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Water diffusivity in rhyolitic glasses as determined by in situ IR spectroscopy

Abstract The dehydration rate of hydrous rhyolitic glasses at 475–875 °C was measured by in situ infrared (IR) spectroscopy in order to determine the diffusion coefficient of water in rhyolitic glasses. The IR spectra of glass thin sections were obtained at 90-s intervals during 90 min at high temperatures, and the change in absorbance at 3550 cm^{-1} corresponding to total water was monitored. The diffusion coefficients obtained from dehydration rates of the rhyolitic glasses are considered to be averaged value over the water-concentration profile in the sample. The averaged apparent diffusion coefficients increase with the initial total water content from 0.20 μm^2 s^{-1} for 0.7 wt% to 0.37 μm^2 s^{-1} for 2.8 wt% at 700 °C. The apparent activation energy for the diffusion of total water decreases with increasing initial water content from 112 ± 6 kJ mol^{-1} for 0.7 wt% to 60 ± 17 kJ mol^{-1} for 4.1 wt%. Assuming a linear relation between the diffusion coefficient of total water and the total water content, the diffusion coefficients at each initial total water content were also determined. The diffusion coefficients of total water at the water contents of 0.7 and 1.9 wt% and at 0.1 MPa were best fitted by $\ln D = [(12.9 \pm 0.8) - (111\,500 \pm 6400)/RT]$ and $\ln D = [(10.6 \pm 0.4) - (86\,800 \pm 2800)/RT]$, respectively, and are in agreement with previous data (D in μm^2 s^{-1}, T in K). The present in situ IR dehydration experiment is a rapid and effective method for the determination of water diffusivity at high temperatures.

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Introduction

Knowledge of water diffusion in silicate melts and glasses is important for understanding volcanic processes. One controlling factor of volcanic eruption is nucleation and growth of bubbles in ascending magma, and the rates of the bubble nucleation and growth in magma are directly related to water diffusion rate (e.g. Sparks et al. 1994). Thus, we need to determine the diffusion coefficient of water in silicate melts and glasses in order to model the bubble nucleation and growth quantitatively.

The diffusivity and the diffusion mechanism of water species in silicate melts and glasses have been investigated by many authors (e.g. Delaney and Karsten 1981; Karsten et al. 1982; Lapham et al. 1984; Zhang et al. 1991; Jambon et al. 1992; Watson 1994; Behrens and Nowak 1997; Nowak and Behrens 1997; Zhang 1999; Zhang and Behrens 2000). The diffusion coefficient has often been obtained on the basis of water-concentration profile in quenched silicate glasses after dehydration and hydration experiments and coupling experiments, using the Boltzmann–Matano method (Nowak and Behrens 1997) or the fitting method (Zhang et al. 1991; Zhang and Behrens 2000). The dehydration rate of glass slab was also used to determine the apparent outward diffusivity of water (Jambon et al. 1992).

We report here a new method for determining the diffusion coefficient of water. In this method, glass thin sections are heated on a heating stage under an FT–IR microscope and the dehydration rates of the thin sections are monitored by in situ IR spectroscopy. Based on monitored dehydration rates, the diffusion coefficients of water are estimated. This method has the following advantages over the previous quench technique; (1) it can analyze the dehydration directly at high temperature; and (2) it has the potential to obtain kinetic data at

Table 1 Chemical composition of natural obsidian (Nat.)

	Nat.
SiO_2 (wt%)	77.3
Al_2O_3	13.0
CaO	0.5
FeO^a	0.5
MgO	0.1
TiO_2	0.1
MnO	0.0
Na_2O	3.8
K_2O	4.7
Total[b]	100
Density (gl^{-1})	2320
Water content (wt%)[c]	0.74

[a] Total iron as FeO
[b] Recalculated to 100%
[c] Total water content based on Karl Fisher titration described in Okumura et al. (2003)

high temperature. On the other hand, the disadvantage of our method is that the dependence on water content cannot be observed directly, because this method analyzes water-concentration profile in the glass slab as an average. In this study, diffusion coefficients of total water at 475–850 °C and at 0.1 MPa are obtained based on dehydration rates measured by in situ IR spectroscopy, and then the obtained diffusivities are compared with the results of previous studies.

