

Diffusion of water and oxygen in quartz: reaction–diffusion model

Robert H. Doremus*

Materials Science & Engineering Department, Rensselaer Polytechnical Institute, Troy, NY 12180, USA

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Abstract

A mechanism of diffusion of isotopically tagged water in crystalline quartz by molecular diffusion and network exchange is compared to previous experiments. Three experimental factors are explained by this mechanism. (1) The apparent diffusion coefficient is proportional to the fugacity of the water vapor in the gas phase. (2) The ratio of apparent diffusion coefficients at 800°C in deuterium–hydrogen exchange to ^{18}O – ^{16}O exchange is $4.7(10)^5$. (3) Below 700°C the measured diffusion coefficients become time dependent. This diffusion–exchange mechanism is valid for a wide variety of crystalline and amorphous oxides. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Water in oxides can influence their mechanical properties such as creep and viscosity. Dissolved water and oxygen in oxides determine their oxidation state [1], and can, therefore, influence their optical absorption and chemical reactivity. Transport of water and oxygen in minerals and melts is important in geological processes such as circulation of water in geological formations, partitioning between mineral phases, bubble formation in magmas, hydrolytic weakening, and rheology of rocks. Diffusion can influence the determination of temperature from ^{18}O concentrations [2].

Transport of water and oxygen in quartz has been previously measured with isotopic exchange and diffusion of tagged water molecules (D_2O and H_2^{18}O) and oxygen ($^{18}\text{O}_2$). The results of these experiments

have been interpreted in terms of network diffusion of constituents such as OH^- and O^{2-} [3,4]. However, a number of experimental results are not consistent with this mechanism. (1) At temperatures below about 630°C the measured diffusion coefficients for D_2O in quartz are higher than expected from extrapolation from higher temperatures [5]. (2) The diffusion coefficients for H_2^{18}O are much lower than those for D_2O [3,5,6]. (3) The diffusion coefficients of H_2^{18}O are directly proportional to the water fugacity [6,7]. (4) In some experiments the diffusion coefficient of H_2^{18}O is higher at shorter diffusion times at a particular temperature [6]. A mechanism of simple network diffusion is inconsistent with these results.

A mechanism of molecular diffusion of water in silica glass and its isotopic exchange with network atoms was proposed in 1969 [8], and recently expanded and compared to new experimental data [9]; the mechanism was also applied to the diffusion of oxygen in silica glass [10] (see also [11]). In the

* Tel.: +1 518 276 6372; Fax: +1 518 276 8554; E-mail: doremr@rpi.edu

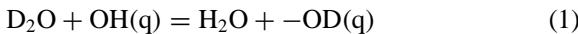
present paper I show that the results on diffusion of water and oxygen in quartz can be understood in terms of this model of molecular diffusion and isotopic exchange with the silicon–oxygen network of quartz. Farver and Yund have suggested that molecular water is involved in diffusion of H_2^{18}O in quartz [7], and molecular models of water in quartz have led to the conclusion that molecular diffusion of water in quartz is a likely mechanism [12,13]. Zhang et al. have proposed molecular diffusion of water in rhyolitic glasses and quartz [14,15].

The equations for diffusion and network exchange are first briefly reviewed as they are pertinent to experiments on quartz. More details are in [9] and [10]. Then these equations are applied to the experimental data on diffusion of water and oxygen in quartz. Finally the results are discussed and compared to diffusion of water and oxygen in other oxides.

2. Equations

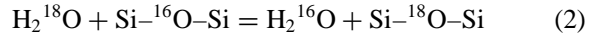
2.1. Network exchange

The experimental results on quartz are all of the following type. There is a fixed concentration of exchangeable atoms in the quartz, either OH groups for D_2O or network ^{16}O for H_2^{18}O . Tagged water molecules in the gas phase dissolve molecularly in the quartz and diffuse in it. The isotopic groups (either deuterium or ^{18}O) exchange with the appropriate hydrogen or ^{16}O in the quartz. There is enough water in the gas phase so its isotopic composition does not change with time. The total concentration S_T of exchangeable groups (either $\text{D} + \text{H}$ or $^{16}\text{O} + ^{18}\text{O}$) in the quartz is fixed and does not change with time. A biatomic reaction is assumed for the reaction rates of the forward and reverse reactions. The exchange of deuterium for hydrogen can be written as:



in which q means a group bonded in the quartz network. In the quartz sample of Kats discussed here, the hydrogen and deuterium ions compensate for the extra charge on aluminum ions four coordinated in the silicon–oxygen network, as shown by a detailed analysis of infrared spectra [5]. The total concentration of $\text{OH} + \text{OD}$ remains constant throughout

the experiments, as shown by the spectra. In the exchange for tagged oxygen the reaction is:



The exchange takes place with oxygen atoms bonded in the silicon–oxygen network; their total concentration ($^{16}\text{O} + ^{18}\text{O}$) remains constant.

