, 0.1 GPa, 0-2.5 wt% H$_2$O$_t$, using $K$ from Equation (7c), $D_{H_2O_m}$ can be expressed as (Ni et al. 2009b):

$$D_{H_2O_m}^{haploandesite} = \exp\left(-12.27 - 13.91X - \frac{18172 - 73136X}{T}\right)$$

where $T$ is in K and $X$ is the mole fraction of H$_2$O$_t$ on a single oxygen basis. $D_{H_2O_t}$ for haploandesite melts (also for Andesite 2 in Table 1, judging from similarity in $D_{H_2O_t}$ in the two melts in Fig. 10) can be calculated from the above $D_{H_2O_m}$ using Equation (13) with $K$ from Equation (7c), but only under the limited conditions of 743-873 K, 0.1 GPa, 0-2.5 wt% H$_2$O$_t$.

For other silicate melts (such as basalt and trachyte), the equilibrium constant $K$ for Reaction (1) has not been characterized. Hence, no $D_{H_2O_m}$ values or equations have been reported in the literature, and only $D_{H_2O_t}$ values and expressions under limited conditions are obtained. These are summarized below.

**Basalt melts.** For basalt melts (compositions 13 and 14 in Table 1), the investigations are limited (Zhang and Stolper 1991; Okumura and Nakashima 2006; Persikov et al. 2010) and the range of H$_2$O covered in experiments is only ≤ 1.1 wt%. Assuming $D_{H_2O_t}$ is proportional to H$_2$O$_t$ and ignoring the pressure effect on the diffusivity (the validity of this assumption needs confirmation), Zhang et al. (2007) summarized the data and expressed $D_{H_2O_t}$ as follows at 673-1773 K, ≤ 1 GPa and ≤ 1.1 wt% H$_2$O$_t$:

$$D_{H_2O_t}^{basalt} = C_w \exp\left(-8.56 - \frac{19110}{T}\right)$$

where $T$ is in K and $C_w$ is wt% of H$_2$O$_t$. The recent high temperature data on a haplobasalt melt (62.2 wt% SiO$_2$, 10.5 wt% Al$_2$O$_3$, 6.8 wt% MgO; 14.2 wt% CaO and 6.3 wt% Na$_2$O) by Persikov et al. (2010) are about 0.17 times those on a MORB melt (composition 13 in Table 1).
by Zhang and Stolper (1991) when compared at 1 wt% H_2O assuming. It is not clear whether this difference is due to the significant compositional difference between the two melts, or due to the different H_2O concentration coverage, or due to experimental uncertainties.

**Trachyte melts.** For trachyte melt (composition 12 in Table 1), there has been only one study (Freda et al. 2003). The equilibrium constant K for Reaction (1) for trachyte melts has not been characterized. Assuming D_{H_2O} is proportional to H_2O, Zhang et al. (2007) summarized the data and expressed D_{H_2O} as follows at 1334-1601 K, 1 GPa and ≤ 2 wt% H_2O:

\[ D_{H_2O}^{\text{trachyte}} = C_w \exp \left( -10.90 - \frac{17975}{T} \right) \]  

(23)

where \( T \) is in K and \( C_w \) is wt% of H_2O. The H_2O diffusivity in trachyte melt is slightly (by a factor of about 3) higher than that in andesite melt with a similar SiO_2 content. Combining this observation with the small difference in the H_2O diffusivity between metaluminous rhyolite and peralkaline rhyolite, it appears that H_2O diffusivity in silicate melts depends primarily on the SiO_2 content, and the effects of other components, such as alkalinity, are minor (though still noticeable).

**Self-diffusion of H_2O.** The above discussion is on the chemical diffusion or effective binary diffusion of H_2O, when there is a chemical concentration (or chemical potential) gradient in H_2O. Limited data on the self-diffusion of H_2O, or exchange of H_2O and H_2O in a chemically homogeneous system (i.e., without H_2O chemical concentration gradients), are available (e.g., Nowak and Behrens 1997). The theoretical analysis by Zhang et al. (1991b) showed that the self-diffusivity of H_2O (\( D_{H_2O-H_2O} \)) can be written as follows if H_2O is the diffusing species:

\[ D_{H_2O-H_2O} = D_{H_2O} \frac{X_m}{X} = D_{H_2O} \frac{X_m}{X} \left( \frac{dX_m}{dX} \right) \]  

(24)

where \( X \) and \( X_m \) are mole fractions of H_2O and H_2O on a single oxygen basis. The ratio (\( X_m/X \)) can be calculated as follows (Eqn. 13 in Zhang 1999b):

\[ \frac{X_m}{X} = \frac{8X}{8X + K(1 - 2X) + \sqrt{K^2(1 - 2X)^2 + 16KX(1 - X)}} \]  

(25)

where \( K \) is the equilibrium constant of Reaction (1). The calculation of \( dX_m/dX \) can be found from Equation (13). The values of \( X_m/X \) and \( dX_m/dX \) are shown in Figure 3 for \( K = 0.5 \), and vary from 0.5 at 0 wt% H_2O to 0.67 at 7 wt% H_2O. Hence, at low H_2O, the D-H self-diffusivity \( D_{H_2O-H_2O} \) is about 0.5 times \( D_{H_2O} \) (Doremus 1969; Zhang et al. 1991b). At higher H_2O, \( D_{H_2O-H_2O} \) is closer to \( D_{H_2O} \) (such as 0.7 times \( D_{H_2O} \)). The data of Nowak and Behrens (1997) are consistent with the above results. This analysis shows that under some conditions, self-diffusivity is smaller than chemical diffusivity, although some studies showed that self-diffusivity is often greater than chemical (effective binary) diffusivity (Lesher 1990, 1994; Zhan 1993; Van der Laan et al. 1994).

**All natural silicate melts.** For rhyolite to andesite melts in the calc-alkaline series, Behrens et al. (2004) provided an expression of H_2O diffusivity at 1 wt% H_2O, Okumura and Nakashima (2006) related the H_2O diffusivity at 0.7 wt% H_2O to NBO/T (ratio of non-bridging oxygen to tetrahedrally coordinated cations) in the melt, and Ni et al. (2009a) presented a new diffusivity expression specifically for intermediate temperatures (700-900 K). In all three studies, a single parameter (silica content or NBO/T) is used to characterize the complicated melt composition variation, which is clearly a simplification.

H_2O diffusivities at 1 wt% H_2O in various melts are summarized in Figure 11. Continuing the effort of Behrens et al. (2004) and Ni et al. (2009a), we use H_2O diffusivity data from 116
experiments by IR profiling method except for basalt melts, and arrive at the following general model for $D_{H_2O}^t$ at 1 wt% $H_2O_t$:

$$\ln D_{H_2O}^t = 12.06 + 14.75 AI - 42.22 Si + 2.716 P \times Si - \frac{42021 - 45407 Si + (7409 Si - 1593) P}{T} \quad (26)$$

where $D$ is in m$^2$/s, $T$ is in K, $P$ is in GPa, $Si$ is the cation mole fraction of Si, and $Al = Na+K-Al$ where Na, K and Al are cation mole fractions. One additional compositional parameter Al is used in the above fitting compared to the models of Behrens et al. (2004) and Ni et al. (2009a).

The above expression reproduces all the literature data for rhyolite-peralkaline rhyolite-dacite-andesite-haploandesite-trachyte composition within a factor of 2, covering 676-1629 K and 0-1.9 GPa (Fig. 11). Equation (26) can also be used to estimate the $H_2O_t$ diffusivity at <1 wt% $H_2O_t$ at intermediate temperatures and ≤ 3 wt% $H_2O_t$ at high temperatures with the aid of proportionality assumption. The data on basalt melt (Zhang and Stolper 1991) cannot be modeled well using a simple compositional dependence. The reason is not clear. The data of Okumura and Nakashima (2004, 2006) are not included in the fitting because they are not based on measured profiles.
To develop a more general expression of H$_2$O diffusivity in all natural silicate melts at both high and low H$_2$O$_t$ for geological applications, more experimental data are necessary. The critical data include diffusion in basalt melts at high H$_2$O$_t$ at both high and intermediate temperatures, and in andesite melts at high H$_2$O$_t$ and intermediate temperatures. Furthermore, it is necessary to resolve the dependence of $D_{\text{H}_2\text{O}_t}$ on H$_2$O$_t$ content in high-temperature andesite melts by careful experiments. More data on peralkaline melts from basanite to phonolite to further confirm that the effect of peralkalinity is small would also greatly help. For specific modeling involving a melt that is very different from studied melts (such as lunar basalt – Saal et al. 2008; Zhang 2009), it is essential to obtain at least a few data points to verify that the compositional difference does not lead to very different H$_2$O diffusivities.

**Some clarifying points.** Below are some additional points of clarification:

1. Although we often say that $D_{\text{H}_2\text{O}_m}$ is proportional to H$_2$O$_t$ at low H$_2$O$_t$ (≤ a couple of percent), meaning that $D_{\text{H}_2\text{O}_m}$ approaches zero as H$_2$O$_t$ approaches zero, it is just an approximation. In theory, $D_{\text{H}_2\text{O}_m}$ approaches $D_{\text{OH}}$ as H$_2$O$_t$ approaches zero ($d[H_2O_m]/d[H_2O_t]$ would be so small so that OH diffusion will dominate). That is, if species equilibrium is reached, $D_{\text{H}_2\text{O}_m}$ is linear with H$_2$O$_t$ with a very small intercept $D_{\text{OH}}$, but $D_{\text{OH}}$ is so small that it has not been resolved experimentally in natural melts discussed above. However, in a soda lime silicate melt (74 mol% SiO$_2$, 10 mol% CaO, and 16 mol% Na$_2$O) and a float melt (72.5 mo% SiO$_2$, 0.4 mol% Al$_2$O$_3$, 3.3 mol% MgO, 9.8 mol% CaO, and 13.7 mol% Na$_2$O), $D_{\text{H}_2\text{O}_m}$ is independent of H$_2$O$_t$ concentration at 0.02 to 0.25 wt% H$_2$O$_t$ (Behrens 2006), possibly indicating that the $D_{\text{OH}}$ limit is reached, as well as fairly large $D_{\text{OH}}$ values for these sodic melts.

2. The proportionality relation at low H$_2$O$_t$ and Equation (13) holds only when there is rough equilibrium between H$_2$O$_m$ and OH for Reaction (1). Because the reaction rate constant increases with increasing temperature and H$_2$O$_t$, equilibrium is reached at relatively high temperature but not low temperature. For a given temperature, the proportionality applies at high H$_2$O$_t$ but not very low H$_2$O$_t$; what can be considered as very low H$_2$O$_t$ depends on the temperature. For example, Jambon et al. (1992) showed that for rhyolite melt, at 0.114 wt% H$_2$O$_t$ and 783 K, Equation (13) and the proportionality relation do not hold. Therefore, regarding point (1), in many cases the proportionality relation may already be inapplicable before H$_2$O$_t$ becomes so low that $D_{\text{OH}}$ becomes important.

3. H$_2$O$_m$ diffusivity is a modeling parameter that depends on the accuracy of the equilibrium constant $K$, which in turn depends on the accuracy of the infrared calibration to measure species concentrations. On the other hand, H$_2$O$_t$ diffusivity is constrained by the length and shape of the measured H$_2$O$_t$ concentration profiles. Hence, if $K$ values in a melt are improved in the future, one cannot simply use the new $K$ values in the above equations in conjunction with $D_{\text{H}_2\text{O}_m}$ above to calculate $D_{\text{H}_2\text{O}_t}$, because the $D_{\text{H}_2\text{O}_t}$ diffusivities themselves are based on the specific $K$ values. That is, internal consistency must be maintained for accurate calculation of $D_{\text{H}_2\text{O}_t}$. The expressions of $K$ values listed above should still be used to calculate $D_{\text{H}_2\text{O}_t}$ unless a new $D_{\text{H}_2\text{O}_m}$ expression is obtained by using the new $K$ values.

4. If different experimental methods are applied to characterize $D_{\text{H}_2\text{O}_m}$ as a function of H$_2$O$_t$ content (i.e., using concentration profiles), the diffusivity values at given T-P-H$_2$O$_t$ and melt composition conditions should be independent of the method (such as diffusion couple, dehydration, hydration, etc.) However, some methods can only obtain average diffusivities (e.g., mass loss or gain methods), and different averages may have different meanings, leading to different diffusivities. For example, under the same conditions, the average $D_{\text{H}_2\text{O}_t}$ value during dehydration experiments (during
which H_2O diffuses out) and that during hydration experiments (during which H_2O diffuses in) are different (Moulson and Roberts 1961; Zhang et al. 1991a; Wang et al. 1996; Zhang 1999b; Figure 3-33 in Zhang 2008). If the surface H_2O during hydration experiments is the same as the initial H_2O during dehydration experiments, and the minimum H_2O_t concentration is zero, and if \( D_{H_2O_t} \) is proportional to H_2O_t, then (Zhang et al. 1991a; Wang et al. 1996):

\[
\begin{align*}
D_{in} &= 0.619D_{X_i} \\
D_{out} &= 0.347D_{X_i} \\
D_{in} &= 1.78D_{out}
\end{align*}
\] (27a) (27b) (27c)

where \( D_{X_i} \) is \( D_{H_2O_t} \) at the initial H_2O_t content of the sample during dehydration, and \( D_{X_s} \) is \( D_{H_2O_t} \) at the surface H_2O_t content of the sample during hydration. Ni and Zhang (2008) showed how to derive the general relation between \( D_{out} \) and \( D_{X_i} \).

