Available online at www.sciencedirect.com
ScienceDirect
Earth and Planetary Science Letters 254 (2007) 69–76
EPSL
www.elsevier.com/locate/epsl

Molecular H_2O as carrier for oxygen diffusion in hydrous silicate melts

H. Behrens [a,*], Y. Zhang [b], M. Leschik [a,c], M. Wiedenbeck [d], G. Heide [c], G.H. Frischat [c]

[a] *Institut für Mineralogie, Universität Hannover, Callinstr. 3, D-30167 Hannover, Germany*
[b] *Department of Geological Sciences, The University of Michigan, Ann Arbor, MI 48109-1063, USA*
[c] *Institut für Nichtmetallische Werkstoffe, TU Clausthal, Zehntnerstr. 2a, D-38678 Clausthal-Zellerfeld, Germany*
[d] *GeoForschungsZentrum Potsdam, Telegrafenberg, D-14473 Potsdam, Germany*

Received 3 September 2005; received in revised form 12 November 2006; accepted 13 November 2006
Available online 22 December 2006
Editor: R.D. van der Hilst

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 H_2O 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 H_2O and ^{18}O 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. H_2O profiles were analyzed by infrared spectroscopy and ^{18}O profiles by SIMS. ^{18}O 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 H_2O diffusion, not due to the self diffusion of oxygen itself. With this confirmation, experimental data on H_2O diffusion in silicate melts can be used to infer ^{18}O diffusion under hydrothermal conditions, and hydrothermal oxygen diffusion data in silicate minerals can be used to infer H_2O diffusivity, as long as the concentration or solubility of H_2O in the given phase is known.

Keywords: oxygen diffusion; hydrous silicate melts; rhyolite; H_2O diffusion; oxygen and hydrogen isotopes

1. Introduction

Many authors have carried out ^{18}O "self" diffusion experiments under hydrothermal conditions [2–9]. During such an experiment, an ^{18}O-enriched H_2O fluid surrounds or is in contact with a mineral, glass or melt, and ^{18}O diffuses into the condensed phase. After the experiment, the isotopic ratio R ($\equiv {}^{18}O/({}^{16}O+{}^{18}O)$) 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 ^{18}O diffusivity. Related phenomena are the hydrolytic weakening of quartz [10,11] and enhanced cation diffusivities in framework silicates such as feldspars [12–14].

* Corresponding author. Tel.: +49 511 762 8054; fax: +49 511 762 3504.
E-mail address: h.behrens@mineralogie.uni-hannover.de (H. Behrens).

0012-821X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.epsl.2006.11.021

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 H_2O diffusion for which a quantitative theory has been proposed.

It is well established that molecular H_2O (hereafter referred to as H_2O_m) is the mobile species responsible for transporting the H_2O component in silicate melts [25–31] although some details about migration of H_2O in the melts remain debated [25,32,33]. OH is essentially immobile but may be consumed or regenerated by an interconversion reaction between H_2O and OH. Hence, diffusion of H_2O is a classical diffusion-reaction problem [34]. The diffusion coefficient of total H_2O (H_2O_t, including both H_2O_m and hydroxyl) can be expressed as:

$$D_{H_2O_t} = D_{H_2O_m} \cdot dX_{H_2O_m}/dX_{H_2O_t}. \quad (1)$$

Where X refers to the mole fraction of the species or component in the melt calculated on a single oxygen basis. Because H_2O contains oxygen, the diffusion of H_2O_m leads to an oxygen flux. A number of authors [1,7,9,18,22–24] have proposed that ^{18}O diffusion from a hydrothermal fluid into silicate melt, glass, quartz and feldspar is carried by H_2O_m, with anhydrous oxygen and OH being essentially immobile except for local ^{18}O–^{16}O isotopic exchange reactions between H_2O_m and other oxygen species. That is, ^{18}O 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 $D_{^{18}O}$ (the apparent ^{18}O diffusivity) is complicated, an approximate expression is as follows [1]:

$$D_{^{18}O} \approx D_{H_2O_m} \cdot X_{H_2O_m}. \quad (2)$$

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

$$D_{^{18}O} \approx D_{H_2O_t} \cdot X_{H_2O_m} \cdot dX_{H_2O_t}/dX_{H_2O_m}. \quad (3)$$