At a particular location in the quartz crystal the rate of change of the concentration S^* of tagged groups is:

$$\frac{\partial S^*}{\partial t} = k(C^*S - CS^*) \quad (3)$$

in which k is a reaction rate coefficient and C^* is the concentration of molecularly dissolved tagged water in the quartz, and S and C are the concentrations of untagged groups in the quartz network and dissolved molecularly, respectively. Eq. 3 assumes that the exchange reaction (Eq. 2) is pseudo-first order, because the concentration of network oxygen is constant. Furthermore, in tracer exchange there are no chemical gradients, so there is no net chemical reaction nor any effects of changing thermodynamic activities. The total concentrations are:

$$S_T = S^* + S \quad \text{and} \quad C_T = C^* + C \quad (4)$$

in which C_T is the total concentration of molecularly dissolved water in the quartz. The total concentration of network groups S_T (either $\text{OH} + \text{OD}$ or $^{16}\text{O} + ^{18}\text{O}$) is uniform and constant with time, as described above. It is also assumed that C_T is uniform and constant with time. In these isotopic exchange experiments this assumption is valid because the rate of molecular diffusion of the dissolved water is rapid enough to transport it well beyond the region in the quartz in which exchange is taking place. Furthermore any change in the fugacity of the water vapor is rapidly reflected in a change of the concentration C_T of molecularly dissolved water. From Eqs. 3 and 4:

$$\frac{\partial S^*}{\partial t} = k(C^*S_T - C_T S^*) \quad (5)$$

2.2. Local equilibrium

Consider now the concentration of dissolved water at the quartz surface. It is assumed that the dissolved water is in equilibrium with the water in

the surrounding gas phase, so that the concentration of dissolved water at the surface is proportional to the water vapor fugacity in the gas (Henry's law), which is constant with time. It is also assumed that all the water molecules in the gas phase are tagged. Then the concentration of tagged molecules dissolved molecularly at the quartz surface is C_T , and is constant with time. Eq. 5 then becomes at the quartz surface:

$$\frac{\partial S^*}{\partial t} = kC_T(S_T - S^*) \quad (6)$$

Integration of this equation from $t = 0$ to t gives the concentration S_0^* of exchanged network groups at the quartz surface:

$$S_0^* = S_T[1 - \exp(-C_Tkt)] \quad (7)$$

This equation shows that at long times ($C_Tkt \gg 1$) the surface network groups are completely exchanged with the dissolved tagged groups. However, at shorter times the surface groups are not entirely exchanged. For example, if $C_Tkt \sim < 0.5$, then $S_0^* = S_T(C_Tkt)$ at the surface, so the surface concentration of tagged groups in the network increases proportional to time. Thus at long times the exchange reaction is at local equilibrium at each point in the quartz, but there is still a gradient of tagged dissolved water molecules into the quartz, and of network tagged groups.

The equation of continuity for diffusion of dissolved tagged water molecules, including the exchange reaction, is [16]:

$$\frac{\partial C^*}{\partial t} = D \frac{\partial^2 C^*}{\partial x^2} - \frac{\partial S^*}{\partial t} \quad (8)$$

in which C^* is the concentration of dissolved water in the quartz at distance x and time t , and D is its diffusion coefficient. For the condition of local equilibrium of the last paragraph exchange reactions 1 or 2 are governed by an equilibrium constant K :

$$K = \frac{CS^*}{C^*S} \quad (9)$$

at equilibrium, the isotopic ratio is the same in the dissolved and network species, so $K = 1$, and from Eqs. 4 and 9, for all x and t :

$$\frac{S^*}{S_T} = \frac{C^*}{C_T} \quad (10)$$

The quantity measured in the diffusion experiments is S^* , the concentration of network isotope. To derive equations for the apparent diffusion of S^* from Eq. 8, the differentials from Eq. 10 are:

