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An experimental investigation on diffusion of water in haplogranitic melts

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Abstract The diffusivity of water has been investigated for a haplogranitic melt of anhydrous composition $\text{Qz}_{28}\text{Ab}_{38}\text{Or}_{34}$ (in wt %) at temperatures of 800–1200°C and at pressures of 0.5–5.0 kbar using the diffusion couple technique. Water contents of the starting glass pairs varied between 0 and 9 wt %. Concentration-distance profiles for the different water species (molecular water and hydroxyl groups) were determined by near-infrared microspectroscopy. Because the water speciation of the melt is not quenchable (Nowak 1995; Nowak and Behrens 1995; Shen and Keppler 1995), the diffusivities of the individual species can not be evaluated directly from these profiles. Therefore, apparent chemical diffusion coefficients of water (D_{water}) were determined from the total water profiles using a modified Boltzmann-Matano analysis. The diffusivity of water increases linearly with water content <3 wt % but exponentially at higher water contents. The activation energy decreases from 64 ± 10 kJ/mole for 0.5 wt % water to 46 ± 5 kJ/mole for 4 wt % water but remains constant at higher water contents. A small but systematic decrease of D_{water} with pressure indicates an average activation volume of about $9 \text{ cm}^3/\text{mole}$. The diffusivity (in cm^2/s) can be calculated for given water content (in wt %), T (in K) and P (in kbar) by

$$\log D_{\text{water}} = (-4.81 - 0.045 \cdot C_{\text{water}} + 0.027 \cdot C_{\text{water}}^2) - (3378 - 483 \cdot C_{\text{water}} + 46.9 \cdot C_{\text{water}}^2 + 47.5 \cdot P)/T$$

in the ranges $1073 \text{ K} \leq T \leq 1473 \text{ K}$; $0.5 \text{ kbar} \leq P \leq 5 \text{ kbar}$; $0.5 \text{ wt \%} \leq C_{\text{water}} \leq 6 \text{ wt \%}$. The absence of alkali concentration gradients in the glasses after the

experiments shows that interdiffusion of alkali and H^+ or H_3O^+ gives no contribution to the transport of water in aluminosilicate melts. The H/D interdiffusion coefficients obtained at 800°C and 5 kbar using glass pieces with almost the same molar content of either water or deuterium oxide are almost identical to the chemical diffusivities of water. This indicates that protons are transported by the neutral component H_2O under these conditions.

Introduction

Knowledge of the mechanisms of water diffusion in silicate melts and glasses is of fundamental importance for understanding magmatic processes as well as for designing glass products. One of the most impressive processes in nature affected by diffusion of water is degassing of magmas during volcanic eruptions. Nucleation and growth of bubbles in the ascending magma is directly related to the diffusivity of hydrous species in the melt (e.g. Sparks et al. 1994). Diffusion of water in melts also plays an important role for interaction of fluids and magmas, e.g. in subduction zones. Because the solubility of water in silicate melts is much higher than those of other volatiles, e.g. CO_2 or SO_2 (e.g. Holloway and Blank 1994; Carroll and Webster 1994), the composition of the fluids can strongly be altered by diffusion of water into the melt.

It is well known that the water diffusivity in silicate glasses (e.g. Moulson and Roberts 1961; Drury et al. 1962; Haller 1963; Cockram et al. 1969; Burn and Roberts 1970; Tomozawa 1985; Zhang et al. 1991a, b) and melts (Shaw 1974; Jambon 1979; Delaney and Karsten 1981; Karsten et al. 1982; Lapham et al. 1984; Zhang and Stolper 1991) strongly increases with water content. However, despite numerous previous studies the concentration dependence of water diffusion and the mechanisms by which water migrates through the silicate melt structure have not yet been clarified (see Zhang et al., 1991a, for a summary of the discussed models).