Experimental

Starting materials

Rhyolitic obsidian from Higashimotiya, Wadatouge (described by Okumura et al. 2003), was used as the starting material. The chemical composition of the obsidian is listed in Table 1. Its original water content determined by Karl–Fischer titration is 0.74 wt%. The obsidian was cut into small slabs (about $1.5 \times 1.5 \times 4.0$ mm) and sealed in Pt capsules (3 mm ϕ) together with known amounts of deionized water. The capsules with different amounts of water were prepared, then held at 200 MPa and 900 °C for 48 h using an internally heated pressure vessel (IHPV). Based on the water-solubility curve of Moore et al. (1998), the obsidians were estimated to be not saturated with water under our

experimental condition. The water diffusion distance, calculated as $(Dt)^{1/2}$ where D is the total water diffusivity from Zhang and Behrens (2000) and t is the experimental duration (48 h), is about 1 mm. This distance is large enough to reach the centre of the slabs (about $1.5 \times 1.5 \times 4.0$ mm), which can result in uniform distribution of water. After quenching, the capsules were carefully opened and examined under an optical microscope. The run products had almost no crystals and bubbles.

The hydrated obsidians were doubly polished into thin sections to determine water contents. The thin sections were analyzed by FT–IR microspectroscopy (Jasco IRT-30 + FTIR620 Plus) with MCT detector, ceramic IR source and KBr beam splitter. The aperture size of the IR measurement was set to 200×200 μm. The peak intensities (i.e. absorbance) of 5200 (H_2O) and 4500 (OH) cm^{-1} bands after background correction with straight lines and the molar absorptivities of Withers and Behrens (1999) (1.66 and 1.41 l $mol^{-1}cm^{-1}$ for the 5200 and 4500 cm^{-1} bands, respectively) were used to determine the water contents. Their thickness was measured by Laser Scanning Confocal Microscope (KEYENCE, Color Laser 3D Profile Microscope VK-8500 and VK-8510). The IR data and the water contents are listed in Table 2. We analyzed several different points in a thin section to check homogeneous distribution of water, which resulted in a difference of less than 0.2 wt%. The averaged total water contents, 1.9, 2.8 and 4.1 wt%, corresponded to the Run8, Run7 and Run9 samples in Table 2, respectively.

In situ dehydration experiments by IR spectroscopy

In situ IR measurements of water dehydration at 475 to 850 °C and at 0.1 MPa were made using an FT–IR microscope (Jasco MFT-2000; MCT detector, ceramic IR source and KBr beam splitter) with a Linkam TH-1500MH heating stage. Doubly polished thin sections of the natural and hydrated obsidians (Nat., Run7, Run8 and Run9 samples) were used as starting materials. The square thin sections were typically 1.5×1.5 mm in size. The thickness of these thin sections was measured to be 49 to 77 μm by laser scanning confocal microscope.

Before dehydration experiments, the temperature of the heating stage was elevated at a rate of 50 °C min^{-1} and held at a desired temperature (475–850 °C). The error in temperature at the heating stage is estimated to be less than ±1 °C based on the melting of Au (Suzuki and Nakashima 1999). A Pt foil was set on the heating stage at desired temperature, and a reflectance spectrum of the Pt foil was obtained by FT–IR microspectroscopy with an aperture size of 200×200 μm, which was used as a background spectrum for sample measurement. After the background measurement, a sample thin section was placed on the Pt foil in the heating stage. The fluctuation of temperature by setting of the sample thin section was about ±1 °C. Sample measurements were carried out using transmission–reflection (T–R) technique in which the IR light passing through sample being back-reflected by the Pt foil was