$$\frac{\partial C^*}{\partial t} = \frac{C_T}{S_T} \frac{\partial S^*}{\partial t} \quad \text{and} \quad \frac{\partial^2 C^*}{\partial x^2} = \frac{C_T}{S_T} \frac{\partial^2 S^*}{\partial x^2} \quad (11)$$

because S_T and C_T are uniform in time and space. Substituting Eq. 11 in Eq. 8 gives:

$$\frac{\partial S^*}{\partial t} \left(\frac{C_T}{S_T} + 1 \right) = \frac{DC_T}{S_T} \frac{\partial^2 S^*}{\partial x^2} \quad (12)$$

Eq. 12 is the usual continuity equation (Fick's second law) of diffusion with an effective diffusion coefficient D_E :

$$D_E = \frac{DC_T}{(S_T + C_T)} \approx \frac{DC_T}{S_T} \quad (13)$$

Often $C_T \ll S_T$ (the concentration of dissolved water is much less than the concentration of exchanging groups in the network), so that the approximation is valid. From Eq. 13 the effective diffusion coefficient D_E is constant with time and space, so the solutions to Eq. 12 are just those for the usual diffusion problems. Of course the network atoms (S^*) are not actually diffusing; their isotopic concentration changes as a result of diffusion of dissolved water (C^*) and its exchange with network atoms.

The boundary conditions for semi-infinite geometry are: $S^* = S_0^*$ at $x = 0$ for all t ; $S^* = 0$ for $t = 0$ and all x , and S^* approaches zero as x approaches infinity. The solution to Eq. 12 for these conditions is:

$$S^* = S_0^* \operatorname{erfc}(x/2\sqrt{D_E t}) \quad (14)$$

in which erfc is the conjugate error function (see [16], p. 14). The total amount of network atoms exchanged in time t is M^* :

$$M^* = \frac{2S_0^* \sqrt{D_E t}}{\Pi} = \frac{2S_T \sqrt{D_E t}}{\Pi} \quad (15)$$

since we have assumed that all gas atoms are tagged, $C_0^* = C_T$ and for the condition of local equilibrium $S_0^* = S_T$. Eq. 15 is plotted in Fig. 1. The axes can be made dimensionless by dividing M/S_T by L and $D_E t$ by L^2 , where L is a distance.

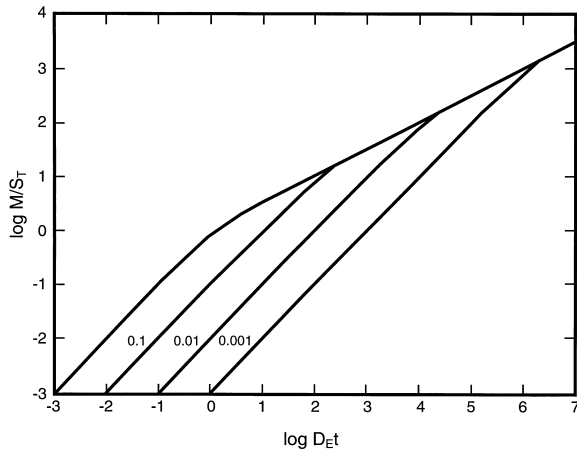


Fig. 1. The total amount M of network atoms exchanged as a function of time t ; log–log plot. The top line is from Eq. 15 for local equilibrium. The numbers on the other lines are values of $kC_T t$; see Eqs. 7 and 17 and 18 for nonequilibrium.

2.3. Nonequilibrium

At shorter times ($C_T k t$ less than about 4) the local equilibrium described above will not hold. Then from Eq. 7 the surface concentration of exchanged groups is smaller than their total concentration S_T . A complete solution to Eq. 8 for this condition is given in [9]. The profiles of S^* versus distance change from that of Eq. 14 to an exponential profile with distance at shorter times [9,10].

$$S^* = kS_T C_T t \exp(-x\sqrt{kS_T/D}) \quad (16)$$

In this regime the total amount M^* of exchanged network atoms is [10,16]:

$$M^* = C_T \sqrt{kS_T D t} \quad (17)$$

The log–log plot of reduced values of M and time in Fig. 1 shows the square root dependence of M on time at longer times (Eq. 15) and the linear dependence at shorter times (Eq. 17). As the exchange coefficient k becomes larger, the amount exchanged increases at a particular time, and the transition to Eq. 15 is at earlier time.