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Zhang et al. (1991a) have demonstrated that the combination of water speciation data with concentration-distance profiling can give new insights into the mechanisms of water diffusion. Assuming that the speciation of water is quenchable during rapid cooling, individual diffusion coefficients for OH groups and for H₂O molecules might be calculated from the profiles of both species measured by near-infrared (NIR) micro-spectroscopy (hereafter "OH" refers to hydroxyl groups, "H₂O" to H₂O molecules and "water" to the chemical component H₂O). Based on their own dehydration experiments with hydrous rhyolitic glasses and on re-interpreted data from diffusion couple experiments with rhyolitic melts (Lapham et al. 1984), Zhang et al. (1991a) concluded that the diffusing species is H₂O. Recently performed *in situ* NIR spectroscopic measurements on hydrous haplogranitic glasses and melts at temperatures up to 800°C and pressures up to 3 kbar (Nowak 1995; Nowak and Behrens 1995; Shen and Keppler 1995) indicate that the speciation of water can strongly change during cooling from run conditions thus suggesting that it may not be possible simply to extrapolate the water diffusion model of Zhang et al. (1991a) to the higher temperatures and water contents important for many silicic magmas.

Previous studies of water diffusion are limited either to low water contents or to small temperature ranges or both. In order to get a more comprehensive view on the mechanisms of water diffusion in aluminosilicate melts we have carried out diffusion couple experiments over an extended temperature range (800–1200°C), pressure range (0.5–5 kbar) and over a wide range of water contents (0–9 wt%). As starting material for our study we have used a haplogranitic glass (labelled AOQ) with normalized anhydrous composition 4.65 wt% Na₂O, 5.68 wt% K₂O, 13.53 wt% Al₂O₃, 76.14 wt% SiO₂ determined by multiple electron microprobe analyses (see Holtz et al. 1992, 1995). The composition is close to the ternary minimum composition in the haplogranite system (Qz-Ab-Or = SiO₂-NaAlSi₃O₈-KAlSi₃O₈) at $P_{\text{H}_2\text{O}} = 2$ kbar (Holtz et al. 1992, 1995).

Diffusion coefficients are calculated using a modified Boltzmann-Matano analysis (Sauer and Freise 1962). The advantage of the applied procedure is that the determination of the position of the Matano-interface is not required. Results obtained by this method are compared to the commonly used form of the Boltzmann-Matano equation. Implications for the mechanisms of water diffusion in polymerized melts are discussed in the second paper (Behrens and Nowak, this issue).

Experimental methods

Starting materials for the diffusion experiments

The dry haplogranitic glass was crushed in a steel mortar and sieved to obtain fractions with grain sizes of 200–500 µm and < 200 µm. The glass powders were cleaned ultrasonically in acetone

and then heated in a platinum crucible up to 800°C to remove organic material. The two fractions were mixed in weight ratio of 1:1 in order to get a powder with a low pore volume. The mixture was inserted in one side welded platinum capsules (35 mm long, 4 mm in diameter, wall thickness 0.2 mm) and compressed with a steel piston. For synthesis of almost dry glasses the loaded capsules were heated in a flame to remove absorbed water and rapidly welded by an electric arc of a tungsten inert gas electrode. For synthesis of hydrous glasses controlled amounts of doubly distilled water (1–9 wt%) or deuterium oxide (4.1 and 6.6 wt%) were inserted into the capsules before welding. These capsules were externally cooled by water during welding. The weights of the welded capsules were controlled after heating for at least one hour at 110°C to test for possible leakage of the capsules.

Syntheses of H-bearing glasses were performed at 1000–1200°C, 5 kbar and 72 h in an internally heated pressure vessel (IHPV) pressurized with Ar. Samples were quenched by turning off the power. This results in initial cooling rates of 200°C/min. Deuterium bearing glasses were produced in a horizontal cold-seal pressure vessel (CSPV) pressurized with Ar. In order to minimize contamination by hydrogen, 200 ml D₂O was injected as a deuterium buffer into the vessel before connecting to the pressure line. The vessel was rapidly pressurized to 1000 bar. Temperature was raised to synthesis conditions (800°C) after closing the vessel. Then the final pressure of 5 kbar was adjusted in the autoclave by opening the valve to the pressure system for a short time. After run durations of 7 days the vessel was cooled by compressed air.

In both apparatuses the samples were quenched isobarically by automatic pumping after opening to the pressure line. At the chosen run conditions the initially inserted amounts of water in the capsules always were below the water saturation limit of the melts (Holtz et al. 1992, 1995) and, thus, in all syntheses 30 mm long bubble free glass blocks were obtained.

