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# Diffusion of a multi-species component and its role in oxygen and water transport in silicates

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## ABSTRACT

An important but poorly understood factor that affects diffusion rates is the role of speciation during diffusion of a multi-species component. The diffusion of such a component is complicated by the different diffusion coefficient of each species and the interconversion reactions among the species. These complexities can be treated by a diffusion equation that incorporates the diffusive fluxes of all species contributing to the concentration of the component. The effects of speciation on the diffusion of the component can be investigated experimentally in some simple cases by measuring concentration profiles of all species developed during diffusion experiments or by studying some of their other consequences.

Experimental data on water diffusion in rhyolitic glasses indicate that although dissolved water is present as two species,  $\text{H}_2\text{O}$  molecules and OH groups, molecular  $\text{H}_2\text{O}$  is the dominant diffusing species at very low to high water concentrations. This explains the apparently complex behavior of water diffusion. Experimental data on oxygen diffusion in some silicates using  $^{18}\text{O}$  tracers in the form of  $\text{H}_2^{18}\text{O}$  are consistent with the idea that  $^{18}\text{O}$  transport is dominated by diffusion of  $\text{H}_2\text{O}$  molecules even at lower water contents (ppm or less). This explains why oxygen transport depends on the presence of water and generally depends on water fugacity linearly. For this mode of oxygen transport, there is a simple theoretical relationship between the effective total oxygen diffusion coefficient and the total water diffusion coefficient that is a function of only the water concentration of the silicate at low water content. This relationship appears to describe quantitatively the existing data over a wide range in water contents and diffusion coefficients in several phases.

## 1. Introduction

The transport of chemical components by volume diffusion in a phase is of fundamental importance in some geological problems and has broad applications in materials science. Many factors that affect diffusion rates (such as temperature, confining pressure, reference frames, and defect concentrations, etc.) are relatively well understood, at least conceptually. However, there remain some aspects of diffusion in geological materials that are poorly understood. In this paper, we discuss the diffusion of a multi-species (i.e., two or more species) component and the role of speciation during diffusion. We first present a general analysis of the multi-species diffusion problem. We then briefly summarize the results of our recent experimental study on the diffusion of water (with two measurable species) in rhyolitic glasses. We devote the rest of this paper to a

discussion of the diffusion of oxygen in the presence of water and the effects of the diffusion of oxygen-bearing hydrous species. We will show that the presence of water and its associated major species (hydroxyl groups and  $\text{H}_2\text{O}$  molecules) can result in distinctive effects if oxygen is transported by these species. In particular, the “self” diffusion coefficient of oxygen in silicates as determined based on the use of  $^{18}\text{O}$  as a tracer during oxygen exchange between silicates and  $\text{H}_2^{18}\text{O}$  vapor will be shown to be strongly dependent on the water pressure or water content even at very low water concentrations. The functional dependence of this “self” diffusion coefficient of oxygen on water content will be derived and a comparison made with existing experimental data.

It is well known that a chemical component in a phase can be present as two or more species; for example, water in silicates may be present as  $\text{H}_2\text{O}$  molecules and/or OH groups [1], and oxygen in

silicates can be classified in many ways, such as bridging oxygen, non-bridging oxygen, and those oxygen atoms that are not associated with tetrahedral Si or Al. The diffusion equation for an  $N$ -species component can be written as follows if cross terms are ignored [2–5]:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \sum_j^N D_j \frac{k_j \partial c_j}{\partial x}, \quad (1)$$

where  $c_j$  and  $D_j$  refer to the concentration and diffusion coefficient of the  $j$ th species of the component;  $c$  ( $\equiv \sum k_j c_j$ ) is the total concentration;  $k_j$  is the coefficient of the  $j$ th species to account for stoichiometry for the interconversion among species. For example, there are two species for the total water component, OH and H<sub>2</sub>O; in this case two OH groups convert to one H<sub>2</sub>O molecule and hence  $k_{\text{OH}} = 1/2$  if  $k_{\text{H}_2\text{O}} = 1$  for a diffusion equation similar to the above. Interconversions among the species do not affect  $c$  and hence do not enter into (1). Equation (1) is in general nonlinear and can only be solved numerically given appropriate initial and boundary conditions and  $N-1$  additional relationships among  $c_1$  to  $c_N$ . The simplest case is that of local equilibrium for reactions among the species. If the concentrations of all the species ( $c_j$ 's) can be measured directly along a diffusion path, the profiles can, in principle, be inverted according to (1) to obtain all the diffusion coefficients ( $D_j$  of the respective species) in the case that the concentrations are not proportional to each other. This can be done by comparing the measured concentration profiles of the species with the numerical solutions of (1), or by employing a Boltzmann-Matano analysis [6], which, in principle, can be used to determine the concentration-dependence of the  $D_j$ 's.

If direct information on speciation is not available, or the effects of speciation are ignored, the diffusion of the component is usually treated as follows (examples will be given below):

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D^* \frac{\partial c}{\partial x} \right), \quad (2)$$

where  $D^*$  is the apparent diffusion coefficient of the component. Comparing (1) and (2),  $D^*$  can formally be expressed as:

$$D^* = \sum_{j=1}^N D_j \frac{k_j \partial c_j / \partial x}{\partial c / \partial x}. \quad (3)$$

In such cases,  $D^*$  depends on all  $c_j$ 's even when all  $D_j$ 's are constant, unless all  $N$  species have identical diffusion coefficients, or all species concentrations are proportional to one another.

We now examine cases in which the presence of multiple species can be demonstrated or inferred to play a role in the diffusion of oxygen and water in silicates.

## 2. Water diffusion during dehydration of rhyolitic glasses

Water in amorphous silicates can be present in at least two forms: H<sub>2</sub>O molecules and OH groups and between them there is assumed to exist a homogeneous equilibrium [1]:



The equilibrium constant ( $K$ ) for the above reaction is [1]:

$$K = [\text{OH}]^2 / \{ [\text{H}_2\text{O}] [\text{O}_{\text{dry}}] \} \quad (5)$$

where  $\text{O}_{\text{dry}}$  represents “anhydrous” oxygen and quantities in brackets represent mole fractions on a single oxygen basis and  $[\text{O}_{\text{dry}}] = 1 - [\text{H}_2\text{O}] - [\text{OH}]$  [ref. 7]. These mole fractions are approximately proportional to the concentrations (in mol/cm<sup>3</sup>) of these species. For simplicity we assume initially that the silicate can be treated as an ideal solution, where mole fractions equal activities and  $K$  is independent of total water content. In this discussion we will ignore problems related to charge balance.

The diffusion equation for water can now be written as [2]:

$$\frac{\partial [\text{water}]}{\partial t} = \frac{\partial}{\partial x} \left( D_{\text{H}_2\text{O}} \frac{\partial [\text{H}_2\text{O}]}{\partial x} + \frac{1}{2} D_{\text{OH}} \frac{\partial [\text{OH}]}{\partial x} \right) \quad (6)$$

where [water] is the total mole fraction of water and always equals  $[\text{H}_2\text{O}] + [\text{OH}]/2$ , and  $D_{\text{H}_2\text{O}}$  and  $D_{\text{OH}}$  are the diffusion coefficients of H<sub>2</sub>O and OH, respectively. If local equilibrium is assumed and  $K$ ,  $D_{\text{H}_2\text{O}}$  and  $D_{\text{OH}}$  are known, (5) and (6) can be used to calculate [H<sub>2</sub>O] and [OH] profiles [3,5]. From (5), H<sub>2</sub>O and OH are not proportional: at low water contents (e.g., < 0.2 wt%), OH is the dominant species; at higher water contents (e.g., > 4 wt%), H<sub>2</sub>O is the dominant species [1,7]. This

feature of non-proportionality allows determination of both  $D_{\text{H}_2\text{O}}$  and  $D_{\text{OH}}$  from measured  $\text{H}_2\text{O}$  and OH profiles.