At very low X_{H_2Ot} (<0.001) which are typically found in nominally water-free minerals, this equation simplifies to

$$D_{^{18}O} \approx D_{H_2O_t} \cdot X_{H_2O_t}/2. \quad (4)$$

Hence, $D_{^{18}O}$ is typically orders of magnitude smaller than D_{H_2Ot} and the ^{18}O profile is much shorter than the H_2O_t profile. Therefore, across the ^{18}O profile, H_2O_t is roughly constant, leading to constant $D_{^{18}O}$ and an error function shape of the profile [4–8]. On the other hand, when surface X_{H_2Ot} is large (as for hydrous melts in contact with a fluid), $D_{^{18}O}$ approaches D_{H_2Ot} and the length of ^{18}O profile is a significant portion of that of the H_2O_m profile. That is, along the ^{18}O profile, X_{H_2Ot} and hence $D_{^{18}O}$ vary significantly, leading to deviation of the shape of the ^{18}O profile from an error function. Numerical simulations show that when surface X_{H_2Ot} is <0.01, ^{18}O profile is essentially indistinguishable from an error function profile. When surface X_{H_2Ot} 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 ^{18}O and hydrous species. If the hypothesis is correct, the two profiles would be related such that the ^{18}O profile can be calculated from the H_2O_t profile. In this study, we report such a confirmation by experiments in which ^{18}O-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 H_2O_t and ^{18}O were measured: H_2O_t as the sum of OH and H_2O_m by infrared spectroscopy, and $^{18}O/^{16}O$ by secondary ion mass spectrometry. R is calculated from $^{18}O/^{16}O$. We fit profiles of both H_2O_t and R assuming (i) H_2O_m is the diffusing species for both H_2O_t and ^{18}O, and (ii) diffusivity of H_2O_m is an exponential function of H_2O_t content [1]. Verification of the theory requires that both H_2O_t and R profiles would be well fit by a single expression of D_{H_2Om}.

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.% H_2O_t was run at 1085 K whereas in two other experiments a water-poor (0.04 wt.% H_2O_t) synthetic glass with a similar composition was used (Table 1). The starting fluid for the experiments at 1136 K and 1085 K contained $D_2^{18}O$, with D/(D+H)=0.80 and R=0.855. In

Table 1
Composition of glasses (wt.%)

Sample name sources	EDF Erevan Dry Fountain, Armenia	EDFS synthetic
SiO_2	76.78 (0.32)	76.32 (0.28)
TiO_2	0.10 (0.02)	0.01 (0.02)
Al_2O_3	12.77 (0.13)	13.27 (0.19)
FeO [a)]	0.52 (0.03)	0.01 (0.01)
MnO	0.09 (0.01)	0.00 (0.01)
MgO	0.07 (0.01)	0.01 (0.01)
CaO	0.56 (0.02)	1.11 (0.06)
Na_2O	4.08 (0.07)	4.24 (0.11)
K_2O	4.55 (0.07)	5.11 (0.11)
H_2O [b)]	0.16	0.04
Sum	99.67	100.11
M_{glass} (g/mol) [c)]	32.49	32.56

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.

[a] Total iron is given as FeO.

[b] The H_2O content was determined from the peak height of the IR absorption band at 3570 cm^{-1} using the calibration of Leschik et al. [35].

[c] Molar mass of anhydrous glass is calculated on single oxygen basis, and is needed for calculating the mole fractions of total H_2O [40].

the experiment at 1041 K, the starting water was a 1:1 mixture of $H_2^{18}O$ with normal hydrogen and $R=0.95$ and D_2O with normal oxygen and $D/(D+H)=0.999$, leading to $R\approx0.48$ and $D/(D+H)\approx0.50$.

Hydrothermal hydration experiments were carried out in rapid-quench externally heated pressure vessels at 100 MPa argon pressure. The capsule was stored in the water-cooled part of the vessel during heating. After reaching the target temperature the capsule was rapidly inserted into the hot part by rotating the vessel. To terminate the experiment, the sample was rapidly returned to the cold part. The experimental conditions are listed in Table 2. After cooling the samples were sectioned perpendicular to the polished surface. H_2O and D_2O 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^{-1} (H_2O) and 2650 cm^{-1} (D_2O) 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. $^{18}O/^{16}O$ 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 ^{18}O surface concentrations vary widely. Only the profile with the highest surface $^{18}O/^{16}O$ ratio has been used in data treatment.