Table 2 The results of IR ananlyses for hydrated obsidians

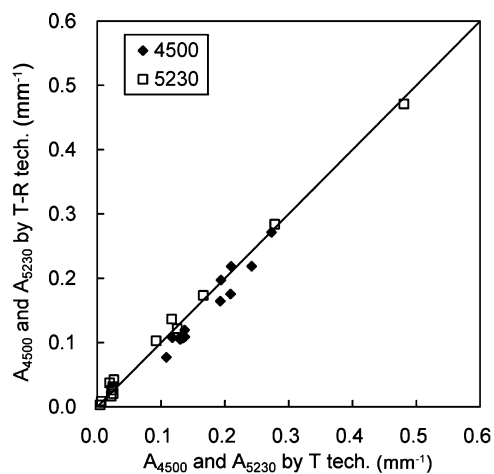| Sample	Absorbance 4500 cm^{-1}	Absorbance 5200 cm^{-1}	Thickness (μm)	OH (wt%)	H_2O (wt%)	Total H_2O (wt%)
Run7-1-02	0.013	0.015	49	1.5	1.4	2.9
Run7-1-03	0.012	0.015	49	1.4	1.4	2.8
Run7-1-04	0.012	0.014	49	1.4	1.4	2.7
Run8-1-01	0.018	0.012	76	1.3	0.8	2.1
Run8-1-02	0.018	0.012	77	1.3	0.7	2.1
Run8-1-03	0.018	0.012	78	1.3	0.7	2.0
Run8-2-01	0.015	0.008	69	1.3	0.6	1.9
Run8-2-02	0.014	0.008	70	1.3	0.6	1.9
Run9-2-01	0.022	0.039	75	1.6	2.4	4.0
Run9-2-02	0.023	0.041	77	1.6	2.5	4.1
Run9-2-03	0.023	0.041	78	1.6	2.5	4.1
Run9-3-01	0.020	0.036	68	1.6	2.4	4.1
Run9-3-02	0.020	0.036	69	1.6	2.4	4.1

collected. A problem for this technique is that some part of the light may not be passing through the sample, as described by Nowak and Behrens (1995). In order to investigate this effect, the absorbances (peak heights) at 4500 and 5230 cm^{-1} for hydrous rhyolitic glasses obtained by transmission–reflection (T–R) technique were compared with those obtained by transmission (T) technique (Fig. 1). Since the comparison shows good agreement, we assumed that the light without passing through the sample was not influential in the IR spectra collected by T–R technique. It should be noted that the IR absorbance by T–R technique corresponds to twice the thickness of the sample.

Sample measurement was started just after the sample setting. Fifty scans were accumulated to obtain an IR spectrum with a spectral resolution of 4 cm^{-1} in the 700–7000 cm^{-1} region. The sample measurement was automatically repeated by a software program (Jasco, interval measurement program) at 90-s intervals during 90 min, yielding 60 successive spectra for an experiment. Since 50 scans took about 70 s, the IR spectrum obtained represents the average for the 70 s. It is assumed that the IR spectrum was obtained 35 s after starting an IR analysis.
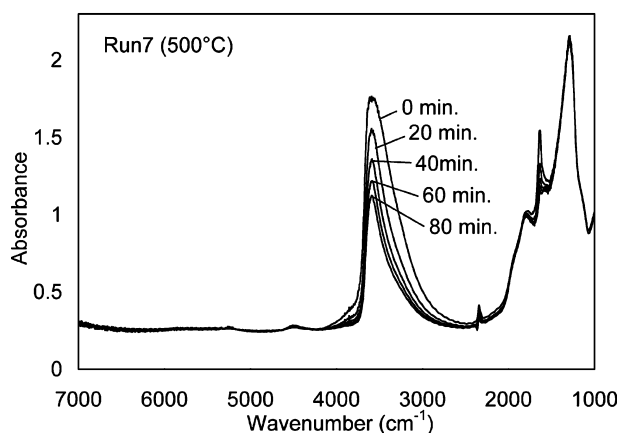
Results

We carried out 20 runs for four samples with 0.7–4.1 wt% water. Because the melting of samples and bubble formation occurred at high temperature, experiments at high temperatures cannot be carried out successfully. The experiment of the Run9 sample with high water content (4.1 wt%) could only be performed at < 575 °C.

Typical successive spectra obtained by in situ IR measurement are shown in Fig. 2. The absorption bands of water species are found at 5200, 4500, 3550 and 1630 cm^{-1}, corresponding to H_2O, OH, OH + H_2O and H_2O, respectively (e.g. Stolper 1982). The intensities of these absorption bands (absorbances) were measured to obtain dehydration rate of rhyolitic glass except for the 5200 cm^{-1} band, because the absorbance at 5200 cm^{-1}

was too weak to be measured during the heating experiment.

