Molecular $\text{H}_2\text{O}$ as carrier for oxygen diffusion in hydrous silicate melts

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Abstract

Dissolved water is known to dramatically enhance oxygen diffusion in silicate melts, glasses and minerals. A quantitative theory has been developed to explain this phenomenon by transport via molecular $\text{H}_2\text{O}$ diffusion [Y. Zhang, E.M. Stolper, G.J. Wasserburg, Diffusion of a multi-species component and its role in the diffusion of water and oxygen in silicates, Earth Planet. Sci. Lett., 103 (1991) 228–240]. Here we report experimental confirmation of the theory for rhyolitic melts by measuring both $\text{H}_2\text{O}$ and $\text{O}^{18}$ diffusion profiles in a single experiment. In sorption experiments at 100 MPa and temperatures from 1041 to 1136 K isotopically enriched water diffused into doubly polished rhyolitic glass wafers. $\text{H}_2\text{O}$ profiles were analyzed by infrared spectroscopy and $\text{O}^{18}$ profiles by SIMS. $\text{O}^{18}$ diffusivities were found to be 1–2 orders of magnitude slower than bulk water diffusivities but 3–4 orders of magnitude faster than Eyring diffusivities calculated from viscosity. The data show that oxygen “self” diffusion under hydrothermal conditions is due to molecular $\text{H}_2\text{O}$ diffusion, not due to the self diffusion of oxygen itself. With this confirmation, experimental data on $\text{H}_2\text{O}$ diffusion in silicate melts can be used to infer $\text{O}^{18}$ diffusion under hydrothermal conditions, and hydrothermal oxygen diffusion data in silicate minerals can be used to infer $\text{H}_2\text{O}$ diffusivity, as long as the concentration or solubility of $\text{H}_2\text{O}$ in the given phase is known.

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1. Introduction

Many authors have carried out $\text{O}^{18}$ “self” diffusion experiments under hydrothermal conditions [2–9]. During such an experiment, an $\text{O}^{18}$-enriched $\text{H}_2\text{O}$ fluid surrounds or is in contact with a mineral, glass or melt, and $\text{O}^{18}$ diffuses into the condensed phase. After the experiment, the isotopic ratio $R (\equiv \frac{\text{O}^{18}}{\text{O}^{16} + \text{O}^{18}})$ is measured as a function of distance from the surface in contact with the fluid. Experimental data show that the presence of water dramatically enhances $\text{O}^{18}$ diffusivity. Related phenomena are the hydrolytic weakening of quartz [10,11] and enhanced cation diffusivities in framework silicates such as feldspars [12–14].

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Various hypotheses have been proposed to explain the dramatic enhancement of oxygen diffusion in silicate melts [1,15–24]. The most often discussed explanations are based on the enhancements induced by fast proton transients [18–20] or hydrous species as carriers of oxygen [21–24]. The former is a qualitative idea and has not been developed into a quantitative theory. The latter hypothesis suggests that hydrothermal oxygen “self” diffusion data actually reflect transport via H₂O diffusion for which a quantitative theory has been proposed.

It is well established that molecular H₂O (hereafter referred to as H₂Oₐ) is the mobile species responsible for transporting the H₂O component in silicate melts [25–31] although some details about migration of H₂O in the melts remain debated [25,32,33]. OH is essentially immobile but may be consumed or regenerated by an interconversion reaction between H₂O and OH. Hence, diffusion of H₂O is a classical diffusion-reaction problem [34]. The diffusion coefficient of total H₂O (H₂Om, including both H₂Oₐ and hydroxyl) can be expressed as:

$$D_{\text{H}_2\text{O}_m} = D_{\text{H}_2\text{O}_a} \cdot \frac{dX_{\text{H}_2\text{O}_m}}{dX_{\text{H}_2\text{O}_a}}.$$  

Where X refers to the mole fraction of the species or component in the melt calculated on a single oxygen basis. Because H₂O contains oxygen, the diffusion of H₂Oₐ leads to an oxygen flux. A number of authors [1,7,9,18,22–24] have proposed that ¹⁸O diffusion from a hydrothermal fluid into silicate melt, glass, quartz and feldspar is carried by H₂Oₐ, with anhydrous oxygen and OH being essentially immobile except for local ¹⁸O–¹⁶O isotope exchange reactions between H₂Oₐ and other oxygen species. That is, ¹⁸O transport from a hydrothermal fluid into a silicate melt, glass or mineral is controlled by coupled diffusion and exchange. Detailed quantitative aspects of this mechanism have been developed by Zhang et al. [1] but experimental evidence has, until now, been missing. Although an accurate general expression for D₁⁸O (the apparent ¹⁸O diffusivity) is complicated, an approximate expression is as follows [1]:

$$D_{\text{D}} \approx D_{\text{H}_2\text{O}_m} \cdot X_{\text{H}_2\text{O}_m}.$$  