3. Experimental results

Profiles of H_2O_t and R are shown in Fig. 1. The surface H_2O_t content is roughly in agreement with H_2O solubility data indicating about 4 wt.% H_2O can be dissolved in rhyolitic melts at 100 MPa in the investigated temperature range [35–42]. H_2O_t profiles clearly do not follow an error function, indicating strong dependence of H_2O diffusivity on H_2O_t content, as shown by numerous previous studies [25–32]. The ^{18}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 R values. This is expected because the length of the R profile is significant compared to that of the H_2O_t profile. Typically, the R

Table 2
Experimental conditions and fitting results

Exp #	T (K)	P (MPa)	Starting glass	C_{H_2Ot} initial (wt.%)	R fluid initial	D/(D+H) fluid initial	Time (s)	X_{H_2Ot} surface	C_{H_2Ot} surface (wt.%)	Best-fit [a)] a	D_0 based on H_2O_t fit	D_0 based on ^{18}O fit
1	1041	100	EDFS	0.04	≈0.48	≈0.50	2160	0.0756	4.33	34	1.89±0.02	1.95±0.05
2	1085	100	EDF	0.16	0.855	0.80	1830	0.0775	4.44	25	4.01±0.07	4.98±0.12
3	1136	100	EDFS	0.04	0.855	0.80	900	0.0750	4.29	18	10.5±0.3	11.8±0.2

Notes. 2σ uncertainties are shown for D^0 values obtained by fitting. Although fitting errors on D_0 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%.