The integral absorbance of the 3550 cm^{-1} band was measured as a peak area after baseline correction with a straight line. The maximum integral absorbance error of the 3550 cm^{-1} band is estimated to be 1.5, because the peak area was determined by integrating the peak height with the error of 0.001 from 2500 to 4000 cm^{-1}. Typical temporal changes in absorbance at 3550 cm^{-1} are shown in Fig. 3. The absorbance decreased with time and the decrease rate is greater at higher temperatures. Initial values of the absorbance are not the same at different temperature runs for a sample with the same initial water content. This is because the decrease rate in absorbance is different at

Fig. 2 Successive infrared (IR) spectra obtained by in situ heating experiments for a synthetic water-containing obsidian of 2.8 wt% total water (*Run7 sample*) at 500 °C. The spectra after 0, 20, 40, 60 and 80 min are shown
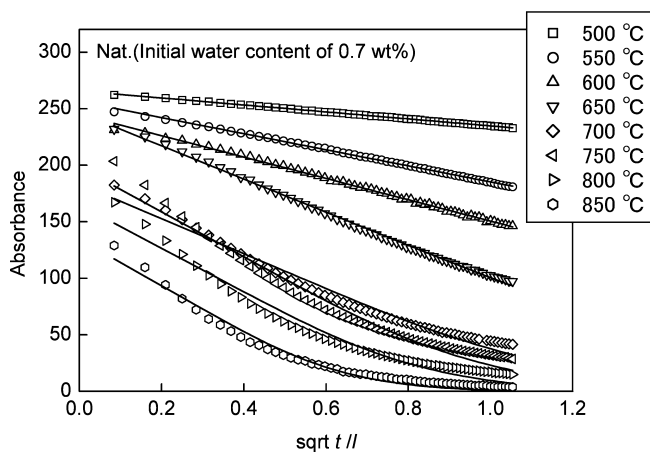

Fig. 1 Comparisons of the absorbances at 4500 and 5230 cm^{-1} obtained by transmission–reflection technique (*T–R tech.*) and those by transmission technique (*T tech.*). The absorbances are normalized by sample thickness to mm^{-1} (A_{4500} and A_{5230}). The thickness for the T–R technique was assumed to be twice the measured sample thickness

Fig. 3 Typical IR results of in situ dehydration experiments. Temporal changes in the integral absorbance at 3550 cm^{-1} of the natural obsidian of 0.7 wt% total water (*Nat.* samples) are shown as a function of square root of time normalized by the sample thickness. The dehydration rate (Abs vs. $\sqrt{t}/l$) is used to determine the diffusion coefficient according to Eq. (1). The *solid lines* represent the results of fitting by Eq. (1)

different temperatures and IR data represent the average for 70 s. This difference is, however, not influential in the later discussion in this study dealing with dehydration rates.

The absorbances of the 4500 and 1630 cm^{-1} bands were measured as peak heights after baseline corrections with straight lines. The absorbance errors of the 4500 and 1630 cm^{-1} bands are within 0.001, which is estimated from the noise level of the background spectrum. The uncertainty of the absorbance at 1630 cm^{-1} is also caused by the method of baseline correction due to a complicated background around 1630 cm^{-1}. However, this uncertainty does not influence the relative change in the absorbance as long as the background around 1630 cm^{-1} does not change. Typical temporal changes in absorbance at 4500 (OH) and 1630 (H_2O) cm^{-1} for the Run8 sample with 1.9 wt% total water at 500 °C are shown in Fig 4. Both the absorbances decreased with time.

Discussion

Water speciation during dehydration experiments

The water speciation is important to understand the diffusion mechanism, because water is present in silicate melts and glasses as at least two species (OH and H_2O) which have different diffusivity, and because the water species react with each other (Zhang et al. 1991; Zhang and Behrens 2000). For water in silicate glasses, OH diffusion is very slow and H_2O is the main diffusing species (Zhang et al. 1991). Behrens and Nowak (1997) inferred that water transport in silicate glasses and melts was mainly due to the diffusion of H_2O with the reaction between H_2O and OH pair (adjacent two OH groups).
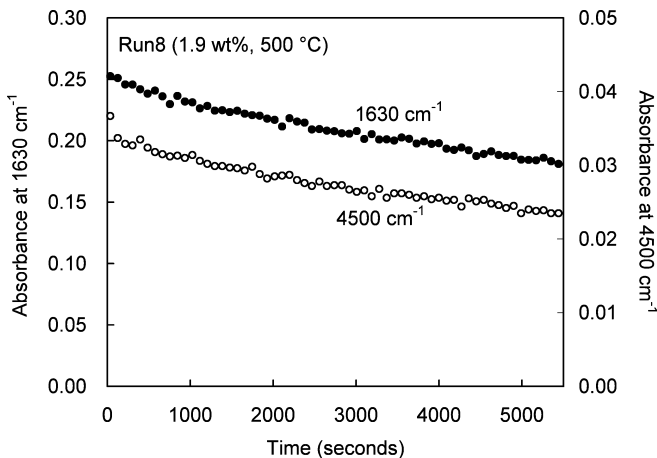
Fig. 4 Temporal changes in peak height at 4500 (OH) and 1630 (H_2O) cm^{-1} for a synthetic water containing obsidian of 1.9 wt% total water (*Run8* sample) at 500 °C are shown as a function of time