The water contents of the quenched glasses were determined by Karl-Fischer titration. The analytical procedure is described in detail by Holtz et al. (1992, 1995) and Behrens (1995). The homogeneity of the water distribution in the hydrous glass blocks was tested by analysing pieces (10–20 mg) from both ends and from the centre of each glass block. Differences in water content from one end to the other were below 5% relative for most of the glass blocks. For one sample a larger difference of 10% relative over 30 mm was observed. However, this only corresponds to a variation of 0.15 wt% water along a piece of 6 mm length with an average of 6.96 wt% water which was used in the diffusion experiment AOQD023 (Table 1). Quantities of water added in the capsules for synthesis and the average water contents of the obtained glasses measured by Karl-Fischer titration always were in good agreement (less than 10% relative for a glass block with 1.27 wt%, less than 5% relative for glass blocks with water contents 2–9 wt%).

Preparation of water diffusion samples

The diffusion couple technique described by Lapham et al. (1984) was used to obtain one dimensional infinite medium water concentration-distance profiles. Different preparation techniques were applied for testing the influence of preparation on the obtained diffusion profiles. Starting materials for the diffusion experiments were either glass cylinders (2.9 mm in diameter, 5–6 mm long) or rectangular glass blocks (contact area 2.8 · 2.8 mm, 6 mm long) prepared from the dry and hydrated glass blocks described above. Furthermore noble metal coated glass cylinders (4 mm in diameter, 6 mm long) prepared as described by Lapham et al. (1984) were used in some runs. For measurement of chemical diffusion of water, water rich samples were contacted with dry samples or samples of low water content. For H/D interdiffusion experiments one hydrated glass block and one containing nearly the same molar concentration of deuterium oxide were contacted. All contact planes for the diffusion experiments were polished with 3 µm diamond paste. The contact planes were marked with some grains of

Table 1 Experimental parameters and determined water diffusion coefficients of the diffusion couple experiments. Only the diffusion coefficients printed in boldface were considered to determine D_0 and E_0 for the different water contents using the Arrhenius equation. The diffusion coefficients printed in light belong to diffusion experiments at 0.5 and 1 kbar or to short time experiments. (*Prep. tech.*: preparation technique, *cyl*: cylinders, *t_n*: nominal run duration, *t_e*: effective run duration, *M*: Matano-interface)

Sample no.	C_{water} [wt %]	Prep. tech.	T [°C]	P [kbar]	t_n [min]	t_e [min]	Shift of M [mm]	D_{water} [10^{-7} cm ² /s]							
								0.5 wt %	1 wt %	1.5 wt %	2 wt %	3 wt %	4 wt %	5 wt %	6 wt %
AOQD011	7.87 Co ³ /0.02	Blocks	800	5.0	14.0	14.0	0.023	—	—	—	—	0.87	1.37	2.11	3.38
AOQD017	7.75 / 2.35	Blocks	800	5.0	120.0	125.5	0.000	—	—	—	—	0.78	1.66	2.85	4.89
AOQD001	5.65 / 1.55	Drilled cyl.	850	5.0	180.0	182.7	0.114	—	—	—	0.61	1.06	1.62	—	—
AOQD002	5.71 / 1.38	--	850	5.0	360.0	362.7	0.125	—	—	—	0.50	0.96	1.61	—	—
AOQD021	1.95 / 0.02	Blocks	900	1.0	600.0	605.8	0.023	0.25	0.47	0.85	—	—	—	—	—
AOQD022	6.61 / 0.02	--	900	5.0	360.0	365.8	0.493	0.20	0.39	0.62	0.89	1.59	2.75	4.64	7.64
AOQD010	3.50 / 0.02	Drilled cyl.	1000	1.0	60.0	63.2	0.018	0.42	0.71	1.03	1.46	—	—	—	—
AOQD009	3.46 / 0.02	--	1000	5.0	60.0	63.2	0.035	0.20	0.35	0.51	0.70	—	—	—	—
AOQD024	6.80 / 0.17	Coated cyl.	1000	5.0	120.0	126.5	0.256	0.35	0.61	0.85	1.10	1.80	3.23	6.04	11.00
AOQD016	2.12 / 0.02	Blocks	1100	0.5	720.0	726.5	0.085	0.64	1.18	1.71	—	—	—	—	—
AOQD012	9.05 Co ³ / 0.02	--	1100	5.0	6.0	12.5	0.127	0.53	0.82	1.16	1.48	2.25	3.15	4.43	6.33
AOQD005	6.44 / 0.01	Drilled cyl.	1100	5.0	30.0	33.5	0.061	0.40	0.57	0.77	0.97	1.58	3.06	6.92	—
AOQD015	7.35 / 3.75	Blocks	1100	5.0	30.0	36.5	0.148	—	—	—	—	—	—	—	—
AOQD013	7.25 / 0.03	--	1100	5.0	120.0	126.5	0.460	0.50	0.85	1.29	1.68	2.80	4.32	7.31	15.28
AOQD023	6.96 / 0.17	Coated cyl.	1100	5.0	120.0	126.5	0.455	0.46	0.91	1.34	1.72	2.73	4.29	7.03	14.10
AOQD014	2.07 / 0.05	Blocks	1100	5.0	720.0	726.5	0.097	0.41	0.81	1.24	1.76	—	—	—	—
AOQD003	5.89 / 1.50	Drilled cyl.	1150	5.0	30.0	33.7	0.040	—	—	—	—	—	—	—	—
AOQD006	5.85 / 0.04	--	1200	5.0	30.0	33.8	0.076	0.78	1.28	1.81	2.32	3.74	6.59	12.64	—
AOQD020	6.91 / 0.04	Blocks	1200	5.0	60.0	66.9	0.216	0.63	1.24	1.92	2.72	4.35	6.58	11.13	20.00
AOQD004	8.60 / 2.17	Drilled cyl.	1200	5.0	0.0	3.8	0.025	—	—	—	—	—	—	—	—