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

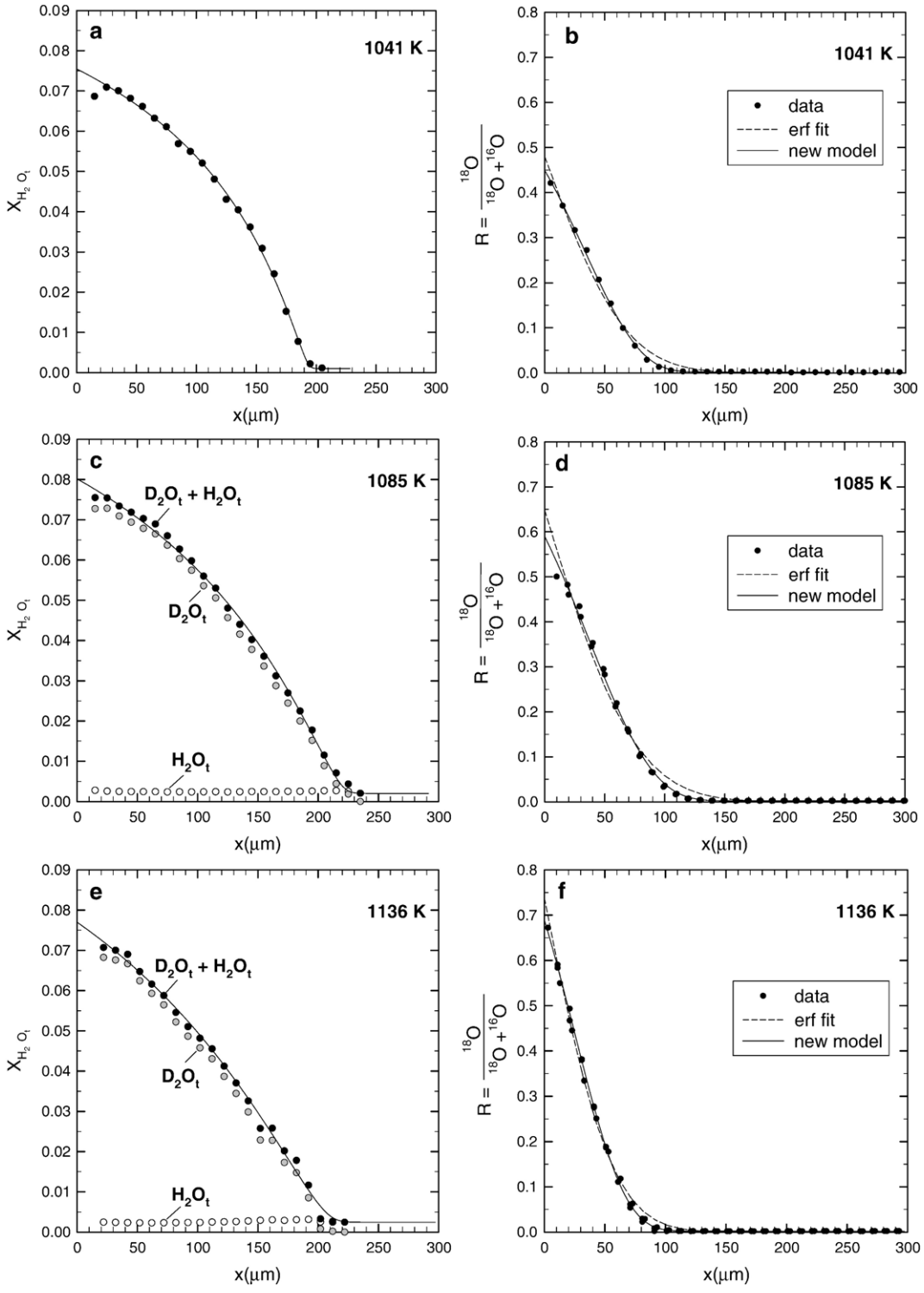

Fig. 1. a–e. H_2O_t and ^{18}O profiles generated by hydrothermal experiments. The H_2O_t profiles (sum of both isotopes) clearly differ from an error function profile, and no error function fit is tried. The ^{18}O profiles appear to be of error function shape, but the error function fit (dashed curves) shows small systematic deviation, especially at $x \approx 80$ to 100 μm (low H_2O_t content) where the data show more rapid decrease towards the background value of 0.002. The solid curves are fits of both H_2O_t and R profiles by assuming H_2O_m is the only diffusing species and $D_{H_2Om} = D_0 \exp(aX_{H_2Ot})$. The best-fit values of a and D_0 are listed in Table 2. No adjustments to the surface position of the H_2O_t profile were made to match D_{H_2Om} from the H_2O_t and R profiles.

profile extends to about one half of the H_2O_t profile (Fig. 1).

4. Fitting concentration profiles

The model to fit the concentration profiles of both H_2O_t and ^{18}O is based on Zhang et al. [1]. Assuming molecular H_2O is the diffusing species and there is local equilibrium between OH and molecular H_2O species, the diffusion equation for H_2O_t is:

$$\frac{\partial X_{H_2O_t}}{\partial t} = \frac{\partial}{\partial x}\left(D_{H_2O_m}\frac{\partial X_{H_2O_m}}{\partial x}\right), \quad (5)$$

where t is time, and x is the space coordinate along the direction of diffusion. The diffusion equation for R presuming H_2O_m is the diffusing species requires additional approximation. Assuming (i) $^{18}O/^{16}O$ ratio is the same for different oxygen species in the melt (e.g., there is isotopic equilibrium and the fractionation factor is very close to 1) and (ii) total oxygen concentration is roughly constant, the diffusion equation for ^{18}O is:

$$\frac{\partial R}{\partial t} \approx \frac{\partial}{\partial x}\left(D_{H_2O_m}\frac{\partial (R\cdot X_{H_2O_m})}{\partial x}\right) - R\frac{\partial}{\partial x}\left(D_{H_2O_m}\frac{\partial X_{H_2O_m}}{\partial x}\right). \quad (6)$$

The apparent $D_{^{18}O}$ based on the above equation depends on various conditions. A relatively simple approximation is $D_{^{18}O} \approx D_{H_2Om}\cdot X_{H_2Om}$ (i.e., Eq. (2)). Numerical simulations show that the accuracy of this approximation depends largely on H_2O_t. For example, $D_{^{18}O}$ exceeds $D_{H_2Om}\cdot X_{H_2Om}$ by less than 10% relative when $X_{H_2Ot}<0.01$, but by up to 40% when X_{H_2Ot} increases to 0.1.