There have also been many studies on obsidian hydration near room temperatures (e.g., Friedman and Long, 1976; Cole an Chakraborty 2001; Riciputi et al. 2002; Anovitz et al. 2004, 2006, 2008). These studies are not discussed here because (i) they do not seem to fit neatly into the diffusion data trends by higher-temperature data, probably due to effects of disequilibrium that cannot be treated simply, and (ii) our focus here is on silicate melts at high temperatures to intermediate temperatures (e.g., > 600 K), not surface processes at room temperatures.

**MOLECULAR H_2 DIFFUSION**

In terrestrial magmas, hydrogen is typically oxidized and hence in the form of the hydrous component. Under extremely reducing conditions, the hydrogen component may be present in the elemental form as molecular H_2. Diffusion of molecular H_2 is different from that of H_2O and may play a role under very low \( f_{O_2} \). In this section, diffusion of molecular H_2 is reviewed for completeness of coverage, and also for discussing the possible role of H_2 diffusion relative to H_2O diffusion in natural silicate melts.

H_2 has not been detected as a dissolved gas species in terrestrial silicate melt because it is easily oxidized in natural melts when there is ferric iron present. To understand H_2 diffusion, it is necessary to avoid H_2 oxidation so that pure molecular H_2 (that is, the ratio of H_2/H_2O is \( >> 1 \)) diffusion can be characterized. Therefore, H_2 diffusion experiments must be conducted under very reducing conditions. Under such reducing conditions, iron in natural melts would be significantly reduced to metallic Fe, which would complicate the experiments. Hence, extensive and reliable H_2 as well as D_2 diffusion data are available only for pure silica glass. There are more data on D_2 diffusion (Lee et al. 1962; Lee 1963; Perkins and Begeal 1971; Shelby 1977) than on H_2 diffusion (Barrer 1941; Lee et al. 1962; Lee 1963; Shang et al. 2009).

Molecular H_2 diffusion data on other melts and glasses are limited and their reliability is uncertain. Chekhmir et al. (1985) tried to infer molecular H_2 diffusivity in albite melt based on reduction-induced color change (by reducing CO_2 to graphite). Gaillard et al. (2002, 2003a,b) investigated the kinetics of reduction of Fe^{3+} to Fe^{2+} by molecular H_2 in rhyolite melts, and tried to infer molecular H_2 diffusivity (Gillard et al. 2003b). Because the mechanisms of these complicated process (including solution, reactions and diffusion) are not well quantified (e.g., what the redox reaction kinetics are, whether the redox reaction plays a role in limiting the entire process, how the process depends on H_2 fugacity), it is not clear whether the inferred molecular H_2 diffusivity data are correct. The activation energy for “molecular H_2 diffusion” inferred by Chekhmir et al. (1985) is 113 kJ/mol (clearly too high, more likely reflect molecular H_2O diffusion), and by Gillard et al. (2003b) is about 40 kJ/mol (more reasonable). Even though
it is not clear whether the estimated H\textsubscript{2} diffusivities by Gaillard et al. (2003b) are correct, the method used by Gaillard et al. (2003a,b) has great potential because they were able to measure both molecular H\textsubscript{2} and OH bands by infrared spectroscopy (the H\textsubscript{2} peak at 415 mm\textsuperscript{-1} is weak in IR spectra but detectable), and it may hence be possible to treat the problem quantitatively in a similar fashion as in Zhang et al. (1991a) to understand both the redox reaction and diffusion. In the discussion below, we focus on H\textsubscript{2} and D\textsubscript{2} diffusion in silica glass (in the glass science literature, silica glass is sometimes referred to fused quartz, or even simply “quartz”), rather than the unverified semi-quantitative data by Chekhmir et al. (1985) and Gillard et al. (2003b).

Most experimental data on H\textsubscript{2} and D\textsubscript{2} diffusion in silica glass are based on permeation experiments, in which gas permeates from one side of a glass (in contact with hydrogen gas of, e.g., 90 kPa) to the other side (a vacuum line connected to a mass spectrometer). It takes some time for the gas to diffuse through the glass and reach a steady state. Hence, there is a pre-steady-state stage, during which the gas flux builds up; there is also a post-steady-state stage, during which the gas flux gradually decays to zero. Permeability (SI units: mol·m\textsuperscript{-1}·s\textsuperscript{-1}·Pa\textsuperscript{-1}) is directly obtained from the experimental flux and pressure gradient (pressure difference in two chambers divided by the thickness of the glass wafer) at steady-state permeation. Diffusivity may be calculated either from the measured permeability and solubility, or from the non-steady state decay after the steady-state permeation terminates (or build-up at the beginning of the permeation experiments). Because absolute concentrations are difficult to measure accurately, the error in the solubility often dominates the error in the diffusivity if the solubility is needed to estimate the diffusivity. In addition, pre-existing OH in the silica glass may contribute to the permeation flux, and dissolved hydrogen molecules (including both H\textsubscript{2} and D\textsubscript{2}) may react with silica to form bound hydrogen such as OH or SiH (Shelby 1994). Hence, experimental data must be carefully examined so that these effects are avoided. Shelby (1977) showed that once these effects are accounted for, D\textsubscript{2} (and H\textsubscript{2}) diffusivities can be obtained consistently.

Even though several groups investigated H\textsubscript{2} permeation and diffusion in silica in 1910-1940, as summarized in Barrer (1941), these earlier data were often an order of magnitude off (Shang et al. 2009) and are not discussed here. Lee et al. (1962) measured the diffusivity of H\textsubscript{2} and D\textsubscript{2} and found the data at T > 1073 K are scattered and do not follow the trend defined by lower-temperature data. This was explained by a possible reaction of H\textsubscript{2} or D\textsubscript{2} with silica network at high temperature. They also found that the diffusivity determined at the decay stage of the permeation experiments is more reliable than that determined from the build-up stage, likely because the sample is more fully annealed at the decay stage. Lee (1963) investigated the effect of impurities in the silica glass and obtained new H\textsubscript{2} and D\textsubscript{2} diffusivity data at 600-1300 K. The effect of impurities including Al\textsubscript{2}O\textsubscript{3} (ranging from 0.1 to 160 ppm) and OH (10 to 3000 ppm) in silica glass turned out to be small as long as care is taken to avoid possible reactions and to use only the steady state and post-steady-state data. The data in Lee et al. (1962) are not discussed further because the work was superseded by Lee (1963). Perkins and Begeal (1971) reported D\textsubscript{2} (and noble gas element) diffusivities in silica glass at 298-448 K. Shelby (1977) determined D\textsubscript{2} diffusivities in various silica glasses at 450-1000 K, and the differences were found to be no more than 0.17 log units (0.38 ln units) (these are highly reproducible experiments with internal precision better than 10\% relative, or 0.04 log units). Shang et al. (2009) developed a new technique and obtained H\textsubscript{2} diffusivities at 296-523 K. All of these studies were conducted at low pressures (often less than one atmosphere pressure).

Figure 12 compares all the H\textsubscript{2} and D\textsubscript{2} diffusion data in Lee (1963), Perkins and Begeal (1971), Shelby (1977), and Shang et al. (2009). Data scatter is small; the maximum minus minimum at a given temperature is about 0.4 in lnD. At high temperatures, H\textsubscript{2} and D\textsubscript{2} diffusion was investigated by the same author (Lee 1963) on the same silica glass, and it was found that H\textsubscript{2} diffusivity is greater than D\textsubscript{2} diffusivity, as expected, but by only about 20\%, not the theoretical 41\% difference based on the square root of mass relation. The difference of 20\% is
large enough to be distinguished in the same glass by the same author when self-consistency is high, but roughly within error when results from different silica glasses and different authors are compared. At lower temperatures (<500 K), H$_2$ diffusivity is apparently smaller than D$_2$ diffusivity, and the difference can reach 20% relative (except for one point at room temperature that deviates more). This difference is probably due to differences between various silica glasses (such as different OH content), and accuracy of the solubility models used. Because there are more data on D$_2$ diffusion and they are all obtained by similar permeation methods with more careful assessment of glass composition, the uncertainties on D$_2$ diffusivities are smaller.

Fitting H$_2$ and D$_2$ diffusion data (Shang et al. 2009; Shelby 1977) by the Arrhenian relation leads to:

\[
D_{\text{silica melt}}^{\text{H}_2} = \exp \left( -\left(16.471 \pm 0.070\right) - \frac{(5363 \pm 33.4)}{T} \right) \tag{28}
\]

\[
D_{\text{silica melt}}^{\text{D}_2} = \exp \left( -\left(17.228 \pm 0.042\right) - \frac{(4996 \pm 21.8)}{T} \right) \tag{29}
\]

where $D$ is in m$^2$/s, $T$ is in K, and errors are given at the 2σ level. The activation energy for H$_2$ or D$_2$ diffusion is low, of the order 41-45 kJ/mol.

However, the relation between D$_2$ diffusivity and temperature is slightly non-Arrhenian (e.g., Shelby 1977), which can be captured well by the following expression:

\[
D_{\text{silica melt}}^{\text{D}_2} = T \cdot \exp \left( -\left(24.546 \pm 0.031\right) - \frac{(4480.5 \pm 16.1)}{T} \right) \tag{30}
\]
where \( D \) is in \( m^2/s \), and \( T \) is temperature in K. The above equation reproduces all experimental \( D_2 \) diffusion data in silica melt and glass within 24% (2\( \sigma \) error in \( \ln D \) is 0.20, which is mainly due to differences between different silica glasses). The implied Arrhenian activation energy from the above equation depends somewhat on temperature as \( R(4480.5+T) \) based on the above equation where \( R \) is the universal gas constant and \( T \) is temperature in K. That is, the activation energy varies from 39.7 to 45.6 kJ/mol from 300 to 1000 K.

When compared with diffusivities of neutral noble gas molecules in silica melt (Swets et al. 1961; Frank et al. 1961; Perkins and Begeal 1971), \( H_2 \) and \( D_2 \) diffusivities are between that of He and Ne (Fig. 12). Furthermore, the activation energy for \( H_2 \) and \( D_2 \) diffusion is similar to that for Ne diffusion and is greater than that for He diffusion.

Below, we evaluate the possible role of molecular \( H_2 \) diffusion to the diffusion of the hydrogen component (including \( H_2O_m \) and OH). In the presence of \( H_2 \), one-dimensional diffusion of total hydrogen component can be expressed as (following Zhang et al. 1991b):

\[
\frac{\partial C_{\text{total H}}}{\partial t} = \frac{\partial}{\partial x} \left( D_{H_2} \frac{2\partial C_{H_2}}{\partial x} + D_{H_2O_m} \frac{2\partial C_{H_2O_m}}{\partial x} \right)
\]  

(31)

where \( C \) is concentration in \( mol/m^3 \), \( C_{\text{total H}} \) is total H concentration (moles of H atoms per \( m^3 \)), \( D_{H_2} \) and \( D_{H_2O_m} \) are molecular \( H_2 \) and molecular \( H_2O_m \) diffusion coefficients, and OH diffusion is ignored as discussed earlier. The factor of 2 in the above equation is due to the fact that each \( H_2 \) molecule or \( H_2O_m \) molecule contains two H atoms and the hydrogen atoms are used to represent the hydrogen component. Comparing the above equation with

\[
\frac{\partial C_{\text{total H}}}{\partial t} = \frac{\partial}{\partial x} \left( D_{\text{total H}} \frac{\partial C_{\text{total H}}}{\partial x} \right)
\]

(32)

where \( D_{\text{total H}} \) is the total H diffusivity, we obtain:

\[
D_{\text{total H}} \frac{\partial C_{\text{total H}}}{\partial x} = D_{H_2} \frac{2\partial C_{H_2}}{\partial x} + D_{H_2O_m} \frac{2\partial C_{H_2O_m}}{\partial x}
\]

(33)

Assuming local chemical equilibrium between various hydrogen species (including \( H_2 \), \( H_2O_m \), and OH), then,

\[
D_{\text{total H}} = 2D_{H_2} \frac{\partial C_{H_2}}{\partial C_{\text{total H}}} + 2D_{H_2O_m} \frac{\partial C_{H_2O_m}}{\partial C_{\text{total H}}}
\]

(34)

Hence, the ratio of the molecular \( H_2 \) diffusion contribution to the molecular \( H_2O_m \) contribution is (again assuming local chemical equilibrium among species):

\[
\text{Ratio} = \frac{D_{H_2}}{D_{H_2O_m}} \frac{\partial C_{H_2}}{\partial C_{H_2O_m}} = \frac{D_{H_2} C_{H_2}}{D_{H_2O_m} C_{H_2O_m}}
\]

(35)

The last equal sign in the above equation holds if \( H_2 \) concentration is proportional to that of \( H_2O_m \) (e.g., uniform oxygen fugacity). If the ratio equals 1, the two species contribute equally. If the ratio is smaller than 1, molecular \( H_2O_m \) diffusion contributes dominantly. If the ratio is greater than 1, molecular \( H_2 \) diffusion contributes dominantly. The contribution of \( H_2 \) to total H diffusion depends on the concentration ratio of \( H_2/H_2O_m \) and the diffusivity ratio.