We have reported an experimental study of the diffusion of water at 400–550 °C by dehydrating natural rhyolitic glasses with initially known and uniform water contents [5]. After partial dehydration, we determined the concentration profiles of both  $\text{H}_2\text{O}$  and OH by Fourier transform infrared spectroscopy. Based on these concentration profiles, we obtained a relationship between  $K$  and  $[\text{water}]$  by a polynomial fit of the actual  $K$  vs.  $[\text{water}]$  along diffusion profiles of all samples at a single temperature, to account for deviations from ideality [7] and departure from local equilibrium at low water content. The relationship is reasonably approximated by local equilibrium at high temperatures and high water contents. The concentration profiles were compared with the numerical solution of equations (6) and (5) where  $K$  in (5) was from the fit. Figures 1a, b compare calculated profiles (with different  $D_{\text{OH}}/D_{\text{H}_2\text{O}}$  ratio) to measured profiles for one sample with 0.8 wt% initial water heated at 490 °C for 11.4 days. Figure 1a shows the best fit to the data for  $D_{\text{OH}}/D_{\text{H}_2\text{O}} = 1$ ; in this case  $\text{H}_2\text{O}$  and OH diffuse at the same rate and the total water profile is linearly dependent on an error function. It is evident that the fit is a poor one, consistent with previous observations that total water concentration profiles cannot be fit with a constant apparent diffusion coefficient for total water ( $D_{\text{water}}^*$ ) [8–14] and that  $D_{\text{water}}^*$  must be a strong function of water concentration [8–17]. The fit improves as  $D_{\text{OH}}/D_{\text{H}_2\text{O}}$  decreases and an almost perfect fit is obtained at  $D_{\text{OH}}/D_{\text{H}_2\text{O}} = 0$  (Fig. 1b). To illustrate the dependence of the difference between the model calculated profiles and the measured profiles in more detail, we show  $1 - r^2$  (where  $r$  is the correlation coefficient and  $1 - r^2$  is proportional to the sum of the square of residuals) of the fit for different values of  $D_{\text{OH}}/D_{\text{H}_2\text{O}}$  in Fig. 1c. The minimum lies near  $D_{\text{OH}}/D_{\text{H}_2\text{O}} = 0$ , indicating that  $\text{H}_2\text{O}$  is the dominant diffusing species for this sample. The same procedure has been followed for other samples and similar results were obtained even for a sample with 0.2 wt% initial water in which the  $\text{H}_2\text{O}$  concentration is minute compared to that of OH. All the results show that  $D_{\text{OH}}$  is negligible compared to  $D_{\text{H}_2\text{O}}$ , and that  $D_{\text{H}_2\text{O}}$  is

approximately independent of water concentration at 400–550 °C and with a range of 0.2 to 1.7 wt% total water. Hence, we conclude that  $\text{H}_2\text{O}$  is the diffusing species and that the OH concentration profile is generated by local reactions that interconvert OH and  $\text{H}_2\text{O}$ . Such reactions thus try to maintain local equilibrium and also provide the diffusing species. This conclusion based on experimental data in which the species concentrations were measured is in general accord with that of Doremus [18,19] and some more recent discussions [3,17,20–23].

Based on (3),  $D_{\text{water}}^*$  is related to  $D_{\text{OH}}$  and  $D_{\text{H}_2\text{O}}$  in the following manner [2]:

$$\begin{aligned} D_{\text{water}}^* &= D_{\text{H}_2\text{O}} \frac{\partial[\text{H}_2\text{O}]/\partial x}{\partial[\text{water}]/\partial x} + D_{\text{OH}} \frac{\partial[\text{OH}]/\partial x}{\partial[\text{water}]/\partial x} \\ &\approx D_{\text{H}_2\text{O}} \frac{d[\text{H}_2\text{O}]}{d[\text{water}]} + D_{\text{OH}} \frac{d[\text{OH}]}{d[\text{water}]} \quad (7)^* \end{aligned}$$

where  $D_{\text{OH}}$  can usually be ignored but may play a role at extremely low water contents, and the  $\approx$  becomes  $=$  when there is a unique relationship between  $[\text{H}_2\text{O}]$  and  $[\text{water}]$ . At low water concentrations where OH is the dominant species, and assuming constant  $K$ , (7) and (5) can be combined to yield:

$$\begin{aligned} D_{\text{water}}^* &\approx D_{\text{OH}} + 4D_{\text{H}_2\text{O}}([\text{H}_2\text{O}]/K)^{1/2} \\ &\approx D_{\text{OH}} + 4D_{\text{H}_2\text{O}}[\text{OH}]/K \\ &\approx D_{\text{OH}} + 8D_{\text{H}_2\text{O}}[\text{water}]/K. \quad (8) \end{aligned}$$

As indicated above,  $D_{\text{OH}} \ll D_{\text{H}_2\text{O}}$ , so that when  $[\text{water}] \gg KD_{\text{OH}}/(8D_{\text{H}_2\text{O}})$ , the contribution of  $D_{\text{OH}}$  becomes negligible and  $D_{\text{water}}^* \approx 8D_{\text{H}_2\text{O}}[\text{water}]/K$  [3,18]. Therefore, the observed strong (often reported in the literature as linear [13–15]) increase of  $D_{\text{water}}^*$  with water concentration in silicate glasses [8–10,12–14,23] is largely due to the fact that only  $\text{H}_2\text{O}$  molecules are mobile and to the dependence of  $d[\text{H}_2\text{O}]/d[\text{water}]$  on total water concentration at low water content.

\* Note the derivatives in (7). Although we might say that the apparent diffusion coefficient ( $D^*$ ) depends on the “proportions” of the species, we actually mean the derivatives as in (7) in a strict sense. There was an error in equation (3) in [40] that used the following incorrect form (ignoring  $D_{\text{OH}}$ ) without a derivative:  $D_{\text{water}}^* = D_{\text{H}_2\text{O}}[\text{H}_2\text{O}]/[\text{water}]$ , which may cause an error of a factor of two at low water contents. See footnote c in Table 1.