The behavior for nonequilibrium conditions can be described with a time-dependent diffusion coefficient D_T :

$$D_T = DC_T/S_T [1 - \exp(-kC_T t)] \quad (18)$$

At long times $D_T = D_E$ (Eq. 13); at short times $D_T = D/kS_T t$.

3. Comparison with experiments

3.1. Exchange of deuterium for hydrogen

In an excellent study of hydroxyl groups in quartz, Kats monitored with infrared absorption the exchange of hydrogen in quartz with deuterium in D_2O from the vapor [5]. The samples were single crystals of natural quartz cut perpendicular to the optical (c) axis, to expose a direction of more rapid diffusion, and were slabs about 1 mm thick. The experimental results are listed in Table 1, as calculated from the experimental data given in the paper. Some of the values in Table 1 are different from those in [5] as noted in the table. These D_T values are plotted in Fig. 2. The values at the three highest temperatures give the least squares line in the figure and the relation:

$$D_E = 0.27 \exp(-149/RT) \quad (19)$$

with the D_E values in cm^2/s and the activation energy 149 kJ/mole. Experiments at 1000°, 900°, 820°, 700° and 475°C were preceded by heating for 16 h at 1000°C. This treatment appears to reduce the values of D_T at 475°C, contrary to the statement in [5].

Values of the diffusion coefficients at lower temperatures (D_E) calculated from an extrapolation of Eq. 19 are given in Table 2. From Eqs. 13 and 18:

$$D_E/D_T = 1 - \exp(-kC_T t) \quad (20)$$

Table 1

Diffusion coefficients calculated from the experimental results of Kats [5] for water in quartz

Temp (°C)	M/M_D	Time (h)	Sample thickness (cm)	D_T (cm^2/s)
1000	various			$1.79(10)^{-7}$ ^a
900	0.533	5	0.172	$9.16(10)^{-8}$
820	0.521	16.5	0.141	$1.76(10)^{-8}$
700	0.653 ^a	400	0.140	$1.14(10)^{-9}$ ^a
620	0.730	161	0.085	$1.23(10)^{-9}$ ^a
550	0.557	420	0.086	$1.98(10)^{-10}$
500	0.423 ^a	280	0.084	$2.46(10)^{-10}$
475	0.168	424	0.085	$2.62(10)^{-11}$ ^a
400	0.093	425	0.139	$2.14(10)^{-11}$ ^a

^a Different values from those in [5]

D_T values calculated from fig. 4.6 in [16] (see text).

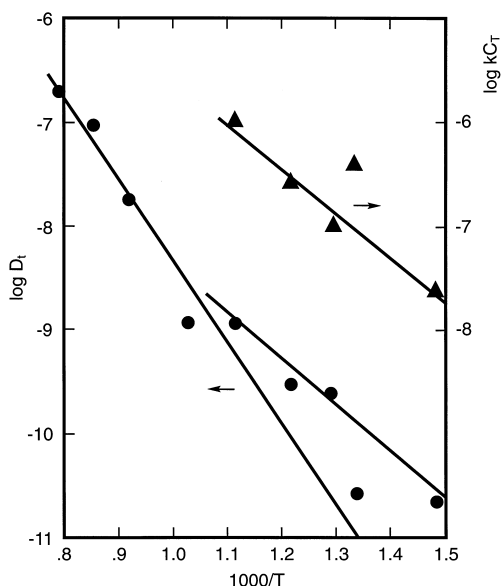


Fig. 2. Log D_T and kC_T as a function of reciprocal temperature. ●, data of Kats [5], see Table 1. ▲, values of log kC_T from Eq. 20 and Table 2 and data of Kats [5].

Values of kC_T calculated at the different lower temperatures from this equation are given in Table 2 and plotted in Fig. 2. If the 475°C point is omitted the values of kC_T give the line in the diagram and the equation:

$$kC_T = 0.064 \exp(-84/RT) \quad (21)$$

with kC_T in s^{-1} and the activation energy in kJ/mole. Including the 475°C point gives an activation energy of about 96 kJ/mole.