In fitting experimental profiles, we applied Eqs. (5) and (6) directly without approximations. A nonlinear multivariable regression program was used to minimize the sum of residual squares [25,28]. For internal consistency and to enable comparison to our previous water diffusion study [28] we have used the equilibrium constant for water speciation in rhyolitic melts from Zhang [40]. D_{H_2Om} in the equations is assumed to increase exponentially with H_2O_t content [28–31]:

$$D_{H_2O_m} = D_0 \exp(aX_{H_2O_t}), \quad (7)$$

where a and D_0 are parameters to be obtained by fitting the profiles. Using parameter a obtained from the H_2O_t profile, the ^{18}O profile is fit separately to obtain D_0. If the model is correct and the data were perfect, D_0 obtained from the ^{18}O profile should be the same as that from the H_2O_t profile.

Best fits of the original data are shown as solid curves in Fig. 1. The fits to both H_2O_t profile and R profile are nearly perfect. The fit to the R profile (solid curves in Fig. 1b, d and f) captures the small deviation from the error function fit (dashed curves in Fig. 1b, d, and f). Further calculations using the theory (but not related to the specific experiments reported here) show that the R profile can deviate from an error function either by terminating more quickly, or with a long tail. A long tail could result from at least two scenarios: (i) when there is local isotopic equilibrium near the surface because of high H_2O content, but little isotopic exchange at low H_2O content; or (ii) when the initial H_2O content in the sample is greater than the surface content. Hence, deviation from an error function does not necessarily reflect multiple diffusion mechanisms.

The values of D_{H_2Om} derived from the H_2O_t profile differ from those derived from the ^{18}O profile by only 3% to 24% (last columns in Table 2). Such a small difference can be accounted for by measurement uncertainty, including those on the position of the interface, spatial resolution, concentrations (such as that due to calibration), etc. For example, the "measured" interface position may differ from the real position by up to 5 μm because of edge chipping for SIMS measurements of ^{18}O profiles, and by up to 20 μm for FTIR measurements of H_2O_t profiles because the edge may not be perfectly vertical and planar [25,28]. Furthermore, measurement spot size is finite, with the spatial resolution of 5–10 μm for SIMS and 30 μm for FTIR measurements. Considering these uncertainties, we

Table 3
Calculated diffusivities (in $\mu m^2/s$)

Exp #	T (K)	Surface X_{H_2Ot}	Surface X_{H_2Ot} [a)]	D_{H_2Om} at surface [b)]	D_{H_2Ot} at surface [b)]	$D_{^{18}O}$ at surface [b)]	$D_{^{18}O}$ based on erf fit
1	1041	0.0756	0.0295	24.7	14.4	0.73	0.63±0.07
2	1085	0.0775	0.0290	27.8	15.8	0.81	0.93±0.06
3	1136	0.0750	0.0260	45.5	24.4	1.18	1.06±0.04

Notes. The errors for the calculated diffusivities are estimated to be <30%.
[a] Calculated after Zhang et al. [49].
[b] Calculated using parameters given in Table 2.

adjusted H_2O_t and R profiles to see whether it is possible to use the same expression of D_{H_2Om} to fit both profiles. This turned out to be relatively easy to achieve. For example, if we adjust only the interface position of the H_2O_t profile, both H_2O_t and R profiles would be fit by exactly the same expression of D_{H_2Om} with adjustment of the interface position of the H_2O_t 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, ^{18}O diffusion profile can be directly calculated with no free parameters from D_{H_2Om} obtained from H_2O_t profile.

As shown in Table 3, the approximate $D_{^{18}O}$ values obtained by fitting an error function to the R profiles are in good agreement with those calculated from the approximate theoretical relation $D_{^{18}O} \approx D_{H_2Om} \cdot X_{H_2Om}$ using X_{H_2Om} at the surface. Furthermore, because $D_{^{18}O}$ is roughly proportional to X_{H_2Om} and because X_{H_2Om} decreases from the surface to the interior, the approximate values of $D_{^{18}O}$ 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_{H_2Ot} and D_{H_2Om} at 1 wt.% H_2O_t 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.% H_2O_t 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 H_2O_t 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% H_2O_t with only two samples having water contents exceeding 1 wt.%. The new