It is interesting to consider the self diffusion of water, such as the diffusion of deuterated water into silica glass already saturated with normal water [24]. In this case there is no chemical concentration gradient and  $[\text{H}_2\text{O}]_{\text{total}}$ ,  $[\text{OH}]_{\text{total}}$ , and  $[\text{water}]_{\text{total}}$  are all constant across an isotopic diffusion profile, where the subscript "total" means inclusion of both hydrogen- and deuterium-bearing species; e.g.,  $[\text{H}_2\text{O}]_{\text{total}} = [\text{H}_2\text{O}] + [\text{D}_2\text{O}] + [\text{HDO}]$ . Assuming local isotopic equilibrium, and ignoring the isotopic fractionation between molecular water and hydroxyl and the difference in the diffusion coefficients of hydrogen- and deuterium-bearing species, the diffusion coefficient for the exchange of D and H ( $D_{\text{D-H}}$ ) can be written as (the detailed derivation is very similar to the case for oxygen "self" diffusion discussed later):

$$D_{\text{D-H}} = D_{\text{H}_2\text{O}}[\text{H}_2\text{O}]_{\text{total}}/[\text{water}]_{\text{total}} + 0.5D_{\text{OH}}[\text{OH}]_{\text{total}}/[\text{water}]_{\text{total}}, \quad (7A)$$

and is constant. Note that  $D_{\text{D-H}}$  is different from  $D_{\text{water}}^*$  in (7) in that (7) contains derivatives while (7A) does not. At low water contents and assuming constant  $K$ ,  $D_{\text{D-H}}$  can be expressed as:

$$\begin{aligned} D_{\text{D-H}} &\approx D_{\text{OH}} + 2D_{\text{H}_2\text{O}}([\text{H}_2\text{O}]/K)^{1/2} \\ &\approx D_{\text{OH}} + 2D_{\text{H}_2\text{O}}[\text{OH}]/K \\ &\approx D_{\text{OH}} + 4D_{\text{H}_2\text{O}}[\text{water}]/K. \end{aligned} \quad (8A)$$

Therefore, if  $\text{H}_2\text{O}$  is the diffusing species,  $D_{\text{D-H}}$  ( $= 4D_{\text{H}_2\text{O}}[\text{water}]/K$ ) is smaller than  $D_{\text{water}}^*$  ( $= 8D_{\text{H}_2\text{O}}[\text{water}]/K$ ) by a factor of 2, as pointed out by Doremus [18]. This expected difference between  $D_{\text{D-H}}$  and  $D_{\text{water}}^*$  is small and hence may be difficult to verify. Nevertheless, this example shows that the self diffusion coefficient might be *smaller* than the chemical diffusion coefficient of the same component; it is interesting to compare this with recent reports that suggest that the self diffusion rate is usually equal to or greater than the chemical diffusion rate [25–27].

Although in other systems or under other conditions, the details of water diffusion may differ from those we have presented here, the problem can be treated in a similar fashion. For example, if  $\text{H}_2\text{O}$  is the dominant diffusing species but there is no interconversion between  $\text{H}_2\text{O}$  and  $\text{OH}$  (at low temperature?), or  $\text{OH}$  concentrations are low compared to that of  $\text{H}_2\text{O}$ , then  $D_{\text{water}}^*$  is predicted to

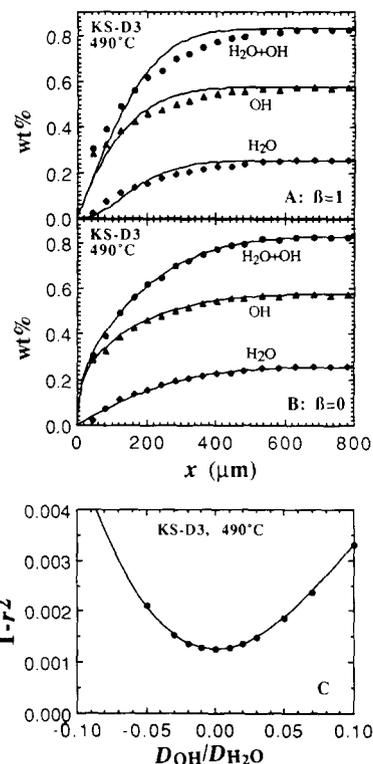


Fig. 1. Water diffusion profiles of KS-D3 (490°C, 18.6 days) fitted by the two species model for different values of  $\beta$  ( $\equiv D_{\text{OH}}/D_{\text{H}_2\text{O}}$ ). (A)  $D_{\text{OH}}/D_{\text{H}_2\text{O}} = 1$ ; (B)  $D_{\text{OH}}/D_{\text{H}_2\text{O}} = 0$ ; (C)  $1 - r^2$  vs.  $D_{\text{OH}}/D_{\text{H}_2\text{O}}$ . See [5] for a full discussion.

be independent of the total water concentration and equal to  $D_{\text{H}_2\text{O}}$  based on (7). If  $\text{OH}$  is both the dominant diffusing species and the dominant chemical species, then  $D_{\text{water}}^*$  will also be independent of total water concentrations and equal to  $D_{\text{OH}}$  based on (7). During hydration of alkali-rich silicates,  $\text{H}_3\text{O}^+$  may exchange with alkali ions and be a major diffusing species [e.g., 28,29], and its behavior could be readily incorporated into the above treatment.

### 3. Oxygen "self" diffusion under hydrothermal conditions

When  $^{18}\text{O}$  is introduced into a silicate (either melt, glass, or mineral) from an  $\text{H}_2^{18}\text{O}$ -bearing fluid phase (as is the case in hydrothermal oxygen "self" diffusion experiments in silicates [30–39]), water will enter the silicate as  $\text{H}_2\text{O}$  and  $\text{OH}$  in amounts that depend on the silicate material, the water fugacity, the total pressure, and the temper-

ature. Oxygen may thus be present in the silicate as at least three species:  $\text{H}_2\text{O}$ ,  $\text{OH}$ , and those oxygen atoms in different sites that are present under completely anhydrous conditions. We will define these latter oxygen atoms as dry oxygen ( $\text{O}_{\text{dry}}$ ), which may itself include many local environments such as bridging, nonbridging oxygen in silicate polymers or isolated oxygen atoms coordinating with network modifiers. In this section we show that if species such as  $\text{H}_2\text{O}$  or  $\text{OH}$  are present and diffusing in the silicate, as they are likely to be in hydrothermal  $^{18}\text{O}$  diffusion experiments, they can contribute significantly to the total  $^{18}\text{O}$  flux and lead to spurious  $^{18}\text{O}$  “self” diffusion coefficients.

Using a speciation-dependent treatment for diffusion, we can write the equation for oxygen diffusion in silicates under hydrothermal conditions as follows:

$$\frac{\partial c^{18}\text{O}}{\partial t} = \frac{\partial}{\partial x} \left( D_{\text{O,dry}} \frac{\partial c^{18}\text{O,dry}}{\partial x} + D_{\text{H}_2\text{O}} \frac{\partial c_{\text{H}_2^{18}\text{O}}}{\partial x} + D_{\text{OH}} \frac{\partial c^{18}\text{OH}}{\partial x} \right) \quad (9)$$

where  $c$  represents concentration (in  $\text{mol}/\text{cm}^3$ ) of the various species. Here the total  $^{18}\text{O}$  concentration is given by  $c^{18}\text{O} \equiv c^{18}\text{O,dry} + c_{\text{H}_2^{18}\text{O}} + c^{18}\text{OH}$ .  $D_{\text{O,dry}}$  is the true self diffusion coefficient of the various structural oxygen atoms not associated with hydrogen. An analogous equation may be written for  $^{16}\text{O}$ . We will ignore any small difference in the diffusion coefficients of the different isotopic species. Other possible oxygen species, such as  $\text{H}_3\text{O}^+$ ,  $\text{CO}_2$  and  $\text{O}_2$ , are not considered here, but they could be readily incorporated in (9).