Our experimental result (Fig. 4) shows that the concentrations of both OH and H_2O decreased with dehydration. Because OH and H_2O have different diffusivity, this result clearly implies that water species react with each other during dehydration and the OH concentration decreased due to its conversion into H_2O. When the reaction between water species is assumed to be H_2O + O $\leftrightarrow$ 2OH, where O is an anhydrous oxygen in silicate structure, the equilibrium constant can be calculated as $K = [OH]^2/[H_2O][O]$, where the brackets represent the mole fraction (e.g. Zhang 1999). The squared absorbance at 4500 cm^{-1} (OH) divided by the absorbance at 1630 cm^{-1} (H_2O) for experimental data in Fig. 4 is roughly constant in the range of 0.024 ± 0.003. This might indicate that the reaction rate under this experimental condition is considered to be fast enough to keep a quasi-equilibrium, because [O] is nearly constant. However, it should be noted that the OH^2/H_2O ratio might increase at lower water contents, because the reaction rate becomes slow.

Overall processes of diffusion and reaction of water species are too complicated to be modelled quantitatively. Therefore, we determine apparent diffusion coefficients of total water in the rhyolitic glasses in the following section, without any assumption for the reaction of water species. The details in overall process of diffusion and reaction of water species will be published elsewhere.

Determination of apparent diffusion coefficient of total water

Apparent diffusion coefficients of total water in hydrous rhyolitic glasses are determined using temporal changes of the absorbance at 3550 cm^{-1} (Fig. 3). Since the 3550-cm^{-1} band corresponds to the total water (OH and H_2O) (e.g. Okumura et al. 2003), the diffusion coefficients obtained in this study should be considered as an "apparent" value for the total water in rhyolitic glasses.

Assuming that the thin sections (about 1.5 × 1.5 mm in size) used in this study are considered as plane sheets and the water concentration at their surfaces remains zero, we can determine the apparent diffusion coefficient using the diffusion-out rate from a plane sheet (Crank 1975, Eqs. 4–20, p. 48):

$$\frac{M_t}{M} = 4\sqrt{\frac{Dt}{\pi l^2}} \cdot \left[1 + 2\sqrt{\pi} \sum_{n=1}^{\infty} (-1)^n ierfc \frac{nl}{2\sqrt{Dt}} \right] , \qquad (1)$$

where M is the initial amount of water in a sample; M_t, the amount of water diffused out from the sample; D, the diffusion coefficient; t, the time; and l, the sample thickness. This equation works for concentration-independent D. The left term in Eq. (1) corresponds to $(Abs_0 - Abs)/Abs_0$, where Abs_0 is the absorbance at initial condition and Abs is the absorbance after t in a series of experiments. Initial absorbance obtained by

in situ IR measurement is not equal to Abs_0, because the sample starts to be dehydrated just after the sample was set at the heating stage. Since the molar absorptivity is dependent on temperature (Keppler and Bagdassarov 1993; Withers et al. 1999), the absorbance measured at room temperature is not also equal to Abs_0. Thus, the initial absorbance Abs_0 was considered to be an unknown parameter as well as the diffusion coefficient D. The values of Abs_0 and D were determined by fitting IR datasets by the Eq. (1) (Fig. 3). The diffusion coefficients obtained are listed in Table 3. Most of fitting errors listed in Table 3 are less than 1% relative and maximally 5% relative. However, these errors are considered to be only parts of the real errors, because there are other sources for experimental and model uncertainties which are difficult to evaluate quantitatively. For example, the D value at 500 °C for Nat. sample (0.7 wt% initial water) was determined in the range of 10% relative of initial absorbance, while the determination of that at 850 °C used the experimental data which covered almost whole range, i.e. ca. 0–100% relative to initial absorbance (Fig. 3).

Another problem is the fact that a diffusion model assuming the concentration-independent D was used for the determination of the diffusion coefficients. Some previous studies (Delaney and Karsten 1981; Nowak and Behrens 1997; Zhang and Behrens 2000) reported the dependence of the diffusion coefficient on the water content. The results of this study also show that the diffusion coefficients seem to increase with initial water contents (Table 3). However, Eq. (1) can be held when M_t/M is between 1 and 0.5 even if the diffusion coefficient depends on the concentration (Wang et al. 1996). Hence, for consistency and better precision, we also used only the data of $M_t/M > 0.5$ for the determination of the diffusion coefficients.