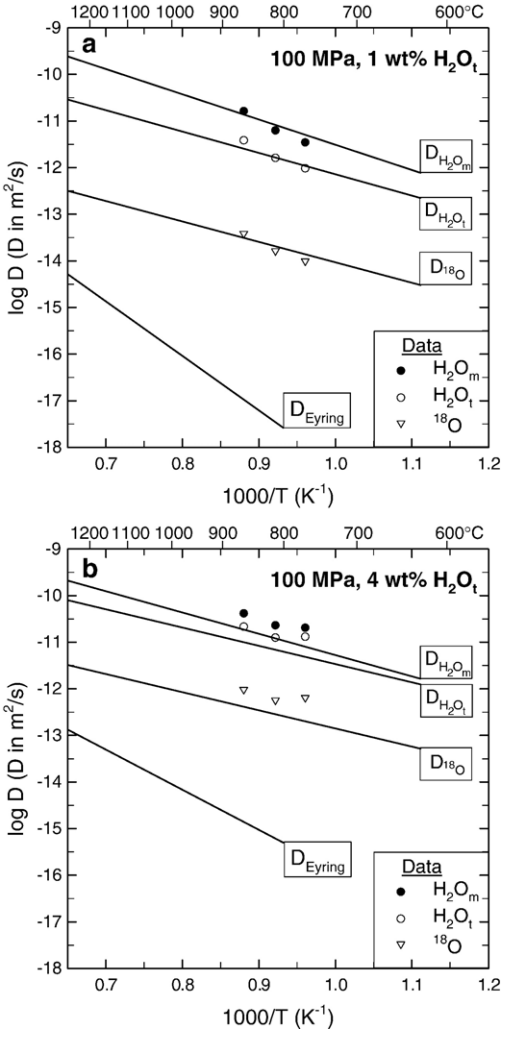

Fig. 2. a, b. Comparison of diffusivities of molecular H_2O, total H_2O, ^{18}O under hydrothermal conditions, and Eyring diffusivities at 1 and 4 wt.% H_2O_t and 100 MPa. Solid curves for D_{H_2Om}, D_{H_2Ot} is based on the model of Zhang and Behrens [28] and $D_{^{18}O}$ is calculated using $D_{^{18}O} \approx D_{H_2Om} \cdot X_{H_2Om}$.

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 ^{18}O and H_2O_t profiles are made for the same experiments, the discrepancy discussed above does not affect the conclusion that ^{18}O is transported by molecular H_2O in rhyolitic melt under hydrothermal conditions.

Fig. 2 shows that $D_{^{18}O}$ in hydrous rhyolitic melts is only 1–2 orders of magnitude less than D_{H_2Ot} but more than three orders of magnitude greater than the

diffusivity calculated from viscosity using the Eyring-relationship:

$$D = \frac{k \cdot T}{\lambda \cdot \eta} \quad (8)$$

where k is Boltzmann constant, λ is jumping distance, and η 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 λ 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 $D_{^{18}O}$ and Eyring diffusivity, the contribution of H_2O as carrier for oxygen is expected to dominate $D_{^{18}O}$ even at low H_2O content down to ppm level (note that Eyring diffusivity obtained from viscosity also depends on H_2O content).

6. Conclusions

The above results confirm that molecular H_2O is the carrier for oxygen transport in rhyolitic melt under hydrothermal conditions. We further infer that molecular H_2O diffusion controls oxygen transport in other silicate melts and glasses, and hydrous species (either molecular H_2O, or OH, or H_3O^+, 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 H_2O (i.e., due to the concentration gradient of H_2O_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 $D_{^{18}O} \approx D_{H_2Om} \cdot X_{H_2Om}$.

In the context of the above conclusions, ^{18}O "self" diffusivity can be calculated from H_2O diffusion data, and vice versa. Data on H_2O 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}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 H_2O and ^{18}O diffusion simultaneously in minerals such as feldspar or quartz to confirm the validity of this hypothesis for minerals.

Acknowledgements

This study was supported by German DFG and the US NSF (EAR-0228752; EAR-0537598). We thank the constructive and insightful comments of an anonymous reviewer.