\( H_2/H_2O_m \) in a given melt depends on the \( H_2/H_2O \) ratio in the gas or fluid phase (which depends on oxygen fugacity \( f_{O_2} \)) and the solubility of \( H_2 \) and \( H_2O \). First, we consider the oxidation reaction in the gas phase:

\[
H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2} O_2(g)
\]

(36)
The equilibrium constant \( K_{H_2-H_2O} \) can be written as:

\[
K_{H_2,4H_2O} = \frac{f_{H_2} f_{O_2}^{1/2}}{f_{H_2O}}
\]

where \( f \) stands for fugacity. Using thermodynamic data in Robie and Hemingway (1995), the equilibrium constant depends on temperature as follows:

\[
K_{H_2,4H_2O} = \exp \left( \frac{6.347 - \frac{29435}{T}}{1} \right) \text{ bar}^{1/2}
\]

where \( T \) is in K. At 298.15 K, \( K_{H_2-H_2O} = 7.6 \times 10^{-41} \text{ bar}^{1/2} \); at 1800 K, \( K_{H_2-H_2O} = 4.5 \times 10^{-5} \text{ bar}^{1/2} \). Hence, at a given \( f_{O_2}, f_{H_2}/f_{H_2O} \) ratio increases with temperature. Oxygen fugacity in natural magmas is often within 2 log units of Ni-NiO (NNO) buffer (Carmichael and Ghiorso 1990). Figure 13a shows \( f_{H_2}/f_{H_2O} \) ratio as a function of temperature along the NNO buffer (plus or minus 2 log units) using the thermodynamic data in Robie and Hemingway (1995) (the NIST-JANAF Thermodaynamic Data Table does not contain data on NiO). It can be seen that \( f_{H_2}/f_{H_2O} \) is often of the order \( 10^{-4} \) to 0.1 in the gas phase in equilibrium with natural melts. Note that the \( f_{H_2}/f_{H_2O} \) ratio is different from the \( H_2/H_2O_m \) concentration ratio in the melt, which also depends on the solubility of \( H_2 \) and \( H_2O \).

To relate the fugacity ratio to the molar concentration ratio of dissolved \( H_2 \) to \( H_2O_m \) concentrations in a melt, it is necessary to know the solubility of both \( H_2 \) and \( H_2O_m \) (not \( H_2O_t \)). Note that resorting to solubility here does not necessarily mean the investigated melt is saturated with respect to molecular or \( H_2 \) or \( H_2O_m \). No reliable data are available for both \( H_2 \) and \( H_2O_m \) solubility and diffusivity in any given melt. There are \( H_2 \) solubility and diffusivity data on

![Figure 13](image-url)
silica melt and glass (Shackelford et al. 1972; Shelby 1977; Shang et al. 2009) but no H$_2$O$_m$ solubility and diffusivity data (though there are extensive H$_2$O solubility and diffusivity data, e.g., Moulson and Roberts 1961; Roberts and Roberts 1964; Doremus 1969, 1973; Tomozawa 1985). There are H$_2$O$_m$ solubility and diffusivity data on rhyolite melt (Zhang et al. 1991a; Zhang 1999b; Ni and Zhang 2008). For a rough estimation, we assume the H$_2$ solubility and diffusivity in silica melt are similar to those in rhyolite melt. The molecular solubilities of H$_2$ (Shackelford et al. 1972) and H$_2$O$_m$ (Zhang 1999b) are as follows:

$$S_{H_2}^{\text{silica melt}} = \exp \left( -13.662 + \frac{1068}{T} \right)$$

$$S_{H_2O_m}^{\text{rhyolite melt}} = \exp \left( -14.193 + \frac{3890}{T} \right)$$

where the solubilities ($S_{H_2}$ and $S_{H_2O_m}$) are in mol·m$^{-3}$·Pa$^{-1}$. Hence, at a given $f_\text{O}_2$ buffer, the molar concentration ratio of [H$_2$]/[H$_2$O$_m$] can be estimated from ($f_{H_2}/f_{H_2O}$)$\cdot(S_{H_2}/S_{H_2O_m})$, as shown in Figure 13b (assuming H$_2$ solubility in rhyolite is the same as that in silica melt). It can be seen that under typical terrestrial conditions, [H$_2$]/[H$_2$O$_m$] is low. Because the ratio of [H$_2$]/[H$_2$O$_m$] is low in terrestrial melts, the total hydrogen component is largely in the form of H$_2$O$_m$ and OH. It is hence appropriate to refer to the total hydrogen component as the hydrous component (but molecular hydrogen can still play a role in the diffusion of the hydrous component, see below). However, in lunar melts that are much more reducing, the [H$_2$]/[H$_2$O$_m$] ratio may be greater than 1, and the total hydrogen component is not simply the hydrous component.

Next, again assuming the H$_2$ diffusivity in rhyolite melt is the same as that in silica melt, using the molecular H$_2$ diffusivity of Shang et al. (2009) (Eqn. 28) and the molecular H$_2$O$_m$ diffusivity of Ni and Zhang (2008) (Eqn. 14), the ratio ($D_{H_2}[H_2]/(D_{H_2O_m}[H_2O_m])$ as a function of temperature and oxygen fugacity buffer is plotted in Figure 13c. It can be seen that when oxygen fugacity is at NNO or higher, diffusion of the total hydrogen component is dominantly due to H$_2$O$_m$ diffusion except for temperatures below 600 K. Under more reducing conditions (that can be encountered in terrestrial melts), at typical magmatic temperatures (≥ 1100 K), H$_2$O$_m$ diffusion still dominates the total hydrogen component flux, but molecular H$_2$ diffusion may dominate the diffusive flux of the total hydrogen component at temperatures below typical magmatic temperatures. It is emphasized that this conclusion is tentative because of the many assumptions involved. Previous experimental diffusion studies (e.g., Shaw 1974; Delaney and Karsten 1981; Karsten et al. 1982; Zhang et al. 1991a; Zhang and Stolper 1991; Nowak and Behrens 1997; Zhang and Behrens 2000; Behrens et al. 2004; Liu et al. 2004b; Okumura and Nakashima 2004, 2006; Ni and Zhang 2008; Behrens and Zhang 2009; Ni et al. 2009a,b; Wang et al. 2009) on the H$_2$O component were conducted without detailed characterization of the oxygen fugacity. Nonetheless, the consistency of these experimental data (e.g., Ni and Zhang 2008) show that H$_2$ diffusion probably did not play a major role in any of these studies. Furthermore, simultaneous H$_2$O and $^{18}$O diffusion studies in the same experiments (Behrens et al. 2007) show that H$_2$O$_m$ that carries O, not H$_2$ that does not carry O, is the diffusing species for the hydrous component. In the future, it will be important to investigate diffusion of the total hydrous component under very reducing conditions with well-characterized oxygen fugacity (e.g., oxygen fugacity that is uniform in the sample and independent of time).

In short, it is possible that molecular H$_2$ diffusion could play a major role in transporting the hydrous component under reducing conditions that may be encountered in terrestrial melts. However, this inference is uncertain at present because of the many assumptions involved. New experimental studies are necessary to resolve this issue.
Zhang et al. (2007) reviewed CO$_2$ diffusion in silicate melts. Not much new work has been published on natural melts since then. For completeness of this chapter and this review volume, a brief summary is provided here. Dissolved CO$_2$ is present in silicate melts in either CO$_2$ molecules or carbonate groups (Fine and Stolper 1985; Blank and Brooker 1994). Hence, CO$_2$ diffusion is also a multi-species diffusion. However, the presence of multiple species seems to contrive to simplify the diffusion properties of CO$_2$, contrary to the case of H$_2$O diffusion (Zhang et al. 2007).

Watson et al. (1982) were the first to investigate tracer diffusion of carbonate (using $^{14}$C tracer diffusion) in silicate melts, and made the surprise discovery that CO$_2$ diffusivity does not depend on the anhydrous melt composition (from a haplobasalt to melt containing 30 wt% Na$_2$O). More extensive $^{14}$C tracer diffusion studies by Watson (1991) confirmed this conclusion but also showed that the diffusivity depends strongly on H$_2$O$_t$. Watson et al. (1982) and Watson (1991) determined concentration profiles using β-track maps made by exposing nuclear emulsion plates to the quenched and sectioned diffusion capsules. As discussed in Mungall (2002), the β-particle range is of the order of a hundred μm (International Commission on Radiation Units and Measurements 1984), much more than initially thought. Hence, tracer diffusion data using β-track maps may be compromised by this effect (those diffusivities extracted from concentration profiles longer than 1 mm are less affected). Furthermore, Zhang et al. (2007) showed that the data are inconsistent with effective binary diffusivities of CO$_2$. Hence, $^{14}$C tracer diffusion data of Watson et al. (1982) and Watson (1991) are not discussed further in quantitative treatment.

Blank (1993), Sierralta et al. (2002) and Nowak et al. (2004) (as well as Fogel and Rutherford 1990, Zhang and Stolper 1991, and Liu 2003) investigated effective binary diffusion of CO$_2$ at CO$_2$ concentration levels of hundreds to thousands of ppm. For the purpose of modeling natural magmatic processes (e.g., CO$_2$ bubble growth in a basalt melt), the effective binary diffusivities of total CO$_2$ are the necessary diffusivities. These studies further confirmed the rough independence of CO$_2$ diffusivity on anhydrous melt composition. This independence is even more surprising considering that CO$_2$ is present as CO$_2$ molecules in rhyolite melt but as CO$_3^{2-}$ ion in basalt melt. Nowak et al. (2004) explained the dependence as follows: Assume molecular CO$_2$ is the diffusing species whereas CO$_3^{2-}$ is roughly immobile. From rhyolite melt to basalt melts, molecular CO$_2$ diffusivity increases (similar to Ar diffusivity), which increases total CO$_2$ diffusivity, but the fraction of dissolved CO$_2$ present as molecular CO$_2$ decreases (the rest is CO$_3^{2-}$), which decreases the total CO$_2$ diffusivity. The two factors roughly cancel each other, leading to a total CO$_2$ diffusivity roughly independent of the anhydrous melt composition. Baker et al. (2005) carried out three carbonate dissolution experiments and measured total CO$_2$ concentration profiles by difference-from-100% method, and two diffusion couple experiments and measured CO$_2$ concentration profiles by FTIR. The compositions for which CO$_2$ diffusion has been investigated are listed in Table 2.

Because of its rough independence of the anhydrous melt composition, CO$_2$ is likely to be the first component for which the diffusivity in various melts can be predicted based on a limited number of studies, which can be compared to the large number of experimental studies on H$_2$O diffusion reviewed in the previous section. Existing experimental data on the effective binary diffusion of CO$_2$ cover 723-1623 K and ≤ 1 GPa. However, they are mostly on dry melts, with only 4 data points on hydrous melts containing ≥ 1 wt% H$_2$O$_t$, of which two points with 5 wt% H$_2$O$_t$ by the reconnaissance experiments of Baker et al. (2005) apparently showed that adding 5 wt% H$_2$O$_t$ does not affect CO$_2$ diffusivity in a trachyte melt, contrary to results by Sierralta et al. (2002) on albite melt and Watson (1991) on other melts. A possible explanation of the discrepancy is that determination of CO$_2$ concentration profiles by the difference-from-100% method used by Baker et al. (2005) does not work well for hydrous
melts and hence CO₂ diffusivities in hydrous trachyte melt are incorrect.

Because total CO₂ diffusivity in all melts are similar to Ar diffusivity in silicic melts (Zhang et al. 2007), and extensive Ar diffusion data in silicic melts are available, covering a wide range of temperature, pressure and H₂O contents (673-1773 K, ≤ 1.5 GPa, and ≤ 5 wt% H₂O), Zhang et al. (2007) used such data to derive the following equation, which is proposed to be applicable for total effective binary diffusivity of CO₂ in basalt to rhyolite melts:

\[
\ln D_{\text{total}, \text{all melts}} = 17367 + 1944.8T - 52.9 \ln 13.99
\]

where \(D\) is in m²/s, \(T\) is in K, \(P\) is in GPa, and \(C_w\) is wt% of H₂O.

Table 2. Chemical composition (wt% on dry basis) for CO₂ diffusion studies.