If local isotopic equilibrium is reached, and if isotopic fractionation among the different oxygen species are small (at a few per mil level) and can be ignored, we have:

$$\frac{c^{18}\text{O,dry}}{c_{\text{O,dry}}} \approx \frac{c_{\text{H}_2^{18}\text{O}}}{c_{\text{H}_2\text{O}}} \approx \frac{c^{18}\text{OH}}{c_{\text{OH}}} \approx \frac{c^{18}\text{O}}{c_{\text{O}}} \equiv R \quad (10)$$

where  $R$  is the  $c^{18}\text{O}/c_{\text{O}}$  ratio in a microscopic volume and can be obtained from a measurement of  $^{18}\text{O}/^{16}\text{O}$ . (If local isotopic equilibria were not reached, then the kinetics of isotopic exchange reactions would have to be considered). Substituting (10) into (9) and assuming  $c_{\text{O}}$  to be approxi-

mately constant across the whole profile and  $c_{\text{O,dry}} \approx c_{\text{O}}$ , we have:

$$\frac{\partial R}{\partial t} = \frac{\partial}{\partial x} \left( D_{\text{O,dry}} \frac{\partial R}{\partial x} + D_{\text{H}_2\text{O}} \frac{\partial \{ R \cdot [\text{H}_2\text{O}] \}}{\partial x} + D_{\text{OH}} \frac{\partial \{ R \cdot [\text{OH}] \}}{\partial x} \right) \quad (11)$$

where  $[\text{H}_2\text{O}]$  ( $\equiv c_{\text{H}_2\text{O}}/c_{\text{O}}$ ) and  $[\text{OH}]$  ( $\equiv c_{\text{OH}}/c_{\text{O}}$ ) are mole fractions of  $\text{H}_2\text{O}$  and  $\text{OH}$  on a single oxygen basis as defined in (5). This is an effective diffusion equation for the isotopic ratio  $^{18}\text{O}/^{16}\text{O}$ . In general, (11) can be solved together with (6) and (5) in a forward calculation given the species diffusion coefficients, similar to the numerical solution of (6) and (5).

If the profiles for  $[\text{H}_2\text{O}]$  and  $[\text{OH}]$  are much broader than the profile of  $R$  (i.e., the relative gradients in  $[\text{H}_2\text{O}]$  and  $[\text{OH}]$  are much smaller than the gradient in  $R$ ), then

$$[\text{H}_2\text{O}] \frac{\partial R}{\partial x} \gg R \frac{\partial [\text{H}_2\text{O}]}{\partial x}, \quad (12)$$

and

$$[\text{OH}] \frac{\partial R}{\partial x} \gg R \frac{\partial [\text{OH}]}{\partial x}. \quad (13)$$

Using (12) and (13), (11) can then be simplified to:

$$\frac{\partial R}{\partial t} \approx \frac{\partial}{\partial x} \left[ \left( D_{\text{O,dry}} + D_{\text{H}_2\text{O}} [\text{H}_2\text{O}] + D_{\text{OH}} [\text{OH}] \right) \frac{\partial R}{\partial x} \right]. \quad (14)$$

The apparent oxygen “self” diffusion coefficient ( $D_{\Sigma\text{O}}^*$ ) for the isotopic ratio  $R$  in this case is then:

$$D_{\Sigma\text{O}}^* \approx D_{\text{O,dry}} + D_{\text{H}_2\text{O}} [\text{H}_2\text{O}] + D_{\text{OH}} [\text{OH}]. \quad (15)$$

Note that in (15) the term  $D_{\text{H}_2\text{O}} [\text{H}_2\text{O}]$  appears, but that  $4D_{\text{H}_2\text{O}} ([\text{H}_2\text{O}]/K)^{1/2}$  appears in (8) at low water contents.  $D_{\Sigma\text{O}}^*$  is thus a linear function of the mole fractions of  $\text{H}_2\text{O}$  and of  $\text{OH}$  given these approximations, but  $D_{\text{water}}^*$  is a linear function of  $[\text{H}_2\text{O}]^{1/2}$ . From the experimental work reviewed above,  $D_{\text{OH}}$  is much smaller than  $D_{\text{H}_2\text{O}}$  and the effective diffusion coefficients of total water and total oxygen are only directly dependent on  $D_{\text{H}_2\text{O}}$  and  $\text{H}_2\text{O}$  concentration. For the relative contributions of  $\text{H}_2\text{O}$  and  $\text{O}_{\text{dry}}$  to the transport of oxygen to be equal would require that  $[\text{H}_2\text{O}] = D_{\text{O,dry}}/D_{\text{H}_2\text{O}}$ . In the case that

$D_{O,dry}/D_{H_2O} = 10^{-6}$  (a case very favorable for  $O_{dry}$  diffusion as will be clear from Fig. 2), then  $[H_2O] = 10^{-6}$ ; which corresponds roughly to the total water mole fraction of  $\sim 2 \times 10^{-4}$  (using  $K = 0.2$ ), or  $\sim 100$  ppm by weight. In other words, since in general  $D_{O,dry} \ll D_{H_2O}$ , it is likely that water will play a leading to dominant role in the effective oxygen diffusion, thus governing the  $^{18}O/^{16}O$  ratio, unless the silicate is unusually water-poor.

It is of interest to compare  $D_{\Sigma O}^*$  with  $D_{water}^*$  in a regime where both  $D_{OH}$  and  $D_{O,dry}$  are effectively zero. Then combining (8) and (15) for low water contents we have [40, but see footnote under eqn. (7) and footnote c in Table 1]:

$$D_{\Sigma O}^*/D_{water}^* \approx [OH]/4 = [water]/2. \quad (16)$$

If OH were both the dominant hydrous species and the diffusing species for water and oxygen diffusion, from (8) and (15) we would have:

$$D_{\Sigma O}^*/D_{water}^* = [OH] = 2[water]. \quad (16A)$$

Hence there were a factor of 4 increase in  $D_{\Sigma O}^*/D_{water}^*$  if the diffusing species were OH instead of  $H_2O$ .

At slightly higher water content and neglecting  $D_{O,dry}$  and  $D_{OH}$ , we have the following more general form for  $D_{\Sigma O}^*/D_{water}^*$  based on (15) and (7):

$$D_{\Sigma O}^*/D_{water}^* \approx [H_2O]d[water]/d[H_2O]. \quad (17)$$

If (12) and (13) are not satisfied (at very high water contents), then the full equation (11) must be used. It also requires that two diffusion equations (11) and (6) be solved simultaneously. In this complicated case, (11) can be rearranged to give the following general form for  $D_{\Sigma O}^*$  of  $R$ :

$$D_{\Sigma O}^* \approx D_{O,dry} + D_{H_2O} \left( [H_2O] + R \frac{\partial [H_2O]/\partial x}{\partial R/\partial x} \right) + D_{OH} \left( [OH] + R \frac{\partial [OH]/\partial x}{\partial R/\partial x} \right). \quad (18)$$

As with the less general expression given in (15), the terms  $D_{H_2O}[H_2O]$  and  $D_{OH}[OH]$  appear in the expression for  $D_{\Sigma O}^*$ . Thus, if either  $D_{H_2O}[H_2O]$  or  $D_{OH}[OH]$  is much larger than  $D_{O,dry}$  then the transport will be governed by the hydrous species. At high water contents and neglecting  $D_{O,dry}$  and  $D_{OH}$ , equations (18) and (7) can be combined to

give the following relationship between  $D_{\Sigma O}^*$  and  $D_{water}^*$ :

$$\frac{D_{\Sigma O}^*}{D_{water}^*} = \left( [H_2O] + R \frac{\partial [H_2O]/\partial x}{\partial R/\partial x} \right) \frac{d[water]}{d[H_2O]}. \quad (19)$$