Combining Eqs. (1) and (2) leads to,

$$D_{\text{D}} \approx D_{\text{H}_2\text{O}_a} \cdot X_{\text{H}_2\text{O}_m} \cdot \frac{dX_{\text{H}_2\text{O}_a}}{dX_{\text{H}_2\text{O}_m}}.$$  

At very low $X_{\text{H}_2\text{O}_a}$ (<0.001) which are typically found in nominally water-free minerals, this equation simplifies to

$$D_{\text{D}} \approx D_{\text{H}_2\text{O}_a} \cdot X_{\text{H}_2\text{O}_a}/2.$$  

Hence, $D_{\text{D}}$ is typically orders of magnitude smaller than $D_{\text{H}_2\text{O}_a}$ and the ¹⁸O profile is much shorter than the H₂O profile. Therefore, across the ¹⁸O profile, H₂Oₐ is roughly constant, leading to constant $D_{\text{D}}$ and an error function shape of the profile [4–8]. On the other hand, when surface $X_{\text{H}_2\text{O}_a}$ is large (as for hydrous melts in contact with a fluid), $D_{\text{D}}$ approaches $D_{\text{H}_2\text{O}_a}$ and the length of ¹⁸O profile is a significant portion of that of the H₂Oₐ profile. That is, along the ¹⁸O profile, $X_{\text{H}_2\text{O}_a}$ and hence $D_{\text{D}}$ vary significantly, leading to deviation of the shape of the ¹⁸O profile from an error function. Numerical simulations show that when surface $X_{\text{H}_2\text{O}_a}$ is <0.01, ¹⁸O profile is essentially indistinguishable from an error function profile. When surface $X_{\text{H}_2\text{O}_a}$ is >0.01, the deviation from an error function begins to be noticeable.

A definitive test for the above hypothesis involves the simultaneous measurement of profiles of both ¹⁸O and hydrous species. If the hypothesis is correct, the two profiles would be related such that the ¹⁸O profile can be calculated from the H₂Oₐ profile. In this study, we report such a confirmation by experiments in which ¹⁸O-labeled (as well as D-labeled) water was diffused into polished rhyolitic glass wafers. Rhyolite was chosen because a large database for water diffusion is available for comparison. After the experiments, both profiles of H₂Oₐ and ¹⁸O were measured: H₂Oₐ as the sum of OH and H₂Oₐ by infrared spectroscopy, and ¹⁸O/¹⁶O by secondary ion mass spectrometry. R is calculated from ¹⁸O/¹⁶O. We fit profiles of both H₂Oₐ and R assuming (i) H₂Oₐ is the diffusing species for both H₂Oₐ and ¹⁸O, and (ii) diffusivity of H₂Oₐ is an exponential function of H₂Oₐ content [1]. Verification of the theory requires that both H₂Oₐ, and R profiles would be well fit by a single expression of $D_{\text{H}_2\text{O}_m}$.

These experiments are relevant not only to understand oxygen diffusion in silicate melts, but also shed some light on the kinetics of hydrogen and oxygen isotope exchange between silicates and other phases. Practical applications of this work include estimation of oxygen diffusivity under hydrothermal conditions from water diffusivity, and vice versa.

2. Experiments and analyses

In the experiments doubly polished rhyolitic glass sections (1 × 5 × 5 mm) were sealed with isotopically enriched water in gold capsules. One natural obsidian containing 0.16 wt.% H₂O was run at 1085 K whereas in two other experiments a water-poor (0.04 wt.% H₂O) synthetic glass with a similar composition was used (Table 1). The starting fluid for the experiments at 1136 K and 1085 K contained D₂¹⁸O, with D/(D+H)=0.80 and R=0.855. In
### Table 1
Composition of glasses (wt.%)