^a These glass blocks were coloured with cobalt

platinum powder (grain size <1 μm). These sample assemblages were sealed in platinum capsules for high temperature diffusion experiments (1100–1200°C) or in gold capsules for low temperature diffusion experiments (800–1000°C). Noble metal tubes with 0.2 mm wall thickness were used because thinner walls often tear due to the sharp edges of the samples. After crimping the capsule material around the samples to remove most of the air, the water cooled capsules were welded with an electric arc of a tungsten inert gas electrode. Before the runs the welded capsules were pressurized in an IHPV at 5 kbar. After this pressure treatment the capsule walls were tested optically for possible fissures to be sure that these capsules would not leak during the following diffusion experiments.

Run conditions

All experiments to study the chemical diffusivity of water were carried out in a horizontally working IHPV with a heating rate of 100°C/min and a cooling rate of 200°C/min except run AOQD011. This run was performed at 800°C and 5 kbar in a CSPV pressurized with Ar. The CSPV can be rotated for rapidly heating the sample in the heated part of the vessel and for rapidly quenching the sample in the water cooled part of the vessel (estimated heating and quench rate: 50°C/s) to minimize the error of diffusion time. Run temperatures were 800–1200°C, run pressures 0.5 to 5 kbar and nominal run durations (t_n) 0–720 minutes (time from reaching the run temperature to the beginning of cooling). The run parameters for these experiments are listed in Table 1. At the chosen $P - T$ conditions the melts were water undersaturated so that the diffusion experiments are not affected by bubble formation and/or dehydration. A Eurotherm-controller/programmer, type 818, controlled the heating programme. The temperature in the sample holder was measured over a distance of 4 cm with three calibrated Ni-CrNi thermocouples (Heraeus Sensor) with an accuracy of $\pm 10^\circ\text{C}$. Furthermore, the temperature distribution in the IHPV sample holder was periodically controlled at 5 kbar by melting experiments of gold and silver wires, using the pressure dependence of the melting points given by Mirwald and Kennedy (1979). Temperature gradients in the sample holder were in all experiments less than 5°C/cm. The pressure was measured with a strain - gauge manometer (accuracy ± 20 bar at 5 kbar). After the run the samples were quenched isobarically by turning off the power of the furnace with directly measured initial cooling rates of 200°C/min.

The two H/D interdiffusion experiments were performed in a CSPV pressurized with Ar. The run temperature was 800°C, run pressure 5 kbar and the nominal run duration (t_n) 60 min (see Table 2). The temperature was measured externally with a calibrated Ni-CrNi thermocouple. The temperature at the sample position was characterized in separate runs using an assembly with three calibrated thermocouples in the interior of the vessel. The accuracy of the sample temperature was better than $\pm 5^\circ\text{C}$ at 800°C. The temperature gradients in the diffusion couples were less than 2°C/cm. A strain gauge manometer measured the pressure with a maximum error of ± 20 bar at 5 kbar. After the run the pressure vessel was cooled down with compressed air. The run pressure was held constant during cooling by automatic pumping.