#### 4. Comparison with previous experimental results

The analysis presented in section 3 can now be applied to experimental data to infer the diffusing species. Oxygen "self" diffusion has been studied extensively using  $^{18}O$  tracers under "dry" and "wet" conditions in crystalline feldspars [30–35,41], crystalline quartz [35–37,42–44], rhyolitic melt [45], silica glass [40,46], potassium-lead silicate glass [47], and potassium silicate glass [48]. In these studies, diffusion profiles of  $R$  or total amounts of exchange of  $^{18}O$  were measured and apparent oxygen "self" diffusion coefficients were determined. There have been no simultaneous determinations of  $R$ ,  $[H_2O]$ , and  $[OH]$  profiles in a single experiment that would allow determination of  $D_{O,dry}$ ,  $D_{H_2O}$  and  $D_{OH}$  and hence the dominant diffusing species. However, there are observations that provide hints to the diffusing species. (1) Reported oxygen "self" diffusion coefficients ( $D_{\Sigma O}^*$ ) are much higher under "wet" conditions than under "dry" conditions (see Fig. 2). (2) When both  $R$  and water concentration profiles have been measured in diffusion experiments, the profile in  $R$  due to diffusion has been found to be restricted to a much shorter linear dimension than the water concentration profile [46]. (3) It has been reported that  $D_{\Sigma O}^*/D_{water}^*$  increases with water content [45]. (4) Most authors have observed that oxygen "self" diffusion coefficients are linearly dependent on or proportional to  $p_{H_2O}$  or  $f_{H_2O}$  (Table 2 and references therein), at least in the low pressure range. (However, a few workers reported no dependence of  $D_{\Sigma O}^*$  on  $f_{H_2O}$ , see [34,37].)

There have been numerous interpretations and speculations on the significance of the enhancement of oxygen diffusion rates in the presence of water and the apparent linear dependence of  $D_{\Sigma O}^*$  on  $f_{H_2O}$ . However, these have often been specific to the matrix material studied. For example, some have proposed that  $H_2O$  was the diffusing species

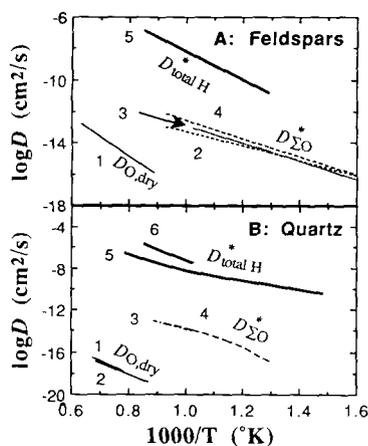


Fig. 2. Comparison of diffusion coefficients of total hydrogen, oxygen under hydrothermal conditions and oxygen under dry conditions. (A) Diffusion coefficients in feldspars. Line 1, oxygen diffusion in anorthite during exchange with  $^{18}\text{O}$ -enriched  $\text{O}_2$  atmosphere [41]; lines 2, 3, and 4, oxygen diffusion in albite, adularia, and anorthite during exchange with  $^{18}\text{O}$ -enriched  $\text{H}_2\text{O}$  at  $f_{\text{H}_2\text{O}}=100$  MPa [30]; line 5, total hydrogen diffusion in adularia at unknown  $f_{\text{H}_2\text{O}}$  [53]. (B) Diffusion coefficients in quartz (modified from fig. 12 in [65], see references therein). Lines 1 and 2, oxygen diffusion in quartz during exchange with  $^{18}\text{O}$ -enriched  $\text{O}_2$  atmosphere; lines 3 and 4, oxygen diffusion in quartz during exchange with  $^{18}\text{O}$ -enriched  $\text{H}_2\text{O}$  at  $f_{\text{H}_2\text{O}}=100$  MPa; line 5, H–D interdiffusion at  $f_{\text{H}_2\text{O}}=2.5$  MPa; line 6, total hydrogen diffusion in quartz at  $f_{\text{H}_2\text{O}}=1$  GPa.

during oxygen “self” diffusion experiments for silica glass [18,19,40], rhyolitic melt [45], and crystalline feldspars [33]; others have suggested that OH was the diffusing species in potassium

lead silicate glasses [47,48]; others have speculated that the effect is due partly to a confining pressure effect and partly to surface reaction [49]; while still others have invoked roles for fast proton transients [44,50], and defects related to  $\text{H}_2$  and  $\text{O}_2$  in hydrothermal oxygen diffusion [35,37,41,51]. The following summarizes the results and observations reported by other workers and discusses them in the framework of our treatment of speciation-dependent diffusion.

(1)  $D_{\Sigma\text{O}}^*$  in quartz and feldspars under wet conditions is found to be many orders of magnitude higher than  $D_{\text{O,dry}}$  but many orders of magnitude lower than  $D_{\text{total H}}^*$  (see Fig. 2 and the references cited therein). We note from Fig. 2 that  $D_{\Sigma\text{O}}^*$  for the dry case is from 4 to 7 orders of magnitude smaller than when  $f_{\text{H}_2\text{O}}=100$  MPa. The presence of water clearly plays a dominating role as was pointed out by previous workers. It should also be noted that  $D_{\text{total H}}^*$  is usually 10 or more orders of magnitude higher than  $D_{\text{O,dry}}$  in the same phase. If we assume that  $D_{\text{water}}^* = D_{\text{total H}}^*$  (we restrict our discussions to Fe-free systems at low  $f_{\text{H}_2}$  in which  $\text{H}_2$  is unlikely to play a dominant role), it is thus plausible in light of our discussion that chemical diffusion of hydrous species could dominate the “self” diffusion of oxygen, even when concentrations of hydrous species are as low as several ppb (eqs. 15 to 17). The observation that  $D_{\Sigma\text{O}}^*/D_{\text{water}}^*$  in amorphous silicates increases with water concentration [45] is also consistent with the notion that oxygen is carried by hydrous species based on (16) to (17).

TABLE 1

Comparison of calculated and observed  $D_{\Sigma\text{O}}^*/D_{\text{water}}^*$

System	$T$ ( $^{\circ}\text{C}$ )	$p_{\text{H}_2\text{O}}$ (MPa)	[water]	$(D_{\Sigma\text{O}}^*/D_{\text{water}}^*)_{\text{meas}}$	$(D_{\Sigma\text{O}}^*/D_{\text{water}}^*)_{\text{calc}}$	References <sup>a</sup>
Quartz <sup>b</sup>	700	400	$\sim 2 \times 10^{-5}$	$(0.8 \text{ to } 15) \times 10^{-6}$	$\sim 1 \times 10^{-5}$	65,36,65
$\text{SiO}_2$ glass	1100	0.092	0.0008	$\sim 0.0008$	0.0004	12,46,12
$\text{SiO}_2$ glass	600	0.1	0.0015	0.0006	0.0008 <sup>c</sup>	12,40,12
$\text{SiO}_2$ glass	1200	0.1	0.0008	0.00044	0.0004 <sup>c</sup>	12,40,12
Rhyolite	850	70	0.061	0.035	0.039	45,45,45
Rhyolite	850	70	0.035	0.050	0.021	45,45,45

$(D_{\Sigma\text{O}}^*/D_{\text{water}}^*)_{\text{meas}}$  are calculated from measured  $D_{\Sigma\text{O}}^*$  and  $D_{\text{water}}^*$ .  $(D_{\Sigma\text{O}}^*/D_{\text{water}}^*)_{\text{calc}}$  are calculated from eqn. (16) except for the last two for which eqn. (17) is used ( $K$  from [5]) because of the high water content.

<sup>a</sup> The 1st reference is for water content, the 2nd for  $D_{\Sigma\text{O}}^*$ , and the 3rd for  $D_{\text{water}}^*$ .