<table>
<thead>
<tr>
<th>Sample name sources</th>
<th>EDF Erevan Dry Fountain, Armenia</th>
<th>EDF synthetic</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>76.78 (0.32)</td>
<td>76.32 (0.28)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.10 (0.02)</td>
<td>0.01 (0.02)</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12.77 (0.13)</td>
<td>13.27 (0.19)</td>
</tr>
<tr>
<td>FeO&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.52 (0.03)</td>
<td>0.01 (0.01)</td>
</tr>
<tr>
<td>MnO</td>
<td>0.09 (0.01)</td>
<td>0.00 (0.01)</td>
</tr>
<tr>
<td>MgO</td>
<td>0.07 (0.01)</td>
<td>0.01 (0.01)</td>
</tr>
<tr>
<td>CaO</td>
<td>0.56 (0.02)</td>
<td>1.11 (0.06)</td>
</tr>
<tr>
<td>Na₂O</td>
<td>4.08 (0.07)</td>
<td>4.24 (0.11)</td>
</tr>
<tr>
<td>K₂O</td>
<td>4.55 (0.07)</td>
<td>5.11 (0.11)</td>
</tr>
<tr>
<td>H₂O&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.16</td>
<td>0.04</td>
</tr>
<tr>
<td>Sum</td>
<td>99.67</td>
<td>100.11</td>
</tr>
<tr>
<td>M&lt;sub&gt;glass&lt;/sub&gt; (g/mol)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>32.49</td>
<td>32.56</td>
</tr>
</tbody>
</table>

Notes. Each analysis is based on 10 measurements using a CAMECA SX100 electron microprobe (conditions: 15 kV acceleration voltage, 6–20 nA beam current, electron beam defocused to 20–40 μm diameter). 1σ uncertainties of microprobe data are given in parentheses.

<sup>a</sup> Total iron is given as FeO.

<sup>b</sup> The H₂O content was determined from the peak height of the IR absorption band at 3570 cm<sup>−1</sup> using the calibration of Leschik et al. [35].

<sup>c</sup> Molar mass of anhydrous glass is calculated on single oxygen basis, and is needed for calculating the mole fractions of total H₂O [40].

### Table 2
Experimental conditions and fitting results

<table>
<thead>
<tr>
<th>Exp #</th>
<th>T (K)</th>
<th>P (MPa)</th>
<th>Starting glass</th>
<th>C&lt;sub&gt;H₂Ot&lt;/sub&gt; initial (wt.%)</th>
<th>R fluid initial</th>
<th>D/(D+H) fluid initial</th>
<th>Time (s)</th>
<th>X&lt;sub&gt;H₂Ot&lt;/sub&gt; surface</th>
<th>C&lt;sub&gt;H₂Ot&lt;/sub&gt; surface (wt.%)</th>
<th>Best-fit&lt;sup&gt;a&lt;/sup&gt;</th>
<th>D&lt;sub&gt;0&lt;/sub&gt; based on H₂O fit</th>
<th>D&lt;sub&gt;0&lt;/sub&gt; based on &lt;sup&gt;18&lt;/sup&gt;O fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1041</td>
<td>100</td>
<td>EDFS</td>
<td>0.04</td>
<td>~0.48</td>
<td>~0.50</td>
<td>2160</td>
<td>0.0756</td>
<td>4.33</td>
<td>34</td>
<td>1.89±0.02</td>
<td>1.95±0.05</td>
</tr>
<tr>
<td>2</td>
<td>1085</td>
<td>100</td>
<td>EDF</td>
<td>0.16</td>
<td>0.855</td>
<td>0.80</td>
<td>1830</td>
<td>0.0775</td>
<td>4.44</td>
<td>25</td>
<td>4.01±0.07</td>
<td>4.98±0.12</td>
</tr>
<tr>
<td>3</td>
<td>1136</td>
<td>100</td>
<td>EDFS</td>
<td>0.04</td>
<td>0.855</td>
<td>0.80</td>
<td>900</td>
<td>0.0750</td>
<td>4.29</td>
<td>18</td>
<td>10.5±0.3</td>
<td>11.8±0.2</td>
</tr>
</tbody>
</table>

Notes. 2σ uncertainties are shown for D<sub>0</sub> values obtained by fitting. Although fitting errors on D<sub>0</sub> are very small, the real error of diffusivities (including uncertainty on the position of the interface, spatial resolution, temperature, etc.) is likely on the order of 30%.

<sup>a</sup> The best-fit <i>a</i> values are somewhat different from those in Zhang and Behrens [28] because <i>a</i> values given there are not well constrained. Data in this study can be used to further constrain the dependence of <i>a</i> on <i>T</i> and <i>P</i>.