<table>
<thead>
<tr>
<th>ID</th>
<th>Comp.</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>FeO</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>P₂O₅</th>
<th>Ref</th>
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<td>1</td>
<td>Rhyolite</td>
<td>76.45</td>
<td>0.08</td>
<td>12.56</td>
<td>1.02</td>
<td>0.08</td>
<td>0.25</td>
<td>4.21</td>
<td>4.78</td>
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<td>2</td>
<td>Rhyolite</td>
<td>77.5</td>
<td>0.07</td>
<td>13.0</td>
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<td>0.04</td>
<td>0.05</td>
<td>0.52</td>
<td>4.10</td>
<td>4.18</td>
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<td>3</td>
<td>Basalt</td>
<td>50.6</td>
<td>1.88</td>
<td>13.9</td>
<td>12.5</td>
<td>0.23</td>
<td>6.56</td>
<td>11.4</td>
<td>2.64</td>
<td>0.17</td>
<td>0.21</td>
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<td>4</td>
<td>Ab</td>
<td>69.03</td>
<td>19.33</td>
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<td>5</td>
<td>AbNa1</td>
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<td>19.24</td>
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<td>7</td>
<td>AbNa3</td>
<td>68.43</td>
<td>18.62</td>
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<td>9</td>
<td>AbNa6</td>
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<td>10</td>
<td>AbNa7</td>
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<td>17.60</td>
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<tr>
<td>11</td>
<td>Rh (CO₂)</td>
<td>75.09</td>
<td>0.22</td>
<td>13.83</td>
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<tr>
<td>12</td>
<td>Da (CO₂)</td>
<td>71.78</td>
<td>0.40</td>
<td>15.31</td>
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<tr>
<td>13</td>
<td>DaAn (CO₂)</td>
<td>66.13</td>
<td>0.68</td>
<td>16.18</td>
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<tr>
<td>14</td>
<td>An (CO₂)</td>
<td>63.37</td>
<td>1.11</td>
<td>16.90</td>
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<tr>
<td>15</td>
<td>AnTh (CO₂)</td>
<td>61.92</td>
<td>1.55</td>
<td>15.22</td>
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<tr>
<td>16</td>
<td>Th (CO₂)</td>
<td>60.48</td>
<td>2.01</td>
<td>14.54</td>
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<tr>
<td>17</td>
<td>Ha (CO₂)</td>
<td>53.55</td>
<td>3.74</td>
<td>16.93</td>
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<td></td>
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<tr>
<td>18</td>
<td>Trachyte</td>
<td>59.9</td>
<td>0.39</td>
<td>18.0</td>
<td>0.89</td>
<td>0.12</td>
<td>3.86</td>
<td>2.92</td>
<td>4.05</td>
<td>8.35</td>
<td>0.21</td>
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</tbody>
</table>

The compositions are listed on the anhydrous basis.


Figure 14 compares experimental data and the above equation, especially the data by Baker et al. (2005) because the comparison with Baker et al. (2005) was not made in Zhang et al. (2007). It can be seen that the calculated line and the experimental data of the same color (the online version) are in rough agreement, except for the two data points at 5 wt% H₂O by Baker et al. (2005) (purple short-dashed line and purple solid squares in Fig. 14; the color can be seen in the online version). Excluding these two data points, the maximum uncertainty of the above equation in predicting \(\ln D_{\text{CO₂, total}}\) (Fogel and Rutherford 1990; Zhang and Stolper 1991; Blank 1993; Sierralta et al. 2002; Nowak et al. 2004; Baker et al. 2005) is 1.13. This 2σ uncertainty is larger than typical experimental data uncertainty (with a 2σ of about 0.6 in \(\ln D\)), because \(D_{\text{CO₂, total}}\) depends weakly on melt compositions, which is ignored in the above treatment. New experimental data on CO₂ diffusion under conditions of high H₂O content are necessary to further constrain CO₂ diffusivities.
Comparison of $CO_2$ and $H_2O$ diffusivities. Comparison between $D_{CO_2, total}$, $D_{H_2O}$, and $D_{H_2O}$ using data and equations summarized above reveal that $D_{H_2O}$ is greater than $D_{CO_2, total}$ and $D_{H_2O}$ is usually greater than $D_{CO_2, total}$ (Fig. 15). This is not unexpected since the effective radius of $H_2O$ molecules (1.37 Å, Shannon 1976; Zhang and Xu 1995) is smaller than the effective radius of $CO_2$ molecules (1.7 Å, Behrens and Zhang 2001; Zhang et al. 2007) that dominates $CO_2$ diffusion. However, because $D_{CO_2, total}$ approaches a non-zero constant but $D_{H_2O}$ approaches essentially zero as $H_2O$ approaches zero, $D_{CO_2, total}$ can become larger than $D_{H_2O}$ at magmatic temperatures at $H_2O < 0.2$ wt% with this content depending temperature, pressure and anhydrous melt composition. In natural silicate melts, $H_2O$ is usually greater than 0.2 wt% and hence $D_{H_2O}$ is greater than $D_{CO_2, total}$.

The diffusion of the two most important volatile components, $H_2O$ and $CO_2$, shows similarities and distinctions (Zhang et al. 2007). In both cases, speciation plays a critical role, the neutral species (molecular $H_2O$ or $CO_2$) is the dominant diffusing species, and the diffusivity of the neutral species increases with $H_2O$. However, there are also major differences. Most importantly, $H_2O$ speciation results in $D_{H_2O}$ that depends strongly on $H_2O$ (as well as melt composition); while $CO_2$ speciation results in $CO_2$ diffusivity that is independent of $CO_2$ concentration, and more surprisingly, even independent of the anhydrous melt composition, which is a blessing for quantifying $CO_2$ diffusion.

**OXYGEN DIFFUSION**

Oxygen is the major constituent and a framework element in silicate melts. Therefore, oxygen diffusivities are essential for characterizing reactions and transport in silicate melts.
Because oxygen can be present in many different components and species, including molecular H₂O, O₂, CO₂, ionic CO₃²⁻ and OH, as well as oxygen bonded to Si, Ti, Al, Fe, Mg, Ca, Na, K, and P (often simplified as bridging oxygen, non-bridging oxygen and free O²⁻), oxygen diffusion kinetics can be complicated but may also yield structural information for silicate melts. Hence, oxygen diffusion has been investigated extensively in the geological, materials science, and glass science literature. However, the various reports can be confusing. Some authors investigated chemical (or effective binary) diffusion of various oxygen species and components, and others investigated self-diffusion of oxygen, which is sometimes due to chemical diffusion of H₂O. In earlier studies, bulk exchange and analytical methods often using mass spectrometry are applied; and in more recent studies, profiling methods typically using the ion microprobe are applied. As a general rule, the studies employing profiling techniques provide more reliable data (e.g., Zhang 2008). In addition to studies by geologists, there is also a significant body of glass and materials science literature on oxygen diffusion. Here, we focus on the geological literature.

Geochemists have investigated oxygen diffusion in melts with natural rock compositions as well as mineral or mineral mixture compositions. Dacite, Dᵢ₃₈An₄₂, Na₂Si₅O₁₀, jadeite and basalt melts have been investigated more systematically. Limited data are available for diopside, CaO-Al₂O₃-SiO₂, nepheline, andesite, and rhyolite melts. Because diffusion under wet conditions and that under dry conditions have different mechanisms, they are discussed separately. ¹⁸O self-diffusion and oxygen chemical diffusion are also discussed separately.

Self-diffusion of oxygen in silicate melts under dry conditions

There is a large literature on oxygen self-diffusion in dry silicate glasses by glass scientists, which is not covered here. Muehlenbachs and Kushiro (1974) were the first in the geological literature to explore self-diffusion of ¹⁸O (or ¹⁸O-¹⁶O exchange diffusion) in various melts at high temperature and room pressure (about 0.1 MPa). Even though the diffusion data turned out to have large errors (see discussion below), the method is introduced below because many other authors used the same or a similar experimental technique. A melt blob suspended from a Pt loop is first equilibrated with a gas (either CO₂ or O₂) of some normal δ¹⁸O in a one-atmosphere furnace. This equilibrated melt is the initial state with known initial ¹⁸O/¹⁶O ratio. Then a gas with a new and constant δ¹⁸O is continuously led into the furnace so that ¹⁸O and ¹⁶O in the gas exchange with those in the melt blob through diffusion. That is, the experiments investigate
the interdiffusivities between $^{18}\text{O}$ and $^{16}\text{O}$, which are also oxygen self-diffusivities. After some duration, the sample is quenched and average $\delta^{18}\text{O}$ in the whole melt blob is measured by mass spectrometry. The result is compared with the analytical solution for diffusion in a sphere:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D t}{r^2}\right)$$

where $M_t$ and $M_\infty$ are the amount of $^{18}\text{O}$ entering the sphere of radius $r$ at time $t$ and time $\infty$. The specific equation is often written in the following form:

$$
\frac{\delta^{18}\text{O}_t - \delta^{18}\text{O}_{\text{gas}}}{\delta^{18}\text{O}_0 - \delta^{18}\text{O}_{\text{gas}}} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D t}{r^2}\right)
$$

where the subscripts 0 and $t$ mean experimental time 0 (i.e., the initial state of equilibration) and time $t$, and the subscript “gas” means the gas phase. The final $\delta^{18}\text{O}$ in the melt is assumed to be the same as that of the gas by treating gas as an infinite reservoir and ignoring isotopic fractionation between the gas and the melt at high experimental temperatures. The above equation is used to fit experimental data of $\delta^{18}\text{O}$ versus $t$, from which the diffusivity is extracted.

Muehlenbachs and Kushiro (1974) reported diffusion data in basalt melt (Fig. 16) and the mineral anorthite at room pressure and 1553–1803 K, as well as andesite, rhyolite, and $\text{Di}_{40}\text{An}_{30}\text{Ab}_{30}$ melts (and plagioclase, anorthite, diopside, enstatite, and forsterite minerals) at 1553 K. The diffusivity does not depend on whether the gas phase is $\text{O}_2$ or $\text{CO}_2$. For basalt melt, the activation energy was found to be 377 kJ/mol, which is very high for a melt. Comparison of different melts at 1553 K indicates that $^{18}\text{O}$ diffusivity in basalt melt is highest, followed by andesite melt and $\text{Di}_{40}\text{An}_{30}\text{Ab}_{30}$ melt (about an order of magnitude lower than in basalt), then rhyolite melt (about three orders of magnitude lower than in basalt) (Fig. 16). The mineral data are not of concern here; they will be discussed in another chapter (Farver 2010, this volume).

**Figure 16.** Oxygen self-diffusivity in dry basalt, andesite, dacite and rhyolite melts. Data sources: Basalt(M), Andesite(M) and Rhyolite(M): room pressure data by Muehlenbachs and Kushiro (1974); Basalt(C): room pressure data by Canil and Muehlenbachs (1990); Basalt(L): 1 GPa data by Lesher et al. (1996); Dacite(T): 1 GPa data by Tinker and Lesher (2001). Calculated line is for dacite at room pressure using Equation (44) to compare with the data by Muehlenbachs and Kushiro (1974) and Canil and Muehlenbachs (1990).
Dunn (1982) used the experimental and analytical approach of Muehlenbachs and Kushiro (1974) and investigated $^{18}$O diffusion in $\text{Di}_{58}\text{An}_{42}$, $\text{Di}_{40}\text{An}_{60}$, and diopside melts at room pressure. Canil and Muehlenbachs (1990) followed with an Fe-rich basalt melt. The activation energy for $^{18}$O diffusion in dry basalt was estimated to be about 251 kJ/mol by Canil and Muehlenbachs (1990), much lower than that of Muehlenbachs and Kushiro (1974), but the two data sets are in good agreement (Fig. 16; compare Basalt(M) and Basalt(C)). This comparison shows that activation energy based on limited data is not reliable especially when there is large data scatter. Compared to more recent diffusion data based on the profiling method, these early data based on bulk gain or loss methods show large scatter ($2\sigma$ error is a factor of 3 in $D$, or about 1.1 in $\ln D$, Fig. 16) and often do not provide much quantitative constraint in our discussion below on how oxygen diffusivities depend on various parameters.

Major advancements in $^{18}$O self-diffusion studies came with the development of the ion microprobe for microscopic measurement of isotopic ratios, although with the requirements of using materials highly enriched in $^{18}$O. Coles and Long (1974) and Hofmann et al. (1974) were the first to apply the ion microprobe to study self-diffusion in minerals. Shimizu and Kushiro (1984) were the first to determine $^{18}$O self-diffusivities in silicate melts by carrying out diffusion couple experiments and by measuring $^{18}$O/$^{16}$O ratios using an ion microprobe. They examined oxygen self-diffusion ($^{18}$O-$^{16}$O exchange diffusion) in jadeite and diopside melts. Rubie et al. (1993), Lesher et al. (1996), Liang et al. (1996), Poe et al. (1997), Reid et al. (2001), Tinker and Lesher (2001), and Tinker et al. (2003) followed the approach of Shimizu and Kushiro (1984). Rubie et al. (1993) and Poe et al. (1997) measured oxygen self-diffusivities in dry $\text{Na}_2\text{Si}_4\text{O}_9$ melt at 1898-2800 K and 2.5-15 GPa, as well as in $\text{Na}_3\text{AlSi}_7\text{O}_{17}$ and albite melts. Lesher et al. (1996) determined oxygen (and silicon) self-diffusion in dry basalt melt at 1593-1873 K and 1-2 GPa. Liang et al. (1996) examined oxygen (as well as Ca, Al and Si) self-diffusivities in various $\text{CaO-}\text{Al}_2\text{O}_3-\text{SiO}_2$ melts at 1773 K and 1 GPa. Reid et al. (2001) studied oxygen (and silicon) self-diffusion in dry diopside melt at 2073-2573 K and 3-15 GPa. Tinker and Lesher (2001) investigated oxygen (and silicon) self-diffusion in dry dacite melt at 1628-1935 K and 1-5.7 GPa. Tinker et al. (2003) reported oxygen (and silicon) diffusivities in dry $\text{Di}_{58}\text{An}_{42}$ melt at 1783-2037 K and 1-4 GPa. These new data generally have higher precision, with the possible exception of Reid et al. (2001) (see below). Studies on wet melts are not summarized here and will be discussed in a later section.