The measured D_T values begin to show a deviation from the high temperature line in Fig. 2 at about

Table 2
Reaction rates of deuterium–hydrogen exchange in quartz, calculated from [5]

Temp (°C)	D_E (cm ² /s)	D_E/D_T	kC_T (per s)
620	$5.37(10)^{-10}$	0.437	$9.9(10)^{-7}$
550	$9.81(10)^{-11}$	0.329	$2.6(10)^{-7}$
500	$2.39(10)^{-11}$	0.0972	$1.0(10)^{-7}$
475	$1.11(10)^{-11}$	0.424	$3.6(10)^{-7}$
400	$7.70(10)^{-13}$	0.0360	$2.4(10)^{-8}$

D_E values extrapolated from high temperature values (see Fig. 2 and text).

D_T from Table 1; kC_T calculated from Eq. 20.

700°C. In silica glass apparent diffusion coefficients of water deviated from the extrapolated coefficients at higher temperatures below about 550°C [17]. In this case the exchange reaction was between dissolved water molecules and Si–O–Si groups [9]; nevertheless the similar deviation temperatures suggest a similar process in crystalline quartz and silica glass. The proximity of these temperatures to the α – β quartz transformation temperature of 573°C appears to be a coincidence.

The above discussion shows that the diffusion results of Kats can be understood in terms of the diffusion-exchange model; the higher apparent diffusion coefficients at lower temperatures result because of the lower exchange rates at lower temperatures, as shown in Fig. 1.

3.2. Exchange of ^{18}O for ^{16}O

There have been several studies of the diffusion of water tagged with ^{18}O into quartz [3,6,7,18]. The profile of ^{18}O exchanged into the silicon–oxygen network was analyzed by SIMS [3,6,7] or a nuclear reaction [18]. At temperatures from 697° to 849°C the results of three studies [3,6,7] at 100 Mpa water pressure and transport parallel to the c -axis of the quartz agreed reasonably well, and give the temperature dependence of the effective diffusion coefficient D_E in cm²/s (least squares):

$$D_E = 7.1(10)^{-3} \exp(-129/RT) \quad (22)$$

with an activation energy of 129 kJ/mole, somewhat less than for the data of Kats. Normal to the rhombohedral plane (1011) the diffusion coefficient is about a factor of two smaller than that parallel to the c -axis at temperatures from 700° to 800°C [5]. Perpendicular to the c -axis the apparent diffusion coefficient of tagged water is about a factor of 100 smaller than for diffusion parallel to the c -axis; the activation energy of combined data from [3] and [5] between 700° and 850°C give a value of about 228 kJ/mole for diffusion perpendicular to the c -axis.

At temperatures below about 700°C the diffusion coefficients measured for $H_2^{18}O$ by different investigators [3,6,7] differ widely, by up to an order of magnitude or more at 500°C. I suggest that the reason for this difference is that the exchange rate between ^{18}O in molecularly dissolved water and ^{16}O

Table 3

Dependence of diffusion coefficients of water in quartz on the time of diffusion below 700°C

Temp (°C)	D (cm ² /s)	Time (h)	Orientation with respect to c -axis	Ref.
500	$1.3(10)^{-17}$	600	parallel	[3]
515	$3.2(10)^{-16}$	287	parallel	[7]
595	$2.2(10)^{-15}$	169	parallel	[7]
600	$1.1(10)^{-15}$	144	parallel	[3]
591	$9.6(10)^{-18}$	135.5	perpendicular	[7]
600	$1.2(10)^{-18}$	672	perpendicular	[3]
600	$3.6(10)^{-14}$	6.37	parallel	[3]
600	$1.0(10)^{-15}$	120	parallel	[3]
700	$9.6(10)^{-15}$	20	perpendicular	[3]
700	$7.0(10)^{-15}$	114	perpendicular	[7]
700	$4.7(10)^{-17}$	43	perpendicular	[7]
700	$2.1(10)^{-17}$	337	perpendicular	[3]

in the quartz network becomes so slow below 700°C that the effective diffusion coefficient D_T becomes time dependent (Eq. 18). In Table 3 some selected data for apparent diffusion coefficients of water in quartz show that when the time of diffusion is similar, results of different investigators are similar, but when diffusion times are different, the diffusion coefficients at shorter times are higher, just as predicted by Eq. 18. This difference is more marked as the temperature becomes lower; even at 700°C there seems to be a small difference. Especially striking is the difference of more than an order of magnitude in measured diffusion coefficients at 600°C for times of 6.37 and 120 h [6].