In order to determine the D values using the data of $M_t/M > 0.5$, we have to choose a time range in which M_t/M was between 1 and 0.5. However, the time range cannot be directly obtained from our experimental dataset, because the initial absorbance Abs_0 is unknown. Thus, we repeated following procedure in order to determine the time range in which $M_t/M > 0.5$ was satisfied. First, all the experimental data were fitted by Eq. (1), and the initial absorbance Abs_0 was determined from the fitting result. Then, the time range satisfying the relation of $M_t/M > 0.5$ was estimated using the Abs_0 value. Afterwards, fitting by Eq. (1) was carried out for the experimental data satisfying the relation of $M_t/M > 0.5$. This was repeated until the relation of $M_t/M > 0.5$ could be satisfied. Typical experimental data used in determining the D values and fitting lines are shown in Fig. 5, and the D values obtained are listed in Table 3 and plotted as a function of temperature in Fig. 6. The diffusion coefficients obtained seem to increase with initial water contents (Fig. 6).

The plotted data as a function of temperature can be fitted by the Arrhenius equation:

$$D = D_0 \exp(-E_a/RT) , \qquad (2)$$

where E_a denotes the activation energy; R, the gas constant; and T, the temperature. The values of $\ln D_0$ and E_a for each sample obtained from the linear regression in the Arrhenius plot are listed in Table 4. The activation energy increases from 60 ± 17 to 112 ± 6 kJ mol^{-1} with decreasing initial water contents from 4.1 to 0.7 wt% (Fig. 7).

Table 3 Experimental data for determination of diffusion coefficient

| Run no.	$C_{initial}$[a] (wt%)	C_{after}[b] (wt%)	Thickness (μm)	T (°C)	All the data			$M_t/M > 0.5$		
					R^{2c}	D^d (μm² s⁻¹)	Error	R^{2c}	D^e (μm² s⁻¹)	Error
Nat.50	0.7	0.6	70	500	0.999	0.0026	0.0001	0.999	0.0026	0.0001
Nat.55		0.5	70	550	0.999	0.0151	0.0001	0.999	0.0151	0.0001
Nat.60		0.5	70	600	0.998	0.0292	0.0003	0.998	0.0292	0.0003
Nat.65		0.3	70	650	0.997	0.0695	0.0006	0.999	0.0745	0.0006
Nat.70		0.2	70	700	0.977	0.1392	0.0034	0.999	0.1988	0.0025
Nat.75		0.1	70	750	0.970	0.1965	0.0056	0.999	0.3121	0.0044
Nat.80		<0.1	70	800	0.967	0.2669	0.0085	0.999	0.4270	0.0088
Nat.85		<0.1	70	850	0.977	0.4585	0.0144	0.997	0.6750	0.0337
Run7-5	2.8	1.2	49	500	0.992	0.0347	0.0005	0.999	0.0401	0.0003
Run7-6		0.4	49	600	0.958	0.0894	0.0030	0.999	0.1642	0.0027
Run7-7		0.2	49	700	0.928	0.2022	0.0107	0.999	0.3691	0.0546
Run8-50	1.9	1.4	77	500	0.998	0.0194	0.0002	0.998	0.0194	0.0002
Run8-55		1.0	69	550	1.000	0.0514	0.0001	0.999	0.0413	0.0001
Run8-60		0.8	77	600	0.999	0.0779	0.0005	0.998	0.0799	0.0007
Run8-65		0.4	69	650	0.985	0.1623	0.0031	0.999	0.1738	0.0024
Run8-675		0.4	69	675	0.971	0.1662	0.0045	0.999	0.2314	0.0039
Run9-475	4.1	2.4	75	475	0.999	0.0404	0.0003	0.999	0.0404	0.0003
Run9-500		2.4	75	500	0.998	0.0349	0.0003	0.998	0.0349	0.0003
Run9-525		2.0	75	525	0.998	0.0580	0.0005	0.998	0.0593	0.0005
Run9-575		1.4	75	575	0.996	0.0997	0.0010	0.999	0.1114	0.0011