The melt that has been most systematically investigated for oxygen self-diffusion is dry dacite even though the number of data points is not extensive (Tinker and Lesher 2001). Figure 17 shows all available experimental data. The data indicate that oxygen self-diffusivity exhibits Arrhenian behavior within the $T$-$P$ range investigated, and increases with increasing pressure from 1 to 4 GPa and then decreases at pressures above 5 GPa. The decrease of the diffusivity with pressure at ≥ 5 GPa may have structural implications, such as possible end of the formation of highly coordinated Si or Al species (Tinker and Lesher 2001). For the purpose of predicting oxygen self-diffusion in dacite melt, there are not enough data at ≥ 5 GPa to constrain the relation. Hence, the data at 1628 to 1935 K and 1 to 4 GPa are fit to obtain the following expression for the self-diffusivity of oxygen in dry dacite melt:

$$\ln D_{\text{dacite melt}}^{^{18}\text{O}} = -(6.57 + 2.148P) - \frac{40830 - 5223P}{T}$$

(44)

where $T$ is in K and $P$ is in GPa. The activation energy decreases with pressure as $(339 - 43P)$ kJ/mol. The activation volume is $-RT\partial(\ln D)/\partial P = -(43.4 - 0.0187) \times 10^{-6}$ m$^3$/mol, a fairly large negative activation volume, in contrast with the positive activation volumes for $\text{H}_2\text{O}$ and $\text{CO}_2$ diffusion. The maximum error by Equation (44) to reproduce the experimental data at 1500-1950 K and ≤ 4 GPa is 0.32 in terms of $\ln D$. Equation (44) cannot be extrapolated at all to $P > 4$ GPa because the linearity between $\ln D$ and $P$ does not hold at higher pressures.
Oxygen self-diffusion in dry $\text{Di}_{58}\text{An}_{42}$ melt has also been examined systematically (Dunn 1982; Tinker et al. 2003). Figure 18 shows all the available data. It can be seen that the data by Dunn (1982) at room pressure are scattered and do not provide much constraint. The $\text{Di}_{58}\text{An}_{42}$ melt is often treated as a basalt-like melt or an FeO-free basalt. However, when oxygen self-diffusivities in dry basalt (solid diamonds and a single plus in Fig. 18) are compared with those in dry $\text{Di}_{58}\text{An}_{42}$, those in basalt are greater by about 1.2 $\ln D$ units. The diffusivity data on $\text{Di}_{58}\text{An}_{42}$ melt by Tinker et al. (2003) at 1738 to 2037 K and 1 to 4 GPa can be expressed as:

\[
\ln D = a - \frac{b}{T}
\]

where $D$ is the diffusion coefficient in m$^2$/s, $T$ is the temperature in K, and $a$ and $b$ are constants.

Figure 17. Oxygen self-diffusion data in dacite melt (Tinker and Lesher 2001).

Figure 18. Oxygen self-diffusion data in $\text{Di}_{58}\text{An}_{42}$ melt compared with those in basalt. Data for $\text{Di}_{58}\text{An}_{42}$ melt are from Dunn (1982) (0.1 MPa; open diamonds) and Tinker et al. (2003) (1.0, 2.0, 3.5 and 4.0 GPa). Data for basalt are from Lesher et al. (1996).
\[
\ln D^{\text{Di-An}_2 \text{ melt}}_{\text{O}} = -10.52 - \frac{26331 - 240P}{T}
\]  
(45)

where \(T\) is in K and \(P\) is in GPa (adding an additional \(P\) term such as that in Equation (44) does not significantly improve the fit). The activation energy is \((219 - 2.0P)\) kJ/mol. The activation volume is \(-RT\partial (\ln D)/\partial P = -2.0 \times 10^{-6}\) m\(^3\)/mol, an order of magnitude smaller than that for oxygen diffusion in dacite melt. The maximum error by the above equation to reproduce the data of Tinker et al. (2003) is 0.18 in terms of \(\ln D\). Extrapolation of the above equation to lower pressures of 0-1 GPa is likely acceptable, but probably not to higher pressures of > 4 GPa.

Rubie et al. (1993) and Poe et al. (1997) studied oxygen self-diffusion in dry Na\(_2\)Si\(_4\)O\(_9\) (or Na\(_2\)O·4SiO\(_2\), NS4) melt. The data (Fig. 19) covering 1893-2800 K and 2.5-15 GPa can be fit by

\[
\ln D^{\text{Na}_2\text{Si}_4\text{O}_9 \text{ melt}}_{\text{O}} = -17.19 - \frac{12693 - 360P}{T}
\]  
(46)

where \(D\) is in m\(^2\)/s, \(T\) is in K, and \(P\) is in GPa. The activation energy is surprisingly low, only about 100 kJ/mol (depending on pressure). The activation volume is negative and small, about \(-3.0 \times 10^{-6}\) m\(^3\)/mol. The maximum error of the above equation in reproducing the experimental data is 0.22 in terms of \(\ln D\).

Three papers explored oxygen self-diffusion in dry basalt melt (Muehlenbachs and Kushiro 1974; Canil and Muehlenbachs 1990; Lesher et al. 1996). However, the earlier data by Muehlenbachs and Kushiro (1974) and Canil and Muehlenbachs (1990) are scattered (Fig. 16). Lesher et al. (1996) reported three data points at 1 GPa and one datum at 2 GPa. Oxygen self-diffusivities at 1593-1873 K and 1 GPa (solid squares in Fig. 16) can be represented by the following equation (Lesher et al. 1996):

\[
\ln D^{\text{basalt melt}}_{\text{O}} = -12.5 - \frac{20447}{T}
\]  
(47)

where \(T\) is in K and \(D\) is in m\(^2\)/s. The activation energy is 170 kJ/mol, smaller than those obtained from other \(^{18}\)O diffusion data in basalt melt at room pressure (377 kJ/mol by Muehlenbachs...
and Kushiro 1974, and 251 kJ/mol by Canil and Muehlenbachs 1990). The large difference in activation energy is likely due to data uncertainty rather than being real. Because the activation volume is highly variable from dacite to D\text{58A}\text{42} melts (−11×10^{-6} to −2.0×10^{-6} m^3/mol; see also Tinker et al. 2003), it is not possible to use information from other melts to constrain the pressure effect on oxygen diffusivity in basalt.

Three papers investigated oxygen self-diffusion in diopside melt (Dunn 1982; Shimizu and Kushiro 1984; Reid et al. 2001). However, the temperature dependence was not constrained: only at two pressures (0.1 MPa by Dunn 1982 and 3 GPa by Reid et al. 2001) were there diffusion data at different temperatures. The data at 0.1 MPa are scattered and those at 3 GPa are strange in that the diffusivity does not change much from 2073 to 2273 K, with an implied activation energy of only 4 kJ/mol (Fig. 20). An error of a factor of 2.5 on individual $D$ values is needed to allow a more reasonable activation energy of about 250 kJ/mol. Hence, the precision of the oxygen self-diffusion data by Reid et al. (2001) is not high. The reason is not clear.

Shimizu and Kushiro (1984) reported oxygen self-diffusion data in jadeite melt at 1673 to 1883 K at 1.5 GPa, and 0.5 to 2.0 GPa at 1673 K (Fig. 21). The diffusivity at 1.5 GPa can be expressed as:

$$\ln D_{\text{jadeite melt}}^{18\text{O}} = -10.84 - \frac{31815}{T}$$

where $D$ is in m^2/s, and $T$ is in K. The activation energy is 265 kJ/mol. At 1673 K, the activation volume is $-6.4\times10^{-6}$ m^3/mol. Assuming the activation volume is independent of temperature, the $P$-$T$ dependence of $^{18}$O diffusivity in jadeite melt may be written as:

$$\ln D_{\text{jadeite melt}}^{18\text{O}} = -10.84 - \frac{32970 - 770P}{T}$$

where $D$ is in m^2/s, $T$ is in K, and $P$ is in GPa.

Liang et al. (1996) investigated the compositional effect of $^{18}$O self-diffusion in various CaO-Al_{2}O_{3}-SiO_{2} melts at 1773 K and 1 GPa. They found that $^{18}$O self-diffusivity increases
with decreasing silica and alumina content, as expected. As NBO/T increases from 0.3 to about 0.9 in CaO-Al₂O₃-SiO₂ system, $^{18}$O self-diffusivity increases by about an order of magnitude.

Figure 22 compares oxygen self-diffusivity in all melts for which the temperature dependence of diffusivity has been determined well at 1 GPa. Oxygen self-diffusivities increase with decreasing SiO₂ and Al₂O₃ contents, or from polymerized to depolymerized melts. From dacite melt (NBO/T ≈ 0.1) to basalt melt (NBO/T = 1), oxygen self-diffusivity increases by two orders of magnitude. It may be inferred that oxygen self-diffusivities depend on oxygen speciation, increasing from bridging oxygen (BO) to non-bridging oxygen (NBO) and then to free oxygen ($O^{2-}$). The diffusivity of each oxygen species may depend on the overall melt composition.

In terms of oxygen self-diffusion, basalt melt (NBO/T = 1) is similar to diopside melt (NBO/T = 2) and Na₂Si₂O₆ melt (NS4 melt, NBO/T = 0.5), whereas dacite melt (NBO/T = 0.1) is similar to jadeite melt (NBO/T = 0) (Fig. 22). But the similarity in each group is not close enough for diffusivities to be merged for a combined fitting. For different melts, there does not seem to be a single compensation temperature where $^{18}$O diffusivities in all melts are the same.

There are not enough data yet to contemplate a general relation between oxygen self-diffusivity and natural melt composition under dry conditions. To achieve such a goal, it is necessary to investigate $^{18}$O diffusion in dry basalt, dry andesite, and dry rhyolite as a function of temperature and pressure systematically (on par with the investigation of dacite melt), and to examine the compositional dependence. In highly polymerized melts (rhyolite and pure silica), it will be important to make the dry system very dry, e.g., less than 50 ppm H₂O (depending on temperature), so that the diffusive flux is due to true $^{18}$O self-diffusion, not H₂O chemical diffusion (see later sections). One may try to use self-diffusivities of other elements such as Si to constrain those of oxygen. However, even though self-diffusivities of oxygen and silicon (both are structural elements) in dry melts are often similar (e.g., Lesher et al. 1996; Poe et al. 1997; Tinker et al. 2003), they may also be significantly different (e.g., Tinker and Lesher 2001; see review by Lesher 2010 and Zhang et al. 2010).

It has been shown that oxygen self-diffusivity in dry melts is similar to the Eyring diffusivity defined as $D = kT/(\lambda \eta)$ where $\lambda$ is the jump distance and $\eta$ is the melt viscosity (e.g., Shimizu
and Kushiro 1984; Tinker et al. 1994; Fig. 27a in this chapter). Therefore, even though $^{18}$O self-diffusion in dry basalt, andesite and rhyolite melts has not been investigated extensively, $^{18}$O self-diffusivity in these dry melts may be estimated using the Eyring equation with a jump distance of $2.8 \times 10^{-10}$ m as long as the melt viscosity can be estimated. In the last 10 years, viscosity models for specific melts have been advanced to high precision (e.g., Zhang et al. 2003 and Hui et al. 2009 for rhyolite melt; Whittington et al. 2009 for dacite melt; Vetere et al. 2006 for andesite melt) and general viscosity models are also available (Hui and Zhang 2007; Giordano et al. 2008) although with larger uncertainties (see Wang et al. 2009 for a comparison of the models of Hui and Zhang 2007 and Giordano et al. 2008). Hence, $^{18}$O self-diffusivities in dry melts can now be estimated with a precision similar to the precision of the viscosity models. For hydrous melts, $^{18}$O “self” diffusivity is much greater than the Eyring diffusivity, and must be understood and predicted in the context of $\text{H}_2\text{O}$ diffusion and the role of $\text{H}_2\text{O}$ in oxygen diffusion (see discussion in a later section).

**Chemical diffusion of oxygen under dry conditions**

Chemical diffusion of oxygen under dry conditions is not well understood. Dunn (1983) reported oxygen chemical diffusion data in nephelinite, alkali basalt and tholeiite melts at 1553 to 1723 K and 0.4 to 2 GPa. Oxidized spheres of glass with $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of 3.7 to 5.8 were packed with graphite powder in a graphite capsule in piston-cylinder experiments. After an experiment, the spheres were retrieved and average FeO concentration in the bulk sample was determined by wet chemical analyses (the $\text{Fe}_2\text{O}_3$ concentration is obtained by difference). Then the diffusivity is estimated using an equation similar to Equation (42). The experimental data of Dunn (1983) on basalt melt are shown in Figure 23. Dunn and Scarfe (1986) used the same approach to obtain diffusivities in an andesite melt at 1623 K and 0.35 to 2 GPa. One possible mechanism for the process in the two reports is as follows: $\text{Fe}_2\text{O}_3$ on the surface of the melt sphere reacts with graphite as:

$$2\text{Fe}_2\text{O}_3(\text{melt}) + \text{C}(\text{graphite}) \rightleftharpoons 4\text{FeO}(\text{melt}) + \text{CO}_2(\text{melt})$$

(50)

Reduction of 1.1 wt% $\text{Fe}_2\text{O}_3$ to produce 1 wt% FeO is accompanied by the production of
0.153 wt% CO₂. Then CO₂ and FeO diffuse into the melt, and Fe₂O₃ in the interior of the melt diffuses to the surface of the melt. In this scenario, the chemical diffusivity determined by Dunn (1983) and Dunn and Scarfe (1986) is related to interdiffusion between CO₂+FeO and Fe₂O₃. Data scatter is considerable in these studies.