It is possible that some of the time dependence of the calculated diffusion coefficients arises because of a reaction layer on the surface of the quartz. At the temperatures and pressures of the experiments there is some solubility of quartz in water, so dissolution and reprecipitation on the crystal surface is possible. However, there is no evidence for such a layer in the published tracer profiles, so it is unlikely that it contributes significantly to the diffusion process. Examination of profiles at lower temperatures should clarify this point.

In a definitive study, Farver and Yund [5] showed that the measured apparent diffusion coefficient of water in quartz is directly proportional to the fugacity of water vapor in the gas phase; this result is just what is expected from the diffusion and exchange mechanism, as shown in Eq. 13 (or Eq. 18). The

effective diffusion coefficient is directly proportional to C_T , the concentration of water dissolved molecularly in the quartz at its surface, which at equilibrium should be proportional to the fugacity of water vapor.

3.3. Different exchanging species

The proposal here is that both the exchange of deuterium for hydrogen [2] and ¹⁸O for ¹⁶O [3–5] are controlled by the diffusion of molecularly dissolved water. The apparent diffusion coefficient D_E at 800°C from Eq. 21 is $3.4(10)^{-14}$ cm²/s, whereas for the data of Kats (Eq. 19) it is $1.6(10)^{-8}$ cm²/s at 800°C, giving a ratio of $4.6(10)^5$. From Eq. 13 the difference between these two apparent diffusion coefficients results from two different factors, the different water vapor pressures and the different exchange capacities (S_T values). In [5] the water vapor pressure was 25 atm, whereas in the data for Eq. 21 it was 1000 atm. Kats reported a concentration of $5.0(10)^{18}$ hydrogen atoms for his natural quartz, and the calculated value of oxygen concentration in the quartz is $5.3(10)^{22}$ atoms/cm³. Thus, the expected ratio between the two kinds of diffusion coefficients is $5.3(10)^{22}(40)/5(10)^{18} = 4.2(10)^5$, in excellent agreement with the measured value of $4.6(10)^5$. This agreement is evidence that the diffusion of molecular water is the controlling mechanism in both kinds of experiments.

Two sets of investigators measured the diffusion of 'dry' tagged oxygen ¹⁸O₂ in quartz [19,20], and

agreed rather well. The apparent diffusion coefficient of oxygen extrapolated to 800°C from [19] was $3.6(10)^{-20}$ cm²/s at an oxygen pressure of 90 torr or 0.118 atm. It is possible that even in these experiments the diffusing species is molecular water. The ratio of apparent diffusion coefficients from Eq. 22 and [19] is $8.8(10)^5$ at 800°C. The ratio of gas pressures in these experiments was $1000/0.118 = 8.5(10)^3$; thus the fraction of water vapor needed in the gas phase to give the diffusion coefficient found in the ¹⁸O₂ experiments was $8.5(10)^3/8.84(10)^5 = 0.0096$, or about $1.1(10)^{-3}$ atm of water vapor pressure. In an analysis of experiments of diffusion of nominally dry oxygen in silica glass [10], it was found that the results when no special precautions were taken to absorb water, were that the gas contained about 0.0045 fraction of water vapor, or about $4.5(10)^{-3}$ atm. Thus it seems possible that the oxygen of [19] and [20] contained this much residual water.

4. Discussion

The experiments provide three factors of strong evidence for the molecular diffusion and exchange mechanism of water in quartz. (1) The apparent diffusion coefficient is proportional to the fugacity of the water vapor. (2) The ratio of diffusion coefficients of water in experiments on deuterium–hydrogen and ¹⁸O–¹⁶O exchange experiments is explained by Eq. 13. (3) Below 700°C the measured diffusion coefficients become time dependent. No other mechanism has been put forward that explains these factors.

These conclusions suggest that in any study of diffusion of gaseous isotopes that can exchange with a solid network (for example water and oxygen in oxides) the time dependence of the diffusion coefficient should be carefully tested over a wide range of diffusion times, especially below 700°C, and diffusion profiles examined carefully for deviations near the sample surface. Another way to detect the diffusion and exchange mechanism is by a reduction of the expected exchange ratio at the sample surface (see Eq. 7). A comparison of Eqs. 7 and 13 shows that this reduction should occur along with the time dependence of the diffusion coefficient. Only a few

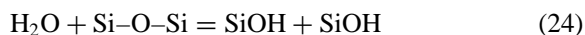
profiles of ¹⁸O are shown in the papers [3,6,7] on water in quartz, mostly at temperatures at or above 700°C, so it is not possible to examine this possibility in these studies. I urge other workers to examine their profiles, especially at 500°C, for a lower surface exchange fraction. Furthermore, possible surface reaction layers (see above) should be examined.