<sup>b</sup> Solubility and diffusion coefficient of water in quartz are controversial (see [57,65–70]). We assumed that  $D_{\text{water}}^* = D_{\text{total H}}^*$  although it has been suggested that in quartz  $D_{\text{total H}}^*$  reflects the exchange diffusion coefficient between  $\text{H}^+$  and alkali ions [57,65].

<sup>c</sup> Calculated values differ from those in [40] by a factor of two (and are in better agreement with experimental data) because there is an error in their eqn. (3) in [40], see footnote under eqn. (7).

Assuming that  $D_{\text{water}}^* = D_{\text{total H}}^*$ , we will show that the values of  $D_{\Sigma\text{O}}^*$  and  $D_{\text{water}}^*$  in some systems for which sufficient data are available are quantitatively consistent with the idea that  $\text{H}_2\text{O}$  is the dominant diffusing species and is responsible for the dramatic increase of the oxygen “self” diffusion coefficient in the presence of water. In Table 1 we list values of  $D_{\Sigma\text{O}}^*/D_{\text{water}}^*$  for various silicates taken from the literature and compare them with the theoretical ratio, calculated using either (16) or (17) and the measured water contents. The “measured” ratios in column 5 are from published experimental data of  $D_{\Sigma\text{O}}^*$  and  $D_{\text{water}}^*$  ( $= D_{\text{total H}}^*$ ). The theoretical values in column 6 at low water content were calculated using the [water] reported from experiments. The justification for neglecting  $D_{\text{O,dry}}$  in these calculations (i.e., for using eqn. 16 or 17) is based on the fact that  $D_{\text{O,dry}}$  is much smaller than  $D_{\Sigma\text{O}}^*$  listed in Table 1 for quartz and silica glass ([42,43] for  $D_{\text{O,dry}}$  in quartz; [52] for  $D_{\text{O,dry}}$  in silica glass). We assume, since  $f_{\text{H}_2\text{O}}$  is high in all cases, that this approximation holds for the other silicates listed in Table 1 as well. It can be seen that the agreement between measured and calculated values of  $D_{\Sigma\text{O}}^*/D_{\text{water}}^*$  is very good for all cases. The worst case is for the rhyolite with [water] = 0.035 where the measured value is a factor of two greater than the calculated value. One silica glass shows a similar discrepancy but in this case the  $R$  profile and hence  $D_{\Sigma\text{O}}^*$  were poorly determined [46]. Considering the wide range in  $D_{\Sigma\text{O}}^*$  (from  $5 \times 10^{-14}$  to  $3 \times 10^{-9}$  cm<sup>2</sup>/s) and in [water] (from  $2 \times 10^{-5}$  to  $6 \times 10^{-2}$ ) we consider the overall agreement to be remarkable and to support the idea that in these cases, mobility of water molecules dominates the apparent “self” diffusion of oxygen.

(2) In silicate minerals, the  $R$  profiles developed during oxygen exchange experiments under hydrothermal conditions ( $f_{\text{H}_2\text{O}} \sim 100$  MPa) can be represented by error functions [30,33–39]. However, in rhyolitic melts, the  $R$  profile under hydrothermal conditions ( $f_{\text{H}_2\text{O}} \sim 70$  MPa) has been stated to deviate from an error function [45]. These observations can be related to the fact that water concentrations in rhyolitic melt are much higher than those in silicate minerals as can be seen in Table 1. At low water contents, since apparent  $^{18}\text{O}$  diffusion coefficients and hence diffusion distances are expected to be much smaller

TABLE 2

Systems in which linear relationships between  $D_{\Sigma\text{O}}^*$  and  $f_{\text{H}_2\text{O}}$  are observed

System	$T$ (°C)	$f_{\text{H}_2\text{O}}$ range (MPa)	Reference
Quartz	700	25 to 350	36
Adularia <sup>a</sup>	650	0.2 to 10	33
K <sub>2</sub> O-SiO <sub>2</sub> glass <sup>b</sup>	714 & 786	0.00025 to 0.0013	48
K <sub>2</sub> O-SiO <sub>2</sub> -PbO	652	0 to 0.0022	47
SiO <sub>2</sub> glass	820	0.00008 to 0.1	40

<sup>a</sup> Above 10 MPa, the data starts to deviate from a linear trend, perhaps due to non-Henrian behavior of dissolved  $\text{H}_2\text{O}$  under high  $f_{\text{H}_2\text{O}}$ .

<sup>b</sup> The original authors concluded  $D_{\Sigma\text{O}}^*$  is proportional to  $(p_{\text{H}_2\text{O}})^{1/2}$  because they incorrectly ignored  $D_{\text{O,dry}}$  at these very low  $p_{\text{H}_2\text{O}}$ .

than those of water based on (15) to (17), the concentrations of hydrous species across the whole  $^{18}\text{O}$  diffusion profile can be treated as constant and the same as the surface concentrations during hydration. Therefore the apparent  $^{18}\text{O}$  “self” diffusion coefficient would be approximately constant across the entire oxygen diffusion profile according to (15) and the shapes of  $^{18}\text{O}$  diffusion profiles would be similar to an error function and not be expected to be useful for distinguishing diffusing species. At high water concentrations,  $^{18}\text{O}$  diffusion distance is expected to be a significant fraction of the water diffusion distance, so  $D_{\Sigma\text{O}}^*$  would increase with total water concentration via (18). Hence  $^{18}\text{O}$  diffusion profiles would be expected to show departures from simple error functions analogous to water diffusion profiles.

(3) A linear relationship between  $D_{\Sigma\text{O}}^*$  and  $f_{\text{H}_2\text{O}}$  has been observed in several systems as summarized in Table 2. At low  $f_{\text{H}_2\text{O}}$  (< 0.003 MPa),  $D_{\Sigma\text{O}}^*$  has been found to be linear to  $f_{\text{H}_2\text{O}}$  for silicate glasses [47,48]. At higher  $f_{\text{H}_2\text{O}}$ ,  $D_{\Sigma\text{O}}^*$  has been found to be proportional to  $f_{\text{H}_2\text{O}}$  for quartz [36] and adularia [33]. (However, Freer and Dennis [34] and Dennis [37] observed no dependence of apparent  $^{18}\text{O}$  “self” diffusion on  $f_{\text{H}_2\text{O}}$  in quartz and feldspars. The reasons for this discrepancy are not clear, and will have to be clarified by further experimentation.) Limited diffusion data in hornblende and apatite suggest  $D_{\Sigma\text{O}}^*$  is proportional to  $f_{\text{H}_2\text{O}}^{1/2}$  [38,39]. These relationships provide hints to the diffusing species. [H<sub>2</sub>O] at the silicate surface during hydrothermal diffusion experiments is expected to be proportional to