References

[1] 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.
[2] S.C. Elphick, C.M Graham, The effect of hydrogen on oxygen diffusion in quartz: evidence for fast proton transients? Nature 335 (1988) 243–245.
[3] B.J. Giletti, M.P. Semet, R.A. Yund, Studies in diffusion—III. Oxygen in feldspars: an ion microprobe determination, Geochim. Cosmochim. Acta 42 (1978) 45–57.
[4] B.J. Giletti, R.A. Yund, Oxygen diffusion in quartz, J. Geophys. Res. 89 (1984) 4039–4046.
[5] B.J. Giletti, K.C. Hess, Oxygen diffusion in magnetite, Earth Planet. Sci. Lett. 89 (1988) 115–122.
[6] J.R. Farver, Oxygen self-diffusion in diopside with application to cooling rate determinations, Earth Planet. Sci. Lett. 92 (1989) 386–396.
[7] S.M. Fortier, B.J. Giletti, Volume self-diffusion of oxygen in biotite, muscovite, and phlogopite micas, Geochim. Cosmochim. Acta 55 (1991) 1319–1330.
[8] E.B. Watson, D.J. Cherniak, Oxygen diffusion in zircon, Earth Planet. Sci. Lett. 148 (1997) 527–544.
[9] J.R. Farver, R.A. Yund, The effect of hydrogen, oxygen, and water fugacity on oxygen diffusion in alkali feldspar, Geochim. Cosmochim. Acta 54 (1990) 2953–2964.
[10] D. Griggs, Hydrolytic weakening of quartz and other silicates, Geophys. J. R. Astron. Soc. 14 (1967) 19–31.
[11] A.K. Kronenberg, S.H. Kirby, R.D. Aines, G.R. Rossman, Solubility and diffusional uptake of hydrogen in quartz at high water pressures: implications for hydrolytic weakening, J. Geophys. Res. 91 (1986) 12,723–12,741.
[12] J.R. Goldsmith, The role of hydrogen in promoting Al–Si interdiffusion in albite ($NaAlSi_3O_8$) at high pressures, Earth Planet. Sci. Lett. 80 (1986) 135–138.
[13] R.A. Yund, Interdiffusion of NaSi–CaAl in peristerite, Phys. Chem. Miner. 13 (1986) 11–16.