Wendlandt (1991) reported oxygen chemical diffusion data in basalt and andesite melts at 1433 to 1633 K and 1 atmosphere with controlled oxygen fugacity (Fig. 23). Mass gain or loss of the spherical sample at an imposed oxygen fugacity was monitored by a high precision electrobalance. Diffusivities were obtained by fitting the variation of the total mass with time using Equation (42). The reaction at the surface is likely 2FeO(melt) + (1/2)O₂ ⇌ Fe₂O₃(melt), then FeO and Fe₂O₃ would interdiffuse in the melt. The diffusivity is hence oxygen chemical diffusivity related to FeO and Fe₂O₃. The data precision is high because weight determination is highly reproducible. However, the initial basalt sample contains 1.03 wt% H₂Oₙ (the initial andesite sample contains 0.44 wt% H₂O). The presence of H₂O in the initial sample may cause two effects:

1. Oxygen diffusivities may be enhanced due to H₂O diffusion, which can carry oxygen (see next section). Based on H₂O diffusivity in basalt (Eqn. 22) and the effect of H₂O diffusion on oxygen diffusion, with 1.0 wt% H₂O, the contribution of H₂O diffusion to oxygen self-diffusion would yield a lnDox of −24.9 at 1633 K, and −25.6 at 1533 K, and −26.5 at 1433 K, which is not enough to account for the high oxygen diffusivities by Wendlandt (1991) (Fig. 23).

2. Because of the presence of H₂O in the initial sample, there would be simultaneous dehydration as O₂ diffuses in or out of the sample. The effect of dehydration on the weight data was not assessed by Wendlandt (1991). Hence, the accuracy of results in this study is uncertain even though the precision is high.

---

Figure 23. Chemical diffusion and oxygen self-diffusion in basalt melt. Oxygen self-diffusion data (open and solid circles) are: 0.1 MPa (C) from Canil and Muehlenbachs (1990); 1.0 GPa (L) from Lesher et al. (1996). The chemical diffusivities are related to O₂ molecular diffusion or FeO effective binary diffusion (see text for discussion): 0.1 MPa (W) from Wendlandt (1991) based on weight gain (filled diamonds; likely reflecting molecular O₂ diffusion and dehydration), which is about a factor of 30 greater than the self-diffusivities; other data are from Dunn (1983), likely reflecting FeO diffusion.
In summary, the much higher apparent oxygen chemical diffusivity by Wendlandt (1991) might be due to complications that are unaccounted for. Furthermore, even if only the data by Dunn (1983) are considered, the scatter is still considerable, which makes it impossible to infer how chemical oxygen diffusivity depends on pressure, or to infer the activation energy. The large scatter in the data of Dunn (1983), Dunn and Scarfe (1986) and Wendlandt (1991) may be partially related to the use of the bulk mass gain or mass loss method, which is prone to complications. Furthermore, part of the difficulty is likely related to the different meanings of oxygen chemical diffusion (such as molecular O$_2$ diffusion, or FeO and Fe$_2$O$_3$ diffusion, or CO$_2$ or H$_2$O diffusion, etc).

**“Self” diffusion of oxygen in the presence of H$_2$O**

In experimental studies or natural systems, H$_2$O is often present: $^{18}$O-enriched H$_2$O may enter the sample of interest from a fluid phase, or H$_2$O may be initially in the sample. Because H$_2$O contains oxygen, the transport of H$_2$O as molecular H$_2$O (or as OH groups) would result in an oxygen flux. Hence, oxygen diffusivity can be affected or controlled by H$_2$O diffusion.

The relation between apparent $^{18}$O diffusivity in silicate melts and the presence of H$_2$O vapor (as well as H$_2$O in the melt) has been explored. DeBerg and Lauder (1980) conducted $^{18}$O-$^{16}$O exchange experiments between melt spheres (composition: 62.2 wt% SiO$_2$ and 37.2 wt% K$_2$O prepared under a vacuum of 0.013 Pa) and an $^{18}$O-enriched O$_2$ or H$_2$O gas, and then extracted $^{18}$O diffusivity. At 1175 K, $^{18}$O diffusivity does not depend on pressure of O$_2$ from 7.5 to 56.3 kPa. On the other hand, the presence of 1.3 kPa of H$_2$O vapor (in addition to 7.5 kPa of O$_2$) yielded an $^{18}$O diffusivity about 2 times the dry $^{18}$O diffusivity at 1093 to 1143 K. The solubility of H$_2$O in this melt is not known. If we assume that the solubility in the potassic silicate melt is roughly the same as that in rhyolite melt (Liu et al. 2005), the solubility at 1.3 kPa of H$_2$O vapor pressure would be about 0.011 wt% (110 ppm). Hence, the observation by DeBerg and Lauder (1980) would imply that when H$_2$O$_{tot}$ concentration is of the order 100 ppm, the contribution to $^{18}$O flux by H$_2$O chemical diffusion is about the same as that of dry oxygen diffusion for this potassic silicate melt at about 1100 K. As H$_2$O partial pressure increases, dissolved H$_2$O$_{tot}$ in the melt increases, and $^{18}$O diffusivity increases. DeBerg and Lauder (1980) concluded that the dissolution and diffusion of O$_2$ in the melt do not play an important role (due to the small solubility and small diffusivity of O$_2$ molecules in the melt), but the dissolution and diffusion of H$_2$O in the melt play a critical role in $^{18}$O diffusion in addition to dry $^{18}$O diffusion. Pfeffer and Ohring (1981) investigated $^{18}$O diffusion in silica in controlled water steam pressure and reached a similar conclusion.

Zhang et al. (1991b) developed the general theory of diffusion of a multi-species component, using the diffusion of H$_2$O and $^{18}$O as specific examples. For $^{18}$O diffusion in the presence of H$_2$O in the sample (either high or low H$_2$O$_{tot}$), because both H$_2$O$_{m}$ and OH carry an oxygen atom, H$_2$O diffusion also carries an $^{18}$O diffusion flux. Because it has been shown from H$_2$O diffusion studies that in silicate melts OH diffusion is negligible compared to H$_2$O$_{m}$ diffusion under almost all conditions, $^{18}$O diffusivity may be viewed as being enhanced by H$_2$O$_{m}$ diffusion alone. In such a case, the general equation for $^{18}$O diffusion can be written as (Eqn. 6 in Behrens et al. 2007 plus the anhydrous diffusion term):

$$\frac{\partial R_i}{\partial t} = \frac{\partial}{\partial x}\left(D_{^{18}O,\text{anhydrous}} \frac{\partial R_i}{\partial x}\right) + \frac{\partial}{\partial x}\left(D_{H_2O_m} \frac{\partial (R_i X_m)}{\partial x}\right) - R_i \frac{\partial}{\partial x}\left(D_{H_2O_m} \frac{\partial X_m}{\partial x}\right)$$

(51)

where $R_i$ is the isotopic fraction of $^{18}$O, $^{18}$O/(^{16}O+^{17}O+^{18}O), $X_m$ is the mole fraction of H$_2$O$_m$ on a single oxygen basis, and $D_{^{18}O,\text{anhydrous}}$ is $^{18}$O diffusivity of oxygen species not associated with H in the presence or absence of H$_2$O. The first term on the right hand side accounts for $^{18}$O diffusive flux due to network oxygen diffusion (not associated with H); the second term accounts for $^{18}$O diffusive flux due to H$_2$O$_m$ diffusion; and the third term accounts for mass...
balance (so that at constant $R_i$ there is no $^{18}$O flux, meaning that the sum of the second and third terms is zero). $D_{^{18}\text{O, anhydrous}}$ is expected to depend on $\text{H}_2\text{O}_t$ concentration because addition of $\text{H}_2\text{O}$ would loosen the melt structure, which would likely cause a higher diffusivity of even anhydrous oxygen species, such as those bonded to Si and Mg. Based on the above equation, $^{18}$O diffusivity can often be estimated as (from Eqn. 15 in Zhang et al. 1991b by removing the OH term):

$$D_{^{18}\text{O}} \approx D_{^{18}\text{O, anhydrous}} + D_{\text{H}_2\text{O}_t} X_m$$

(52)

The $D_{\text{H}_2\text{O}_t} X_m$ term in the above equation is the apparent $^{18}$O “self” diffusivity contributed by $\text{H}_2\text{O}$ diffusion. Using the relation between $D_{\text{H}_2\text{O}_m}$ and $D_{\text{H}_2\text{O}_t}$ (Eqn. 13), the above can be written as:

$$D_{^{18}\text{O}} \approx D_{^{18}\text{O, anhydrous}} + D_{\text{H}_2\text{O}_t} X_m \frac{dX}{dX_m}$$

(53)

where $X$ is the mole fraction of $\text{H}_2\text{O}_t$ on a single oxygen basis. The expression $X_m dX/dX_m$ is shown in Figure 3 for $K = 0.5$. At low $\text{H}_2\text{O}_t$ (e.g., when $X \leq 0.01$), the above can be simplified as (Eqn. 16 in Zhang et al. 1991b):

$$D_{^{18}\text{O}} \approx D_{^{18}\text{O, anhydrous}} + \frac{X}{2} D_{\text{H}_2\text{O}_t}$$

(54)

Zhang et al. (1991b) summarized literature data to evaluate the role of $\text{H}_2\text{O}$ diffusion in $^{18}$O “self” diffusion. Behrens et al. (2007) experimentally investigated $\text{H}_2^{18}$O sorption into a rhyolite melt, from which both $\text{H}_2\text{O}_t$ and $^{18}$O diffusion profiles were measured. Their results show that both $\text{H}_2\text{O}_m$ and $^{18}$O profiles indicate the same $\text{H}_2\text{O}_m$ diffusivity (Fig. 24) under the assumption that $\text{H}_2\text{O}_m$ is the diffusing species and there is chemical and isotopic equilibrium. Thus, their experimental data confirm that $\text{H}_2\text{O}_m$ is the diffusing species in both $\text{H}_2\text{O}_t$ diffusion and $^{18}$O “self” diffusion, as well as the quantitative theory of Zhang et al. (1991b) presented above.

In summary, $\text{H}_2\text{O}$ chemical diffusion (or effective binary diffusion) carries an $^{18}$O flux, which contributes to an apparent $^{18}$O diffusivity. If the $\text{H}_2\text{O}$ content is uniform in the sample and there is no chemical diffusion of $\text{H}_2\text{O}$ (e.g., diffusion couple with similar starting $\text{H}_2\text{O}_t$ but different $^{18}$O/$^{16}$O in the two halves, or sorption of $^{18}$O-enriched $\text{H}_2\text{O}$ into a sample already containing the equilibrium concentration of $\text{H}_2\text{O}$), $^{18}$O/$^{16}$O exchange can still be due to the

Figure 24. Experimental data on $\text{H}_2\text{O}$ and $R_i = ^{18}\text{O}/(^{16}\text{O} + ^{17}\text{O} + ^{18}\text{O})$ profiles (data points) during hydration using $^{18}$O-enriched $\text{H}_2\text{O}$. The solid lines are fit by Equation (11) (for the $\text{H}_2\text{O}$ profile) and Equation (51) (for the $R_i$ profile) assuming $\text{H}_2\text{O}_m$ is the diffusing species and $D_{\text{H}_2\text{O}_m} = D_0 e^{aX}$ with the same $a$ and $D_0$ values for both profiles. From Behrens et al. (2007).
mobility (self-diffusion) of H₂O, and the diffusion may be said to be self-diffusion. In both cases, the diffusing species is H₂O. The resulting ¹⁸O diffusivities from H₂O chemical diffusion and from H₂O self-diffusion are not much different. In the next section, we examine the conditions for ¹⁸O diffusion in natural silicate melts to be true oxygen “self” diffusion or through H₂O diffusion, and quantify apparent ¹⁸O diffusivity in hydrous rhyolite and dacite melts.

“Self” diffusion of oxygen in natural silicate melts in natural environments

Using the theory presented above, if we know both the true ¹⁸O self-diffusivity under dry conditions and the H₂O diffusivity, we can compare \( D_{¹⁸O, anhydrous} \) with \( D_{H₂O, X_m} \), or \( D_{¹⁸O, anhydrous} \) with \( D_{H₂O, t} \frac{dX}{dX_m} \), to determine whether the true ¹⁸O self-diffusion or the apparent ¹⁸O flux due to H₂O diffusion dominates the ¹⁸O flux. Below, we employ data on H₂O diffusion and dry ¹⁸O self-diffusion to evaluate quantitatively the conditions when H₂O diffusion dominates ¹⁸O “self” diffusion.