### 3. Experimental results

Profiles of H₂O<sub>t</sub> and <i>R</i> are shown in Fig. 1. The surface H₂O<sub>t</sub> content is roughly in agreement with H₂O solubility data indicating about 4 wt.% H₂O can be dissolved in rhyolitic melts at 100 MPa in the investigated temperature range [35–42]. H₂O profiles clearly do not follow an error function, indicating strong dependence of H₂O diffusivity on H₂O<sub>t</sub> content, as shown by numerous previous studies [25–32]. The <sup>18</sup>O profiles, although similar to an error function shape to the first order, also deviate slightly and resolvably from error function fits (dashed curves in Fig. 1), in particular at low <i>R</i> values. This is expected because the length of the <i>R</i> profile is significant compared to that of the H₂O<sub>t</sub> profile. Typically, the <i>R</i> sectioned perpendicular to the polished surface. H₂O and D₂O concentration profiles of the sections were determined by Fourier transform infrared spectroscopy (FTIR) at the University of Hannover. Concentrations were derived from the peak height of the band at 3570 cm<sup>−1</sup> (H₂O) and 2650 cm<sup>−1</sup> (D₂O) using calibrations of Leschik et al. [35]. Although different hydrogen isotopes were measured, we did not distinguish these isotopes in fitting the diffusion profiles but use the sum of both. <sup>18</sup>O/<sup>16</sup>O profiles were determined by secondary ion mass spectrometry (SIMS) at GeoForschungsZentrum Potsdam. Details of the analytical conditions are reported elsewhere [35]. When possible, multiple profiles were measured, and these profiles adjusted by shifting the surface position by no more than 3 μm parallel to the diffusion direction to make the multiple profiles consistent. In the experiment at 1041 K the amount of added fluid was probably too low to surround completely the sample and <sup>18</sup>O surface concentrations vary widely. Only the profile with the highest surface <sup>18</sup>O/<sup>16</sup>O ratio has been used in data treatment.
Fig. 1. a–c. H$_2$O$_i$ and $^{18}$O profiles generated by hydrothermal experiments. The H$_2$O$_i$ profiles (sum of both isotopes) clearly differ from an error function profile, and no error function fit is tried. The $^{18}$O profiles appear to be of error function shape, but the error function fit (dashed curves) shows small systematic deviation, especially at $x \approx 80$ to 100 $\mu$m (low H$_2$O$_i$ content) where the data show more rapid decrease towards the background value of 0.002. The solid curves are fits of both H$_2$O$_i$ and R profiles by assuming H$_2$Om is the only diffusing species and $D_{H_2Om}=D_0\exp(aX_{H_2O})$. The best-fit values of $a$ and $D_0$ are listed in Table 2. No adjustments to the surface position of the H$_2$O$_i$ profile were made to match $D_{H_2Om}$ from the H$_2$O$_i$ and R profiles.
Notes. The errors for the calculated diffusivities are estimated to be <30%.

* Calculated after Zhang et al. [49].
* Calculated using parameters given in Table 2.
adjusted H₂Ot and R profiles to see whether it is possible to use the same expression of D_H₂Om to fit both profiles. This turned out to be relatively easy to achieve. For example, if we adjust only the interface position of the H₂Ot profile, both H₂Ot and R profiles would be fit by exactly the same expression of D_H₂Om with adjustment of the interface position of the H₂Ot profile by 2 μm for the 1041 K experiment, by 7 μm for the 1136 K experiment, and by 14 μm for the 1085 K experiment. That is, with very minor adjustments that are within measurement uncertainty, ¹⁸O diffusion profile can be directly calculated with no free parameters from D_H₂Om obtained from H₂Ot profile.

As shown in Table 3, the approximate D_{¹⁸O} values obtained by fitting an error function to the R profiles are in good agreement with those calculated from the approximate theoretical relation D_{¹⁸O} ≈ D_{H₂Om} · X_{H₂Om} using X_{H₂Om} at the surface. Furthermore, because D_{¹⁸O} is roughly proportional to X_{H₂Om} and because X_{H₂Om} decreases from the surface to the interior, the approximate values of D_{¹⁸O} obtained by fitting an error function to the R profiles would be expected to be slightly less than those from theoretical calculation, consistent with the results shown in Table 3.