[14] G. Baschek, W. Johannes, The estimation of NaSi–CaAl interdiffusion rates in peristerites by homogenization experiments, Eur. J. Mineral. 7 (1995) 295–307.
[15] A.H. Eward, The effect of pressure on oxygen isotope exchange in silicates, Chem. Geol. 49 (1985) 179–185.
[16] B.E. Hobbs, Point defect chemistry of minerals under hydrothermal environment, J. Geophys. Res. 89 (1984) 4026–4038.
[17] D.R. Cole, S. Chakraborty, Rates and mechanisms of isotopic exchange, Rev. Mineral. Geochem. 43 (2001) 83–223.
[18] R. Pfeffer, M. Ohring, Network oxygen exchange during water diffusion in SiO_2, J. Appl. Phys. 52 (1981) 777–784.
[19] C.M. Graham, S.C. Elphick, A re-examination of the role of hydrogen in Al–Si interdiffusion in feldspars, Contrib. Mineral. Petrol. 104 (1990) 481–491.
[20] C.M. Graham, S.C. Elphick, Hydrogen in feldspars and related silicates, in: I. Parsons (Ed.), Feldspars and their Reactions, NATO ASI Series, Kluwer, 1994.
[21] K. Wright, R. Freer, C.R.A. Catlow, Water-related defects and oxygen diffusion in albite: a computer simulation study, Contrib. Mineral. Petrol. 125 (1996) 161–166.
[22] J.D.C. McConnell, The role of water in oxygen isotope exchange in quartz, Earth Planet. Sci. Lett. 136 (1995) 97–107.
[23] R.H. Doremus, The diffusion of water in fused silica, in: J.W. Mitchell, R.C. Devries, R.W. Roberts, P. Cannon (Eds.), Reactivity of Solids, Wiley, 1969.
[24] R.H. Doremus, Glass Science, Wiley and Sons, New York, 1973 379 pp.
[25] Y. Zhang, E.M. Stolper, G.J. Wasserburg, Diffusion of water in rhyolitic glasses, Geochim. Cosmochim. Acta 55 (1991) 441–456.
[26] Y. Zhang, E.M. Stolper, Water diffusion in basaltic melts, Nature 351 (1991) 306–309.
[27] M. Nowak, H. Behrens, An experimental investigation on diffusion of water in haplogranitic melts, Contrib. Mineral. Petrol. 126 (1997) 365–376.
[28] Y. Zhang, H. Behrens, H_2O diffusion in rhyolitic melts and glasses, Chem. Geol. 169 (2000) 243–262.
[29] C. Freda, D.R. Baker, C. Romano, P. Scarlato, Water diffusion in natural potassic melts, Geol. Soc. Spec. Publ. 213 (2003) 53–62.
[30] Y. Liu, Y. Zhang, H. Behrens, H_2O diffusion in dacitic melt, Chem. Geol. 209 (2004) 327–340.
[31] H. Behrens, Y. Zhang, Z. Xu, H_2O diffusion in dacitic and andesitic melts, Geochim. Cosmochim. Acta 68 (2004) 5139–5150.
[32] H. Behrens, M. Nowak, The mechanisms of water diffusion in polymerized melts, Contrib. Mineral. Petrol. 126 (1997) 377–385.
[33] R.H. Doremus, Diffusion of water in rhyolite glass: diffusion-reaction model, J. Non-Cryst. Solids 261 (2000) 101–107.
[34] J. Crank, The Mathematics of Diffusion, 2nd editionClarendon press, Oxford, 1975 414 pp.
[35] M. Leschik, G. Heide, G.H. Frischat, H. Behrens, M. Wiedenbeck, N. Wagner, K. Heide, H. Geiβler, U. Reinholz, Determination of H_2O and D_2O contents in rhyolitic glasses using KFT, NRA, EGA, IR spectroscopy, and SIMS, Phys. Chem. Glasses 45 (2004) 238–251.
[36] F. Holtz, H. Behrens, D.B. Dingwell, W. Johannes, H_2O solubility in haplogranitic melts: compositional, pressure, and temperature dependence, Am. Mineral. 80 (1995) 94–108.
[37] P. Papale, Modeling of the solubility of a one-component H_2O or CO_2 fluid in silicate liquids, Contrib. Mineral. Petrol. 126 (1997) 237–251.
[38] G. Moore, T. Vennemann, I.S.E. Carmichael, An empirical model for the solubility of H_2O in magmas to 3 kilobars, Am. Mineral. 83 (1998) 36–42.
[39] S. Yamashita, Experimental study of the effect of temperature on water solubility in natural rhyolite melt to 100 MPa, J. Petrol. 40 (1999) 1497–1507.
[40] Y. Zhang, H_2O in rhyolitic glasses and melts: measurement, speciation, solubility, and diffusion, Rev. Geophys. 37 (1999) 493–516.
[41] N. Tamic, H. Behrens, F. Holtz, The solubility of H_2O and CO_2 in rhyolitic melts in equilibrium with a mixed CO_2–H_2O fluid phase, Chem. Geol. 174 (2001) 333–347.
[42] Y. Liu, Y. Zhang, H. Behrens, Solubility of H_2O in rhyolitic melts at low pressures, J. Volcanol. Geotherm. Res. 143 (2005) 219–235.
[43] F. Schulze, H. Behrens, F. Holtz, J. Roux, W. Johannes, The influence of water on the viscosity of a haplogranitic melt, Am. Mineral. 81 (1996) 1155–1165.
[44] Y. Zhang, Z. Xu, Y. Liu, Viscosity of hydrous rhyolitic melts inferred from kinetic experiments, and a new viscosity model, Am. Mineral. 88 (2003) 1741–1752.
[45] S. Charkraborty, Diffusion in silicate melts, Rev. Miner. 32 (1995) 411–503.
[46] J. Koepke, H. Behrens, Trace element diffusion in andesitic melts — an application of synchroton X-ray fluorexcence analysis, Geochim. Cosmochim. Acta 65 (2001) 1481–1498.
[47] B.T. Poe, P.F. McMillan, D.C. Rubie, S. Chakraborty, J. Yarger, J. Diefenbacher, Silicon and oxygen self-diffusivities in silicate liquids measured to 15 gigapascals and 2800 Kelvin, Science 276 (1997) 1245–1248.
[48] J.E. Reid, B.T. Poe, D.C. Rubie, N. Zotov, M. Wiedenbeck, The self-diffusion of silicon and oxygen in diopside ($CaMgSi_2O_6$) liquid up to 15 GPa, Chem. Geol. 174 (2001) 77–86.
[49] Y. Zhang, R. Belcher, P.D. Ihinger, L. Wang, Z. Xu, S. Newman, New calibration of infrared measurement of dissolved water in rhyolitic glasses, Geochim. Cosmochim. Acta 61 (1997) 3089–3100.