(1) Dacite melt. This melt is considered first because extensive data are available. Figure 25 compares dry ¹⁸O self-diffusivity (Tinker and Lesher 2001) and apparent ¹⁸O diffusivity contributed by H₂O diffusion. First consider a numerical case at 1600 K and 1 GPa (which are close to the covered experimental conditions of both ¹⁸O self-diffusion and H₂O diffusion). From Equation (44), dry ¹⁸O self-diffusivity is \( 3.5 \times 10^{-14} \) m²/s. Based on Equations 18 and 53, about 0.32 wt% H₂O is required to contribute \( 3.5 \times 10^{-14} \) m²/s to the oxygen diffusivity. Because synthesized experimental dry melts typically contain only ≤ 0.1 wt% H₂O, the experimental dry ¹⁸O self-diffusivities at such high temperatures by Tinker and Lesher (2001) are true \( D_{¹⁸O, anhydrous} \). Now consider 1200 K (a more reasonable magmatic temperature for natural dacite) and 1 GPa. Data by Tinker and Lesher (2001) do not cover such a low temperature (metastable melt). Dry ¹⁸O self-diffusivity extrapolated using Equation (44) is \( 2.1 \times 10^{-17} \) m²/s. Based on Equation (18), about 0.05 wt% (500 ppm) H₂O is required to contribute \( 2.1 \times 10^{-17} \)

![Figure 25. Oxygen and H₂O diffusion at 1 GPa in dacite melt. The open circles and the solid line are H₂O diffusion at 0.95 to 1 GPa from Behrens et al. (2004) and Ni et al. (2009b). The two dashed lines are calculated oxygen diffusivities due to H₂O diffusion based on the H₂O diffusivity of Ni et al. (2009b). The filled diamonds (in red in the online version) with a best-fit line (in red in the online version) are experimental ¹⁸O self-diffusion data at 1 GPa from Tinker and Lesher (2001). The dotted line is Eyring diffusivity calculated using the viscosity model of Hui and Zhang (2007) at 0.1 MPa to 1 GPa assuming a jumping distance of \( 2.8 \times 10^{-10} \) m.](image-url)
m²/s to the oxygen diffusivity. The difference at the two temperatures is due to lower activation energy for H₂O diffusion and higher activation energy for dry ¹⁸O diffusion. As the temperature is lowered further, H₂O diffusion would dominate the apparent ¹⁸O “self” diffusion (Fig. 25) at even lower H₂O. Because most natural dacite melts are expected to contain more than 0.2 wt% H₂O, we conclude that apparent ¹⁸O diffusion in natural dacite melts is almost always dominated by H₂O diffusion.

(2) Basalt melt. Both ¹⁸O and H₂O diffusion data are limited on basalt melt. Consider 1600 K and 1 GPa. From Equation (47), dry ¹⁸O self-diffusivity is about 1.1×10⁻¹¹ m²/s. Based on Equation (22), about 1 wt% H₂O is necessary to contribute 1.1×10⁻¹¹ m²/s to apparent ¹⁸O diffusivity. That is, for basalt melt, due to high dry ¹⁸O self-diffusivity and magmatic temperatures, about 1 wt% H₂O is needed for H₂O diffusion to dominate ¹⁸O “self” diffusion. Therefore, in almost all mid-ocean ridge basalt melts (typically containing 0.2 to 0.7 wt% H₂O, but can be up to 1.2 wt%; Dixon et al. 1988; Michael 1988; Workman et al. 2006) and most ocean island basalt melts (often more volatiles than MORB; Dixon et al. 1997; Hauri 2002; Workman et al. 2006), ¹⁸O diffusivity is most likely dominated by true ¹⁸O self-diffusion. However, in pre-eruptive island arc basalt (IAB) melts, and even in melt inclusions in mantle megacrysts likely influenced by subduction, H₂O concentration are 2-6 wt% (Stolper and Newman 1994; Wang et al. 1999; Newman et al. 2000; Gurenko et al. 2005; Wallace 2005), meaning apparent ¹⁸O self-diffusion in these melts is dominated by H₂O diffusion.

(3) Rhyolite melt. There are only limited ¹⁸O diffusivity data in dry rhyolite melt at 1553 K and 0.1 MPa (Muehlenbachs and Kushiro 1974) and the quality of the data is not high (see discussion in an earlier section). On the other hand, H₂O diffusion in rhyolite melt has been investigated extensively (e.g., comprehensive model by Ni and Zhang 2008). Figure 26 compares the contribution to ¹⁸O diffusion by the H₂O flux with that by true network ¹⁸O self-diffusion. Oxygen self-diffusivities by Muehlenbachs and Kushiro (1974) are higher by a factor of about 24 than the Eyring diffusivity for dry melt calculated from the viscosity model of Zhang et al. (2003). If the data by Muehlenbachs and Kushiro (1974) are accurate and the melt was indeed dry (much less than 0.1 wt% H₂O), oxygen flux due to chemical diffusion of H₂O when H₂O content is about 0.1 wt% would be roughly the same as the oxygen flux due to true oxygen self-diffusion. On one hand, oxygen self-diffusivities obtained by Muehlenbachs and Kushiro (1974) are close to effective binary diffusivity of P, which seems to imply the Eyring diffusivity limit. On the other hand, typical “dry” rhyolite glasses (either natural or synthesized) contain ≥ 0.1 wt% H₂O. If the rhyolite used by Muehlenbachs and Kushiro (1974) also contained about 0.1 wt% H₂O, their measurements would actually mean apparent ¹⁸O “self” diffusivity due to H₂O diffusion, implying true dry ¹⁸O self-diffusivities are yet to be determined. Regardless how this issue is resolved, at typical rhyolite melt temperatures (such as 1200 K), H₂O diffusion would dominate oxygen transport at much lower H₂O, such as 10 to 100 ppm level. That means, in natural rhyolite melt in which H₂O content if often 4-6 wt% (e.g., Wallace et al. 2003), diffusive transport of oxygen isotopes is through H₂O diffusion.

There are no ¹⁸O diffusivity data in dry andesite melts, and hence similar quantitative comparisons cannot be carried out. Nonetheless, it is expected that H₂O diffusion plays a more important role in transporting ¹⁸O flux as temperature is lowered and as the melt becomes more silicic. Hence, the behavior of andesite melt is expected to be between that of basalt melt and dacite melt. When H₂O is high enough (e.g., ≥ 0.5 wt%), the apparent ¹⁸O diffusivity in andesite melt is likely dominated by H₂O diffusion. Because pre-eruptive natural andesite melt often contains ≥ 0.5 wt% H₂O, we expect the ¹⁸O flux in natural andesite melt to be often dominated by H₂O chemical diffusion. In summary, in nature, true ¹⁸O self-diffusion is the diffusion mechanism only for relatively dry basalt melt (such as MORB and OIB).

The realization that diffusive transport of ¹⁸O in natural rhyolite and dacite melts is almost always due to H₂O diffusion means it is possible to predict ¹⁸O diffusive transport using Equation
(52) or (53) because H₂O diffusion in these melts has already been investigated well (e.g., Behrens et al. 2004; Liu et al. 2004b; Ni and Zhang 2008; Ni et al. 2009b). For the convenience of the readers, calculated apparent ¹⁸O diffusivities in hydrous rhyolite and dacite melts as a function of $T$, $P$, and H₂O₉ are listed in Tables 3 and 4. In the calculation, the diffusivity of oxygen not associated with H is approximated by Eyring diffusivity. The calculated diffusivities have a 2σ uncertainty of about 0.6 in ln$D$ and may be applied in rough estimation of diffusion rates. For calculation of the ¹⁸O diffusion profile, it is more accurate to use Equation (51).

Prediction of ¹⁸O diffusion in basalt and andesite melts require more experimental work in terms of both H₂O diffusion and dry ¹⁸O diffusion.

Contribution of CO₂ diffusion to ¹⁸O transport in CO₂-bearing melts

Because carbon species (CO₂ molecule and CO₃²⁻) also carry oxygen, oxygen transfer in natural systems may also be realized through the diffusion of these species, especially molecular CO₂. One-atmosphere experiments on ¹⁸O diffusion often use ¹⁸O-enriched CO₂ gas as the source for ¹⁸O (Muehlenbachs and Kushiro 1974; Canil and Muehlenbachs 1990). Not withstanding the quality of such data, one may wonder whether the extracted diffusivity is true ¹⁸O self-diffusivity, or just a reflection of CO₂ diffusion carrying ¹⁸O into the sample. No simultaneous investigation of ¹⁸O and CO₂ diffusion has been carried out yet.

Although experimental data are lacking, the role of CO₂ diffusion in transporting ¹⁸O can be treated similarly as the role of H₂O diffusion in transporting ¹⁸O. However, it is more convenient to consider total CO₂ diffusion rather than the diffusion of CO₂ molecules because $D_{CO₂,total}$ is roughly independent of melt composition. The diffusion equation for the isotopic fraction of ¹⁸O can be written as follows (comparing with Eqn. 51):
where $X_{\text{CaO}_{\text{total}}}$ is mole fraction of total CaO (each CaO contains a single oxygen and two CaO makes one CO$_2$ on a single oxygen basis, and $D_{\text{CO}_2,\text{anhydrous}}$ is diffusivity of CO$_2$ unassociated with carbon. $X_{\text{CaO}_{\text{total}}}$ is calculated as $(C_{\text{CaO}}/22.005)/(C_{\text{CaO}}/22.005 + (100-C_{\text{CaO}}))$ where $C_{\text{CaO}}$ is wt% of CO$_2$ and $W$ is the molar mass of the dry melt on a single oxygen basis (Table 1). $X_{\text{CO}_2,\text{total}}$ may be used instead of $X_{\text{CaO}_{\text{total}}}$, but a factor of 2 would have to be incorporated because each CO$_2$ molecule carries two oxygen atoms. $D_{\text{CO}_2,\text{total}}$ does not depend on CO$_2$ concentration or anhydrous melt composition and hence can be taken out of
the differentials. Based on the above equation, the $^{18}$O diffusivity can often be estimated as (comparing with Eqn. 52):

$$D_{^{18}O} \approx D_{^{18}O,\text{noncarbonated}} + D_{CO_2,\text{total}} X_{CO_2,\text{total}}$$

(56)

The $D_{CO_2,\text{total}} X_{CO_2,\text{total}}$ term in the above equation is apparent $^{18}$O “self” diffusivity contributed by CO$_2$ diffusion. Because $D_{CO_2,\text{total}}$ can be estimated from Equation (41), we examine quantitatively possible contributions by CO$_2$ to $^{18}$O diffusion below.

For rhyolite melt at 1553 K and 0.1 MPa (the condition at which $^{18}$O diffusivity was determined in a CO$_2$ gas by Muehlenbachs and Kushiro 1974), $D_{CO_2,\text{total}}$ is $1.2 \times 10^{-11}$ m$^2$/s from Equation (41). The measured $^{18}$O diffusivity is $4.5 \times 10^{-15}$ m$^2$/s. For CO$_2$ diffusion to contribute to such an $^{18}$O diffusivity, a CO$_2$ concentration of 260 ppm is needed (equivalent to a CO$_2$ partial pressure of 52 MPa). Typical natural rhyolite does not contain this much CO$_2$. We hence conclude that in this case, $^{18}$O diffusivity is not due to chemical CO$_2$ diffusion. This is consistent with the similarity of $^{18}$O diffusivities in CO$_2$ gas and in O$_2$ gas.

For the convenience of readers, contribution to apparent $D_{^{18}O}$ by CO$_2$ chemical diffusion are calculated and listed in Table 5. Note that this table does not give the apparent $D_{^{18}O}$ values as in Tables 3 and 4 where the dry $^{18}$O self-diffusivity has been added or is assessed to be negligible. Table 5 only lists the part of apparent $D_{^{18}O}$ contributed by CO$_2$ chemical diffusion when the CO$_2$ concentration is 100 ppm. The 2σ uncertainty in the calculated values is about 1.1 ln$D$ units. For the full apparent $^{18}$O diffusivity, the anhydrous and non-carbonated true $^{18}$O self-diffusivity and that contributed by CO$_2$ diffusion must be added. Because $D_{CO_2,\text{total}}$ (Equation 41) does not depend on the anhydrous melt composition, Table 5 is roughly applicable to all silicate melts. The contribution to the apparent $^{18}$O diffusivity is proportional to CO$_2$$_{\text{total}}$ concentration (Eqn. 56), which can be used to estimate the contribution to $D_{^{18}O}$ by CO$_2$ chemical diffusion at other CO$_2$$_{\text{total}}$ concentrations. Comparing Table 5 with Tables 3 and 4, the contribution by CO$_2$ chemical diffusion to $^{18}$O diffusion at the 100 ppm CO$_2$ level is not important to dacite melt or rhyolite, with the possible exception of very dry rhyolite melt ($\leq 0.2$ wt% H$_2$O) at very high temperatures ($\geq 1500$ K).

### Table 5. Calculated ln$D_{^{18}O}$ (D in m$^2$/s) contributed by CO$_2$ diffusion at 100 ppm CO$_2$$_{\text{total}}$.