[a] Water contents of experimental starting materials
[b] Water contents after dehydration experiments estimated from absorbance at 3550 cm^{-1}
[c] Correlation coefficient of the fitting analysis in Figs. 3 and 5
[d] Averaged apparent diffusion coefficient of total water determined using Eq. (1) and all the experimental data
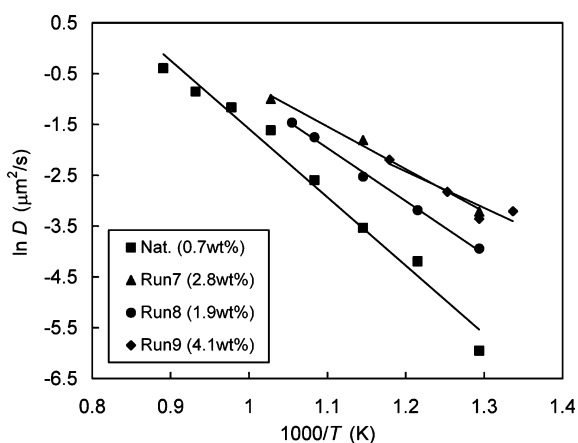[e] Averaged apparent diffusion coefficient of total water determined using Eq. (1) and the data of $M_t/M_0 > 0.5$
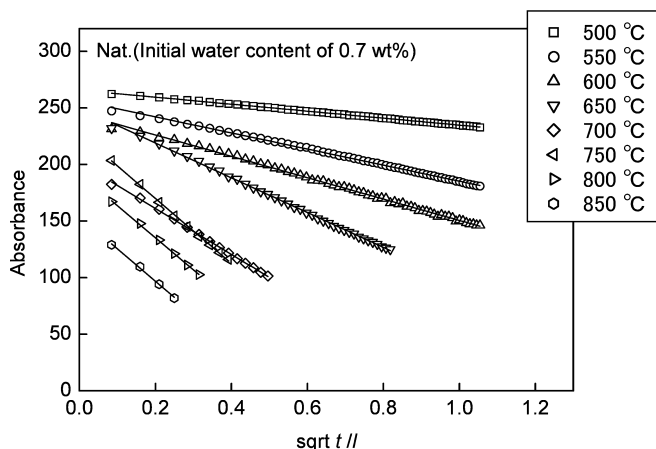
Fig. 5 Typical experimental data satisfying the relation of $(Abs_0 - Abs)/Abs_0 > 0.5$ are shown for *Nat.* samples. The dehydration rate (Abs vs. $\sqrt{t}/l$) is used to determine the diffusion coefficient according to Eq. (1). The *solid lines* represent the results of fitting by Eq. (1)

Table 4 ln D_0 and activation energy E_a obtained from the linear regressions in the Arrhenius plot (Fig. 6)

Sample	$c_{initial}$ (wt%)	ln D_0 ($\mu m^2\ s^{-1}$)	E_a (kJ mol^{-1})
Nat.	0.7	11.8 ± 0.8	112 ± 6
Run7	2.8	7.7 ± 0.9	70 ± 6
Run8	1.9	9.5 ± 0.4	87 ± 3
Run9	4.1	6.0 ± 2	60 ± 17

content is supposed, i.e. $D = D_0 C/C_0$, where D is the diffusion coefficient; D_0 the diffusion coefficient at the initial water content; C the water content; and C_0 the initial water content, it can be shown that averaged diffusion coefficient D_{out} (the value obtained in this study) is related to D_0 by $D_{out} = 0.347\ D_0$ at less than 2 wt% (Zhang et al. 1991; Wang et al. 1996; Zhang 1999).

We applied the above linear relation to our results of Nat. and Run8 samples with initial water contents of < 2 wt%. The obtained apparent diffusion coefficients of water are now plotted as a function of temperature in Fig. 8 together with the results of Zhang and Behrens (2000). The linear regressions for our data give ln $D = [(12.9 \pm 0.8) - (111500 \pm 6400)/RT]$ at 0.7 wt% and ln $D = [(10.6 \pm 0.4) - (86800 \pm 2800)/RT]$ at 1.9 wt%, where D is the apparent diffusivity of total water in $\mu m^2\ s^{-1}$ and T is the temperature in Kelvin (Fig. 8). The agreement is very good considering uncertainties in the model of Zhang and Behrens (2000) and in the diffusivity data obtained in this work.