$f_{\text{H}_2\text{O}}$  in the fluid (Henry's law) and  $[\text{OH}]$  is proportional to  $f_{\text{H}_2\text{O}}^{1/2}$  at low water contents in the ideal case. Therefore, if  $\text{H}_2\text{O}$  is the dominant diffusing species,  $D_{\Sigma\text{O}}^*$  is expected to be proportional to  $f_{\text{H}_2\text{O}}$  (or to  $[\text{water}]^2$  at low water content) according to (15), and  $D_{\text{water}}^*$  to  $f_{\text{H}_2\text{O}}^{1/2}$  (or to  $[\text{water}]$ ) according to (8). If  $\text{OH}$  is the diffusing species,  $D_{\Sigma\text{O}}^*$  is linearly related to  $f_{\text{H}_2\text{O}}^{1/2}$  and  $D_{\text{water}}^*$  is constant. At extremely low  $f_{\text{H}_2\text{O}}$ ,  $D_{\text{O,dry}}$  may play a role and we would have a linear relationship instead of a proportionality. Reported proportionalities or linear relationships between  $D_{\Sigma\text{O}}^*$  and  $f_{\text{H}_2\text{O}}$  in quartz, feldspars, and some silicate glasses (Table 2) suggest that  $\text{H}_2\text{O}$  is the diffusing species in these systems, with some contribution from  $D_{\text{O,dry}}$  in the extremely water-poor glasses. The possible proportionality between  $D_{\Sigma\text{O}}^*$  and  $f_{\text{H}_2\text{O}}^{1/2}$  in hornblende and apatite is consistent with the notion that  $\text{OH}$  is the diffusing species in these minerals. It is perhaps not surprising that  $\text{OH}$  is the diffusing species in these phases because  $\text{OH}$  is a major structural constituent and relatively weakly bound to six or higher coordinated divalent cations (as opposed to  $\text{OH}$  bonded to tetrahedrally coordinated  $\text{Al}$ ,  $\text{Si}$ , or  $\text{P}$  cations in fully polymerized and nominally anhydrous minerals and glasses).

(4) The reported activation energy of  $D_{\Sigma\text{O}}^*$  under wet conditions is usually low (80–200 kJ/mol, [30,31,34–37]) compared to the activation energy of  $D_{\text{O,dry}}$  (200–300 kJ/mol, [41–43]). This is also consistent with the notion that oxygen diffusion under wet conditions involves some species that diffuses more readily than anhydrous oxygen itself. Assuming  $\text{H}_2\text{O}$  is the diffusing species, we can relate the apparent activation energy of  $D_{\Sigma\text{O}}^*$  to the activation energy of  $D_{\text{H}_2\text{O}}$  by the following:

$$\begin{aligned} D_{\Sigma\text{O}}^* &= D_{0,\Sigma\text{O}} e^{-E_{\Sigma\text{O}}/RT} \\ &\approx D_{\text{H}_2\text{O}}[\text{H}_2\text{O}] = D_{\text{H}_2\text{O}}K_{\text{p}}f_{\text{H}_2\text{O}} \\ &= D_{0,\text{H}_2\text{O}} e^{-E_{\text{H}_2\text{O}}/RT}K_{\text{p},0} e^{-\Delta H/RT}f_{\text{H}_2\text{O}} \quad (20) \end{aligned}$$

where  $K_{\text{p}}$  ( $=1/\text{Henry's law constant for water solubility}$ )  $\equiv [\text{H}_2\text{O}]/f_{\text{H}_2\text{O}}$  at equilibrium,  $E$  is activation energy for diffusion, and  $\Delta H$  is the standard state enthalpy change from  $\text{H}_2\text{O}$  vapor to dissolved  $\text{H}_2\text{O}$  in the silicate [7]. Based on (20), the slope in  $D_{\Sigma\text{O}}^*$  vs.  $f_{\text{H}_2\text{O}}$  would give  $D_{\text{H}_2\text{O}}K_{\text{p}}$ . The apparent activation energy for  $D_{\Sigma\text{O}}^*$  at a given

$f_{\text{H}_2\text{O}}$  (i.e., the slope of  $\ln D_{\Sigma\text{O}}^*$  vs.  $1/RT$ ) is the sum of  $E_{\text{H}_2\text{O}}$  and the  $\Delta H$  for  $K_{\text{p}}$  and is greater than  $E_{\text{H}_2\text{O}}$  ( $\Delta H > 0$  since  $K_{\text{p}}$  almost always decrease with temperature), which, in turn, is greater than the activation energy for apparent total water diffusion [5]. Because the activation energy for the diffusion of  $\text{H}_2\text{O}$  is usually low (e.g.,  $\sim 103$  kJ/mol in rhyolitic glasses [5]) and  $\Delta H$  is not expected to be huge ( $\Delta H$  is  $\sim 20$  kJ/mol for albitic and orthoclase melt [7]), the activation energy of  $D_{\Sigma\text{O}}^*$  under wet conditions should usually be low, whereas the activation energy of  $D_{\Sigma\text{O}}^*$  under dry conditions should be higher, reflecting the energy required to break some strong oxygen bonds. This is consistent with observations.

(5) It has been found that  $D_{\Sigma\text{O}}^*$  at  $f_{\text{H}_2\text{O}} = 100$  MPa in different feldspars (albite, orthoclase, and anorthite) are similar [30] (Fig. 2a) but 1 to 2 orders of magnitude higher than in quartz [36,37] (Fig. 2). Since  $D_{\text{total H}}$  for quartz and adularia are similar [53, and Fig. 2], the difference is probably due to a higher solubility of water in general and molecular  $\text{H}_2\text{O}$  in particular in feldspars than in quartz (see eqn. 15). Although no precise water solubility data for feldspars are available, it has been observed that natural feldspars contain much higher total water than natural quartz [54–57], and molecular  $\text{H}_2\text{O}$  has been observed in some colorless natural feldspars [55,56] but never in colorless natural quartz (i.e., only  $\text{OH}$  absorption bands have been observed) by infrared spectroscopy [54, and G.R. Rossman, pers. commun.]. These observations suggest higher water solubility in feldspars than in quartz.

Based on the above discussion, we infer that  $\text{H}_2\text{O}$  is often the diffusing species for  $^{18}\text{O}$  “self” diffusion in amorphous silicates and nominally anhydrous and fully polymerized crystalline silicates under hydrothermal conditions even when the water content is very low. Hence the diffusion mode for  $^{18}\text{O}$  transport under these conditions is chemical diffusion, instead of self diffusion. Although this has been suggested previously for amorphous silicates [18,19,40,45] and speculated upon for crystalline feldspars [33], the quantitative aspects have not been developed previously. Moreover, many other hypotheses, involving roles for fast proton transients [44,50] or for the confining pressure and surface reaction [49], or defects related to  $\text{H}_2$  and  $\text{O}_2$  fugacity [35,37,41,51], have

been proposed to explain these phenomena and observations in fully polymerized crystalline silicates. Although the concentration of defects undoubtedly plays some role, we propose that the major factor in controlling  $D_{\Sigma\text{O}}^*$  in the presence of water is whether the water content in the phase is high enough for  $\text{H}_2\text{O}$  to be the dominant diffusing species. We note that the simultaneous measurement of profiles of  $R$ ,  $[\text{H}_2\text{O}]$  and  $[\text{OH}]$  would provide a definitive means of determining the diffusion coefficients of the various oxygen-bearing species. In the future such measurements will be important for understanding oxygen diffusion under hydrothermal conditions.