<table>
<thead>
<tr>
<th>H$_2$O$_t$ (wt%)</th>
<th>0.1 GPa</th>
<th>0.5 GPa</th>
<th>1 GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000 K</td>
<td>1300 K</td>
<td>1600 K</td>
</tr>
<tr>
<td>0</td>
<td>−39.27</td>
<td>−35.22</td>
<td>−32.69</td>
</tr>
<tr>
<td>0.1</td>
<td>−39.19</td>
<td>−35.15</td>
<td>−32.63</td>
</tr>
<tr>
<td>0.3</td>
<td>−39.01</td>
<td>−35.02</td>
<td>−32.52</td>
</tr>
<tr>
<td>0.5</td>
<td>−38.83</td>
<td>−34.88</td>
<td>−32.41</td>
</tr>
<tr>
<td>1.0</td>
<td>−38.39</td>
<td>−34.54</td>
<td>−32.14</td>
</tr>
<tr>
<td>1.5</td>
<td>−37.95</td>
<td>−34.2</td>
<td>−31.86</td>
</tr>
<tr>
<td>2.0</td>
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<td>−33.86</td>
<td>−31.59</td>
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<tr>
<td>3.0</td>
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<tr>
<td>4.0</td>
<td>−35.74</td>
<td>−32.51</td>
<td>−30.48</td>
</tr>
<tr>
<td>5.0</td>
<td>−35.1</td>
<td>−32.01</td>
<td>−30.08</td>
</tr>
</tbody>
</table>

Each cell lists ln$D_{^{18}O}$ values contributed by CO$_2$ chemical diffusion with $D$ calculated as $D_{CO_2,\text{total}} X_{CO_2,\text{total}}$ at 100 ppm CO$_2$$_{\text{total}}$ and $D_{CO_2,\text{total}}$ from Equation (41). To estimate $D_{^{18}O}$ at other CO$_2$ concentrations, multiply $D_{^{18}O}$ (not ln$D_{^{18}O}$) by the concentration ratio. For example, for 500 ppm CO$_2$, multiply $D_{^{18}O}$ values in this table by 5. Add $D_{^{18}O}$ here to $D_{^{18}O}$ in Tables 3 or 4 (do not add ln$D_{^{18}O}$) would give the full $D_{^{18}O}$ in hydrous and carbonated rhyolite and dacite melts.
Oxygen diffusion and viscosity: applicability of the Eyring equation

Oishi et al. (1975) showed that the $^{18}$O diffusivity in $4Na_2O\cdot3CaO\cdot18SiO_2$, $2CaO\cdotAl_2O_3\cdot2SiO_2$, and $Na_2O\cdot4SiO_2$ melts is inversely proportional to melt viscosity. Shimizu and Kushiro (1984) showed that the Eyring equation relates $^{18}$O diffusivity well with viscosity for dry diopside and jadeite melts (Fig. 27a). $^{18}$O diffusion data in other dry melts (e.g., Liang et al. 1996; Tinker and Lesher 2001; Tinker et al. 2004) also roughly follow the Eyring relation (Fig. 27a) even though in detail there are differences (e.g., Liang et al. 1996; Tinker et al. 2004). Figure 25 shows that the Eyring relation roughly applies to dry dacite melt at 1 GPa (rough agreement between solid diamonds and dotted line). However, Figure 26 indicates either limited experimental $^{18}$O diffusion data in dry rhyolite melt do not represent true $D_{^{18}O, anhydrous}$, or the Eyring relation does not apply to dry rhyolite (comparing solid diamonds and solid circles). Overall, available data largely indicate that the Eyring equation is applicable to $^{18}$O diffusion in dry silicate melts.

For hydrous silicate melts, the available data indicate that the apparent $^{18}$O diffusivity is often orders of magnitude greater than the Eyring diffusivity (or Stokes-Einstein diffusivity or any of the other models of inverse proportionality between diffusivity and viscosity) (Behrens

![Figure 27. Comparison of the Eyring diffusivity with $^{18}$O diffusivity in (a) dry melts, and (b) hydrous rhyolite melts. Note that the scale is base-10 logarithm, not base-e logarithm. Data sources for (a): Shimizu84 = Shimizu and Kushiro (1984); Tinker04 = Tinker et al. (2004); Liang96 = Liang et al. (1996). Data sources for (b): Viscosity model used for the calculation of rhyolite melt viscosity is from Zhang et al. (2003). $H_2O_m$, $H_2O_t$, and $^{18}$O diffusivities are from Behrens et al. (2007) and Ni and Zhang (2008).]
et al. 2007; Fig. 27b). Because natural silicate melts often contain a significant amount of H$_2$O, the results indicate that the application of the Eyring relation in geological melts is very limited. $^{18}$O diffusion in terrestrial silicate melts in natural environments is often dominated by H$_2$O flux and cannot be predicted by the Eyring equation (but can be predicted from H$_2$O diffusivities).

The inapplicability of the Eyring equation to $^{18}$O diffusion in hydrous silicate melts may be explained as follows. In deriving the Eyring equation, one assumption is that the diffusion and viscous flow are controlled by the same mechanism (motion). For the case of dry silicate melts, viscous flow and diffusion of oxygen (the dominant ion in the melt) are both related to structural mobility, and are hence controlled by the same mechanism. However, for the case of wet silicate melts, viscous flow requires network oxygen mobility, but $^{18}$O diffusive flux is carried by the mobility of neutral H$_2$O$_{m}$ molecules, whose motion is not necessarily related to network oxygen relaxation. In the context of this explanation, the Eyring equation cannot be applied as a universal relation; it is necessary to know the diffusion mechanism and diffusing species before assessing whether the equation can be applied. Because most natural melts are hydrous, the applicability of the Eyring relation to natural melts is limited.

**O$_2$ DIFFUSION IN PURE SILICA MELT**

Dissolved molecular O$_2$ in silicate melts may also be referred to as physically dissolved oxygen (meaning no reaction between O$_2$ molecule and other components in the melt or glass because essentially all melts are based on oxygen anions). In natural melts, the oxygen fugacity is low. For example, oxygen fugacity at NNO buffer (about the average oxygen fugacity in typical mantle derived silicate melts), $f_{O_2}$ is only about $3\times10^{-7}$ Pa at 1200 K (calculation based on thermodynamic data of Robie and Hemingway, 1995), lower than that in air by almost 11 orders of magnitude. Therefore, the dissolved O$_2$ concentration in natural silicate melts is expected to be extremely low. However, in industry and in high-temperature experiments carried out in air or in pure oxygen gas, dissolved O$_2$ concentration may be noticeable. Under such conditions, pure molecular O$_2$ diffusion may be studied, and molecular O$_2$ diffusion may contribute significantly to network oxygen diffusion.

We have shown that oxygen diffusion data in natural or nearly natural silicate melts are complicated, but it is still possible to make sense out of most data in terms of contributions by various oxygen species. Oxygen diffusion data in the glass and materials science literature are even messier (e.g., Fig. 9 in the review by Lamkin et al. 1992), likely due to the contributions by the various oxygen species discussed earlier (especially the hydrous component), plus the additional complexity due to molecular O$_2$. Because such data are on melts very different from geological silicate melts, they are not the focus in this volume. Hence, we make no attempt to quantitatively explain the complicated behavior of oxygen diffusivity in various silica and silicate melts in the glass and materials science literature. Below, we briefly discuss molecular O$_2$ diffusion in silica melt for two purposes. First, such data allow us to roughly know the molecular O$_2$ diffusivity (for the completeness of this volume). Secondly, we may use the O$_2$ diffusivity to assess the role of molecular O$_2$ diffusion in oxygen diffusion in natural melts (under oxygen fugacity of terrestrial igneous processes), which turns out to be unimportant due to extremely low oxygen fugacity in natural silicate melts (see below). Molecular diffusion of O$_2$ in silica melt is best understood compared to other silicate melts due to the simple composition of silica.

Even though there have been numerous studies on oxygen diffusion in silica melt/glass, only a limited number of authors reported genuine molecular O$_2$ diffusivities. Norton (1961) carried out molecular O$_2$ permeation experiments in silica glass and obtained molecular O$_2$ diffusivities at 1223 and 1351 K. Hetherington and Jack (1964) made an order of magnitude estimate of molecular O$_2$ diffusivities in silica glass, and the values are consistent with the
results of Norton (1961). Susa et al. (1990) reported diffusivities of molecular O\(_2\) in variously prepared silica films at 1073-1273 K. Lamkin et al. (1992) reviewed oxygen diffusion data in silica and silicate glasses. Kajihara et al. (2004, 2005) systematically investigated molecular O\(_2\) diffusion in silica glass with different OH contents. Kajihara et al. (2008) reviewed diffusion and reaction of interstitial oxygen species in silica glass. Molecular O\(_2\) diffusion data in silica glass are shown in Figure 28. Molecular O\(_2\) diffusivity in low-OH silica glass (Kajihara et al. 2004) can be expressed as follows:

\[
D_{\text{O}_2}^{\text{silica melt}} = \exp\left((19.22 \pm 0.39) - \left(\frac{10727 \pm 482}{T}\right)\right)
\]  

where \(D\) is in m\(^2\)/s, \(T\) is in K and errors are given at the 2\(\sigma\) level. The activation energy for molecular O\(_2\) diffusion is 89±4 kJ/mol, greater than that for Ne diffusion but slightly smaller than that for H\(_2\)O\(_m\) diffusion. Network oxygen diffusivities (such as \(^{18}\)O diffusivities) in silica melts are 5 to 9 orders of magnitude lower than molecular O\(_2\) diffusivity at 900-1700 K (Fig. 1A in Lamkin et al. 1992) and the activation energy is much higher.

To evaluate the role of molecular O\(_2\) in transporting oxygen in natural silicate melts, we compare \(2D_{\text{O}_2}[O_2]\) and \(D_{\text{O}}[O]\) where O\(_2\) means molecular oxygen and O means network oxygen, and the factor 2 is because each molecular O\(_2\) carries two oxygen atoms. Because molecular O\(_2\) solubility in silica melt is about \(10^{-6}\) mol/m\(^3\) at 1 Pa of O\(_2\) pressure (Norton 1961), the solubility at a typical oxygen fugacity of \(10^{-7}\) Pa in natural silicate melt would be of the order \(10^{-13}\) mol/m\(^3\). The network oxygen concentration in silica melt is about 76560 mol/m\(^3\). Hence the concentration ratio of \(2[O_2]/[O]\) is about \(3\times10^{-18}\). Because molecular O\(_2\) diffusivity is no more than 9 orders of magnitude greater than network oxygen diffusivity, at typical oxygen fugacities of natural silicate melts, the ratio of \(2D_{\text{O}_2}[O_2]\) to \(D_{\text{O}}[O]\) is smaller than \(3\times10^{-9}\). Hence, the contribution from molecular oxygen diffusion to oxygen transport is negligible in natural silicate melts. For molecular O\(_2\) to play a significant role in transporting network oxygen, an oxygen fugacity of about 100 Pa or greater is needed.

**Figure 28.** Molecular O\(_2\) diffusivities in silica melts. Susa et al. (1990) and Kajihara et al. (2005) each contain two data sets for slightly different silica melts; these are plotted separately.
SUMMARY AND CONCLUSIONS

Through decades of research, fairly extensive experimental data have been obtained on \( \text{H}_2\text{O}, \text{CO}_2, \) and oxygen diffusion in silicate melts. The variation of diffusivities with temperature, pressure, and melt composition (including water content) has led us to fundamental understanding of diffusion mechanisms and melt structure. \( \text{H}_2\text{O} \) diffusion and \( \text{CO}_2 \) diffusion are both dominated by the diffusion of the respective molecular species. The diffusivity of these two major volatile components increases with temperature and water content, but decreases with pressure. Total \( \text{CO}_2 \) diffusivity increases exponentially with \( \text{H}_2\text{O} \), whereas \( \text{H}_2\text{O} \) diffusivity first increases with \( \text{H}_2\text{O} \) proportionally, and then exponentially. While \( \text{CO}_2 \) diffusivity does not depend much on melt composition except for the \( \text{H}_2\text{O} \) concentration, \( \text{H}_2\text{O} \) diffusivity increases with decreasing silica content at superliquidus temperatures, but the trend at intermediate temperatures is less well defined. \( \text{H}_2\text{O} \) diffusivity also increases slightly with increasing alkalinity. \( \text{H}_2\text{O} \) speciation causes proportionality between \( \text{H}_2\text{O} \) diffusivity and \( \text{H}_2\text{O} \) concentration at low \( \text{H}_2\text{O} \), whereas \( \text{CO}_2 \) speciation leads to independence of total \( \text{CO}_2 \) diffusivity on \( \text{CO}_2 \) concentration, and also causes total \( \text{CO}_2 \) diffusivity to be independent of the anhydrous melt composition. One complexity that needs to be examined in detail in the future is the possible role of molecular \( \text{H}_2 \) diffusion in transporting the hydrous component under reducing conditions.

Oxygen chemical diffusivity depends on the specific diffusion mechanisms and more systematic studies are necessary to understand the various chemical oxygen diffusivities. In the presence of \( \text{H}_2\text{O} \), oxygen “self” diffusion is often controlled by \( \text{H}_2\text{O} \) diffusion. In typical natural silicate melts, especially rhyolite, dacite and andesite melts, \( ^{18}\text{O} \) diffusion is often carried by \( \text{H}_2\text{O} \) diffusion, and hence can be predicted from experimental \( \text{H}_2\text{O} \) diffusivities that have been well characterized in rhyolite and dacite melts. Predicted \( ^{18}\text{O} \) diffusivities in hydrous rhyolite and dacite melts are listed in tables and can be many orders of magnitude greater than the Eyring diffusivity. Only in fairly dry basalt melts (such as MORB and OIB), would \( ^{18}\text{O} \) diffusion occur through true oxygen self-diffusion, in which case the \( ^{18}\text{O} \) self-diffusivity is not much different from the Eyring diffusivity. \( ^{18}\text{O} \) flux carried by \( \text{CO}_2 \) chemical diffusion is also quantitatively evaluated, and the conclusion is that \( \text{CO}_2 \) diffusion does not significantly enhance \( ^{18}\text{O} \) diffusion except under very special conditions. The contribution from molecular \( \text{O}_2 \) diffusion is negligible to network oxygen diffusion under oxygen fugacity encountered in natural silicate melts.

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