Our present new in situ IR method provides a quantitative tool for determining dehydration behaviour of volcanic glasses. Further systematic studies are in progress to understand the competition of diffusion of water species and reaction between water species, and will be reported separately.

Comparison of water diffusivity with previous studies

Since the diffusion coefficient of water is dependent on the total water contents (Delaney and Karsten 1981; Nowak and Behrens 1997; Zhang and Behrens 2000), the apparent diffusion coefficients obtained above should be considered as values averaged over the water-concentration profiles in the samples (Crank 1975; Wang et al. 1996; Zhang 1999). Thus, the averaged apparent diffusion coefficients obtained in this study cannot be directly compared with the diffusion coefficients, including the dependence on the water contents, which were previously reported by some authors (Nowak and Behrens 1997; Zhang and Behrens 2000). However, if the linear relation between the diffusion coefficient and water

Fig. 6 The averaged apparent diffusion coefficients of water in rhyolitic glasses are shown as a function of temperature. The diffusion coefficients were obtained for the data of $M_t/M > 0.5$ using Eq. (1). Uncertainties on the diffusion coefficients from the fittings are smaller than the size of the symbols, except for the data of Run7 at 700 °C (Table 3)
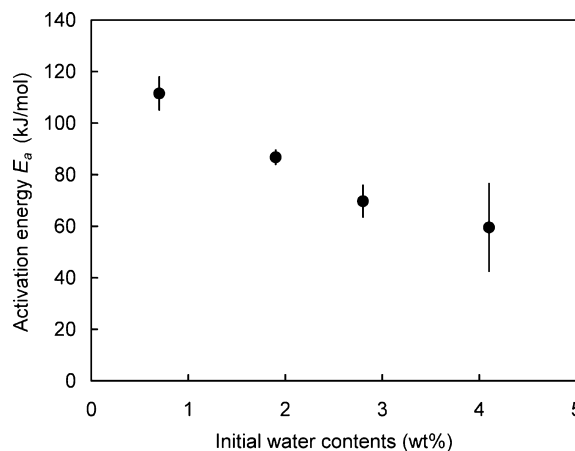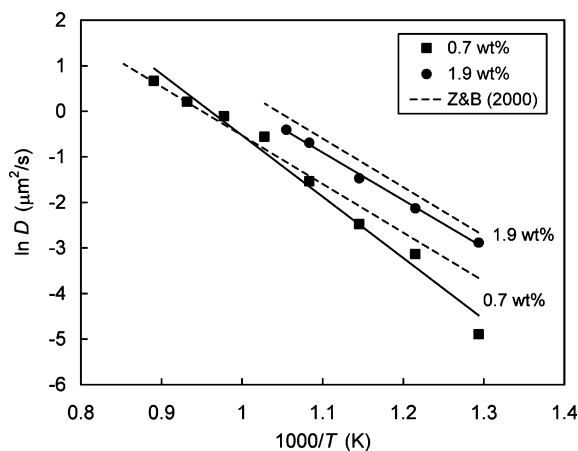

Fig. 7 Activation energy values obtained from the slopes of the linear regressions on the Arrhenius plot (Fig. 6) for different initial water contents. The *error bars* represent standard deviations (2σ)

Fig. 8 Temperature dependence of apparent diffusion coefficients at 0.7 and 1.9 wt% and at 0.1 MPa. *Filled symbols* represent the results of this study, and the *solid lines* are linear regressions for those data. The *dashed lines* are the results of Zhang and Behrens (2000)

Conclusion

The dehydration rates of rhyolitic glasses at a heating stage were measured by in situ IR spectroscopy in order to determine diffusion coefficients of total water in rhyolitic glasses at high temperatures. This method for determining the diffusion coefficient of water has some advantages: (1) it can analyze the dehydration directly at high temperature and (2) it has the potential to obtain kinetic data at high temperature. By applying a diffusion-out model of a plane sheet to our experimental data, the water diffusivities in rhyolitic glasses were determined at 0.7–4.1 wt% and 475–850 °C. The obtained diffusion coefficients show dependences on both the temperature and the initial water content, and their values are similar to the results of previous studies. The apparent activation energy for the diffusion of total water increased from 60 ± 17 to 112 ± 6 kJ mol^{-1} with initial total water content decreasing from 4.1 to 0.7 wt%. The method presented by this study can be applied for the rapid and precise determination of apparent water diffusivities in natural and synthetic glasses with different compositions. The competition of the diffusion and reaction processes of water species at high temperatures can also be investigated by this method.

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