Fortier and Giletti [21] have shown a correlation between apparent diffusion coefficients of water H₂¹⁸O measured at 100 Mpa water pressure and 700°C and 500°C, and the ‘ionic porosity’ of eight crystalline minerals. This porosity *Z* equals one minus the ratio of total spherical volume *V_i* of ions in the mineral in a unit cell to the volume *V_c* of the cell, or:

$$Z = 1 - V_i/V_c \quad (23)$$

The data on quartz fit in this correlation, which suggests that diffusion of molecular water is the controlling mechanism in water diffusion in these minerals. Diffusion of network elements should depend on bond strengths, structure, and similar factors more than on the open volume. Of course detailed studies of each of these minerals are required to give convincing evidence that molecular water is controlling oxygen transport in them. There are other minerals such as micas that do not fit the Fortier and Giletti relation; the mechanisms of hydrothermal diffusion in them are uncertain. I have shown that the experimental results in [22] on diffusion of water in potassium feldspar can result from solubility of molecular water [23]; the authors prefer their original explanation in terms of proton diffusion [24].

Zhang et al. [14] have measured the profiles of water diffusion out of rhyolitic glasses. They found that the diffusion coefficient of dissolved molecular water was much faster than diffusion of network hydroxyls. They assumed a bimolecular reaction between dissolved molecular water and the silicon–oxygen network:



These are exactly the conditions in the fused silica experiments modeled in my 1969 paper [8] (see also [9]); thus the molecular mechanisms proposed for these two glasses are the same. The difference between the two treatments is in the mathematical methods for determining calculated profiles. I

started with an equation similar to Eq. 8 with the assumption that the concentration of reacted OH was much greater than that of dissolved molecular water ($S \gg C$), and solved the resulting equations for the profile of reacted OH (S). In the experiments of Zhang et al. the assumption $S \gg C$ was not valid, so they used a numerical method to solve the continuity equation (Eq. 8 without the last term), using an expression for Eq. 24 to determine concentrations; at equilibrium:

$$K = S^2/C \quad (25)$$

where S is now the concentration of reacted OH groups and C the concentration of dissolved water. Thus the molecular mechanism or model of diffusion and exchange reaction is the same in my treatment and that of Zhang et al.; the difference is in the mathematical methods for determining profiles.

Sharp et al. [25] measured ^{18}O profiles in quartz in contact with C^{18}O_2 vapor. They found diffusion coefficients between those in water and in nominally dry oxygen. Experiments of these authors on ^{18}O profiles in the quartz provide evidence that ^{18}O is not diffusing in the oxygen network. They formed an ^{18}O profile by diffusion from C^{18}O_2 , and then annealed the sample in vacuum. The profile changed very little during this annealing step, with a nominal diffusion coefficient at least a factor of twenty smaller than in the tagged CO_2 vapor. This experiment shows that a constituent of the gas phase, probably water, is responsible for the apparent transport of oxygen in the quartz. Sharp et al. concluded that “There is probably a diffusing species, other than oxygen, that enhances the oxygen diffusion rate in these quartz– CO_2 systems...”

Gautason and Muehlenbachs [26] have shown a correlation of the activation energy of diffusion of nominally dry oxygen in thirteen different crystalline minerals and the ionic porosity Z . Their values of the porosity are higher than those for [21]. Gautason and Muehlenbachs have interpreted their results in terms of ionic diffusion in the mineral networks; in some systems such as zirconates and perovskites there is evidence that the electrical conductivity is related to diffusion of ionic oxygen. Nevertheless I have interpreted some results on diffusion of supposedly dry oxygen in silica glass as resulting from diffusion of residual water [10]. Zhang et al. [15] have sug-

gested that ‘dry’ oxygen diffusion in ‘some silicates’ may result from diffusion of residual water. Thus, the mechanism of the diffusion of oxygen in water-free minerals requires further study for confident acceptance of a mechanism. [RV]

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