5. Comparison with previous data and with Eyring diffusivity

The new experimental data for D_{H₂Ot} and D_{H₂Om} at 1 wt.% H₂Ot obtained in this study are in excellent agreement with those predicted from Zhang and Behrens [28] (Fig. 2a). On the other hand, at 4 wt.% H₂Ot, the new diffusivity data are systematically higher by a factor of 2 (Fig. 2b). There are two possible explanations. One explanation is in the experimental approach. The model of Zhang and Behrens [28] is based on dehydration and diffusion couple experiments whereas in the present study the sorption technique was employed. Although the model used by Zhang and Behrens [28] and by this study does not depend on sorption or dehydration experiments, there might be experimental aspects that were overlooked. For example, in the sorption experiments, there could be surface dissolution during the experiment and re-deposition during quenching. The second, and the more likely explanation, is that the pressure effect in the model is not well constrained, as also pointed out in that paper [28]. Most data with high H₂Ot contents were for pressures of 500 MPa, with only two experiments at 250 MPa. Low pressure experiments (0.1 MPa) are limited to at most 1.7 w% H₂Ot with only two samples having water contents exceeding 1 wt.%. The new results suggest that the pressure dependence of water diffusivity at high water content is more pronounced than predicted. Further research is required to resolve this minor discrepancy. Because the comparisons of ¹⁸O and H₂Ot profiles are made for the same experiments, the discrepancy discussed above does not affect the conclusion that ¹⁸O is transported by molecular H₂O in rhyolitic melt under hydrothermal conditions.

Fig. 2 shows that D_{¹⁸O} in hydrous rhyolitic melts is only 1–2 orders of magnitude less than D_{H₂Ot} but more than three orders of magnitude greater than the
diffusivity calculated from viscosity using the Eyring-relationship:

\[ D = \frac{k \cdot T}{\lambda \cdot \eta} \]  

(8)

where \( k \) is Boltzmann constant, \( \lambda \) is jumping distance, and \( \eta \) is viscosity of hydrous rhyolitic melt [43,44]. The Eyring equation has been shown to be a powerful approach to link melt viscosity to the diffusivity of network formers [45–48], the crucial parameter being the jumping distance. Agreement within a factor of 2 between viscosity and diffusivity data was found for \( \lambda \) values close to the diameter of the silicon tetrahedron [45]. In our calculations we have used \( \lambda = 2 \) Å which was derived by comparison of diffusion couple experiments in the system Ab-Or-Qz (Behrens, unpublished data) with viscosity data for a haplogranitic melt [44]. For anhydrous silicate melts the Eyring diffusivity was found to be close to the diffusivity of oxygen [44,45]. This is obviously not the case for hydrous melts in which oxygen diffusion is decoupled from diffusion of network cations (Al, Si). Due to the large difference between \( D_{\text{H}_2\text{O}} \) and Eyring diffusivity, the contribution of H2O as carrier for oxygen is expected to dominate \( D_{\text{H}_2\text{O}} \) even at low H2O content down to ppm level (note that Eyring diffusivity obtained from viscosity also depends on H2O content).

6. Conclusions

The above results confirm that molecular H2O is the carrier for oxygen transport in rhyolitic melt under hydrothermal conditions. We further infer that molecular H2O diffusion controls oxygen transport in other silicate melts and glasses, and hydrous species (either molecular H2O, or OH, or H3O+, or a combination of these) are responsible for oxygen transport in silicate minerals that contain hydrous component under hydrothermal conditions [1]. Previously reported oxygen “self” diffusion data under wet conditions are due to chemical diffusion of H2O (i.e., due to the concentration gradient of H2O\textsubscript{m} sometimes at minute concentration level), instead of true “self” diffusion (due to the isotopic gradient in a chemically uniform system). Nevertheless, application of the data to calculate rates for oxygen isotope exchange under hydrothermal conditions is still valid as long as they are applied under identical conditions (e.g., the same \( T, \) \( P \), fluid pressure and composition). Under different conditions (e.g., such as different fluid pressure), the applicable diffusivities need to be obtained by interpolation or extrapolation based on theoretical considerations that \( D_{\text{H}_2\text{O}} \approx D_{\text{H}_2\text{O} \cdot \text{H}_2\text{O}} \).

In the context of the above conclusions, \(^{18}\text{O} \) “self” diffusivity can be calculated from H2O diffusion data, and vice versa. Data on H2O diffusion in rhyolitic melt are extensive [25,27,28] and references therein) with additional data from this study. Diffusivity data in other melts are also accumulating [26,29–31], which can be used to estimate \(^{18}\text{O} \) diffusivity in these melts using Eq. (2) provided that water speciation data for the melt are available. In the future it will be an important task to investigate H2O and \(^{18}\text{O} \) diffusion simultaneously in minerals such as feldspar or quartz to confirm the validity of this hypothesis for minerals.

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