We finally note that most so-called "dry" oxygen "self" diffusion experiments in silicates have been conducted by exchange with  $^{18}\text{O}_2$  or  $\text{C}^{18}\text{O}_2$  gas [41–43,52,58]. Under these conditions, if the gas partial pressures were high, leading to relatively high dissolved contents of  $\text{O}_2$  and  $\text{CO}_2$  in the silicates, the  $^{18}\text{O}$  flux might also be partly carried by the chemical diffusion of  $\text{O}_2$  [52] or  $\text{CO}_2$  [58]. The theoretical treatment of this problem would be similar to that given above. In contrast to the quadratic relation between  $[\text{OH}]$  and  $[\text{H}_2\text{O}]$ , the reaction equilibrium between  $\text{CO}_2$  and  $\text{CO}_3^{2-}$  yields a linear relationship between  $[\text{CO}_2]$  and  $[\text{CO}_3^{2-}]$ . Hence, the apparent diffusion coefficient of carbon is predicted to be independent of  $f_{\text{CO}_2}$  or total carbon content and the diffusion profile for carbon to be similar to error functions if  $D_{\text{CO}_2}$  and  $D_{\text{CO}_3^{2-}}$  are constant whether  $\text{CO}_2$  or  $\text{CO}_3^{2-}$  is the diffusing species, in agreement with the results of Watson [59].  $D_{\text{CO}_2}$  and  $D_{\text{CO}_3^{2-}}$  could not be individually resolved from measured  $\text{CO}_2$  and  $\text{CO}_3^{2-}$  profiles. In order to resolve them, experiments would have to be conducted on different silicates with different  $\text{CO}_2/\text{CO}_3^{2-}$  ratios [60] and utilizing knowledge of how  $D_{\text{CO}_2}$  and  $D_{\text{CO}_3^{2-}}$  might vary with bulk composition (similar to the case of NBO and BO discussed in the next section). If  $\text{CO}_2$  or  $\text{CO}_3^{2-}$  is the diffusing species for oxygen, the apparent diffusion coefficient of  $^{18}\text{O}$  is predicted to be proportional to  $D_{\text{CO}_2}$  and  $f_{\text{CO}_2}$  (or total carbon concentration). It has been observed that  $D_{\Sigma\text{O}}^*$  in the presence of  $\text{CO}_2$  depends on  $f_{\text{CO}_2}$  even though the exact relationship is not well-constrained [Z.D. Sharp, pers. commun.], lending some support to this hypothesis.

## 5. Speculations on other systems

We now speculate on the self diffusion of oxygen in volatile-free silicates in which there are three oxygen species: free oxygen ion ( $\text{O}^{2-}$ ), non-bridging oxygen (NBO) and bridging oxygen (BO). The diffusion of  $\text{O}^{2-}$  (such as the exchange of  $^{18}\text{O}^{2-}$  and  $^{16}\text{O}^{2-}$ ) is probably much faster than that of NBO, which, in turn, is probably much faster than that of BO since a bridging oxygen bond is more difficult to break. Assuming local isotopic equilibrium in a system in which chemical composition is identical across diffusion profiles of isotopes, we can readily derive:

$$D_{\text{O,dry}} \approx D_{\text{O}^{2-}}[\text{O}^{2-}] + D_{\text{NBO}}[\text{NBO}] + D_{\text{BO}}[\text{BO}], \quad (21)$$

where  $D_{\text{O,dry}}$  is the bulk self diffusion coefficient of total anhydrous oxygen, and  $D_{\text{O}^{2-}}$ ,  $D_{\text{NBO}}$  and  $D_{\text{BO}}$  are the self diffusivities of these oxygen species.

Shimizu and Kushiro [61] found that at 1650°C and 1.5 GPa, the oxygen self diffusion coefficient is  $6 \times 10^{-7} \text{ cm}^2/\text{s}$  in diopside melt, about 50 times higher than that in jadeite melt. Based on (21), we would explain the fact that the diffusion of oxygen in diopside melt is more rapid compared to a jadeite melt as due to the fact that the concentrations of NBO and  $\text{O}^{2-}$  are high in diopside relative to jadeite melt. That is, although  $D_{\text{NBO}}$  or  $D_{\text{BO}}$  must depend on melt composition and structure, this large variation in  $D_{\text{O,dry}}$  could be due, at least in part, to the change in the dominant diffusing species. Assuming that in diopside melt the contribution of  $\text{O}^{2-}$  and BO to the diffusion of oxygen is negligible and that  $[\text{NBO}]/[\Sigma\text{O}] = 2/3$ , eq. (21) would require that the diffusion coefficient of NBO is about 1.5 times that of bulk oxygen in diopside melt, i.e.,  $D_{\text{NBO}} \approx 9 \times 10^{-7} \text{ cm}^2/\text{s}$ . By the same reasoning,  $D_{\text{BO}}$  is at most the same as the bulk self diffusion coefficient of oxygen in jadeite melt (assuming that the jadeite melt used by Shimizu and Kushiro [61] contains no NBO) and hence is at least 80 times lower than  $D_{\text{NBO}}$ . However, if NBO were present at the 1% level in the jadeitic melt that Shimizu and Kushiro [61] investigated,  $D_{\text{BO}}$  could be even smaller. If valid, this line of reasoning would suggest that the self-diffusion coefficients of oxygen in jadeitic and

other nearly fully polymerized melts would depend strongly on small deviations from stoichiometry. For example, slight changes in melt composition that result in several percent of NBO would increase the diffusion coefficient several times (because  $D_{\text{NBO}} \geq 80D_{\text{BO}}$ ). Therefore extreme care may be necessary to study diffusion in these nearly fully polymerized melts. Although there is a considerable data base for oxygen self diffusion in a variety of melt compositions [61,62, and references therein], the results are not consistent with each other and it is difficult at present to evaluate quantitatively how the bulk oxygen diffusion coefficient varies with melt composition. In view of the potentially sensitive dependence of bulk oxygen self diffusion coefficient on the proportions of  $\text{O}^{2-}$ , NBO, and BO, and the possible presence of minute amount of volatile species, the inconsistencies among different reports could reflect, in part, small differences in melt compositions and experimental techniques. We also note that if this analysis proves to be correct, the measurement of diffusion coefficients might actually help to set constraints on the proportions of NBO in silicate melts.

Besides the cases examined above, there are numerous other possible cases where speciation may play an important role during diffusion. For instance, the presence of 6.2 wt% water has been found to increase the diffusion of Cs in obsidian by 3 to 4 orders of magnitude [63], and the presence of 3 wt% water increases diffusion coefficients of silica in a dacite-rhyolite couple by an order of magnitude [64]. These dramatic increases may be due to changes in the speciation of Cs and Si in the presence of water that result in changes in the relative proportion of various diffusing species.

## 6. Conclusions

When a component is present in a phase as two or more species, the diffusion coefficient of the component is a function of the diffusion coefficients and proportions of all the species. The diffusion of such a component can be treated by a multi-species diffusion equation that can be applied to analyze experimental data to determine or infer the dominant diffusing species. We further note that the diffusion equation which applies to

change of isotopic composition also has a distinctive form when different species are present. This must be taken into account when analyzing experimental results. We have previously shown that molecular  $\text{H}_2\text{O}$  (not OH) is the dominant diffusing species during diffusive dehydration of natural rhyolitic glasses over a wide range of water concentrations. In this paper we have inferred that during hydrothermal oxygen "self" diffusion experiments in crystalline quartz and feldspars, molecular  $\text{H}_2\text{O}$  is the dominant diffusing species and the diffusion mode is chemical diffusion. We conclude that in some systems, especially in the presence of water, it is important to determine the dominant diffusing species and to relate the apparent diffusion coefficient to the concentrations and diffusion coefficients of these species. An understanding of the role of speciation in diffusion not only offers insights to diffusive transport but also helps to relate the diffusion coefficients of seemingly unrelated components (such as the diffusion coefficients of  $^{18}\text{O}$  and water). Since the presence of minute amounts of volatile components and sometimes the slight non-stoichiometry for nominally fully polymerized silicates may greatly enhance the diffusion of oxygen, and perhaps of other components that have intrinsically low diffusion coefficients, stoichiometry and the fugacities of volatile components should be well controlled or monitored in diffusion experiments for such components.

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