The run times were chosen so that the initial water contents at both ends of the diffusion couples were preserved during the experiments. With this infinite medium configuration, simple one dimensional diffusion equations could be applied for calculating the diffusivity of water.

Measurement of water concentration-distance profiles

After quenching, 500 μm thick plates were cut out of the diffusion samples perpendicular to the platinum powder marked interfaces and polished at both sides. Each sample was fixed on a glass plate

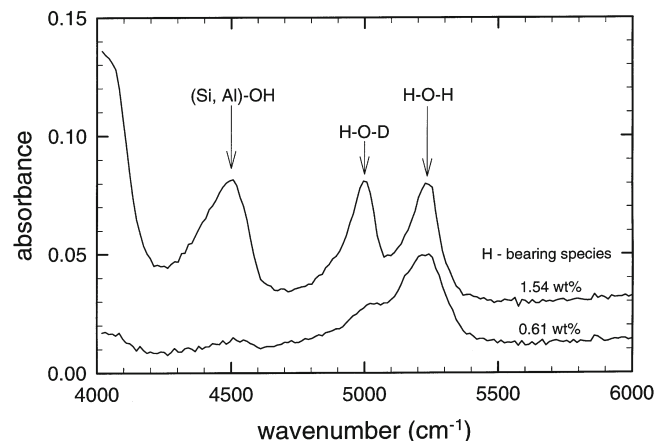
Table 2 Experimental parameters and determined H/D interdiffusion coefficients of the H/D interdiffusion experiments (*prep.tech.* preparation technique, t_n nominal run duration, t_e effective run duration)

Sample no.	c_{water} [wt %]	$c_{\text{deuterium oxide}}$ [wt %]	Prep. tech.	T [°C]	P [kbar]	t_n [min]	t_e [min]	D_{water} [10^{-7} cm ² /s]
IAOQD01	3.75	4.10	Blocks	800	5	60.0	65.5	0.58
IAOQD02	6.10	6.60	Coated cyl.	800	5	60.0	66.5	3.25

with a slit 2 mm wide and 20 mm long. Near-infrared microspectroscopy (Bruker IFS 88 + microscope A 590) has been used to determine the water concentration-distance profiles. Spectra were collected in 50 μm steps adjusted by a digitally controlled xy - table. The spot size of each measurement was approximately 100 μm .

The concentrations of H₂O and OH were determined from the heights of the absorption bands at 5230 cm⁻¹ and at 4500 cm⁻¹, respectively, by using the Lambert-Beer law to obtain the water concentration-distance profiles of the diffusion couple experiments (see Behrens et al. (1996) for details of the applied spectroscopic method). The total water was obtained by summing up both species concentrations. For the calculation of species concentrations we have used an iterative procedure which considers the dependence of the density on water content. The dependence of density on water content and the linear molar extinction coefficients were determined experimentally for the AOQ glass using 40 glasses with the same anhydrous composition and water contents ranging from 1.0 to 8.7 wt % (Behrens et al. in preparation). Density of hydrous AOQ glasses can be described by d [g/L] = 2362 - 14.5 · C_{water} [wt %]. The obtained molar extinction coefficients are 1.79 ± 0.02 L · mole⁻¹ · cm⁻¹ for the H₂O band and 1.56 ± 0.02 L · mole⁻¹ · cm⁻¹ for the OH band.

In the H/D interdiffusion experiments the molar water content was almost constant in the whole assemblage. The H/D exchange profile can be monitored by only measuring the H - bearing species. In addition to (Si,Al)OH and H₂O, HOD must be considered as a third H-bearing species. The HOD has a combined stretching and bending mode excitation at 5020 cm⁻¹ (Fig. 1). The extinction coefficient for this band is not known exactly but for rhyolitic glass Stanton et al. (1986) noted similar extinction coefficients of the combination band for HOD and H₂O. For simplicity we have assumed for the haplogranitic composition that these values are identical. The possible error in the obtained diffusion coefficient due to this assumption only is a few percent relative.

**Fig. 1** NIR absorption spectra of a H/D interdiffusion sample IAOQD01 (thickness = 0.0435 cm) measured at different distances from the platinum layer. H - bearing species correspond to water dissolved as H₂O, HOD and (Si-Al)-OH

Results and data analysis

Water concentration-distance profiles

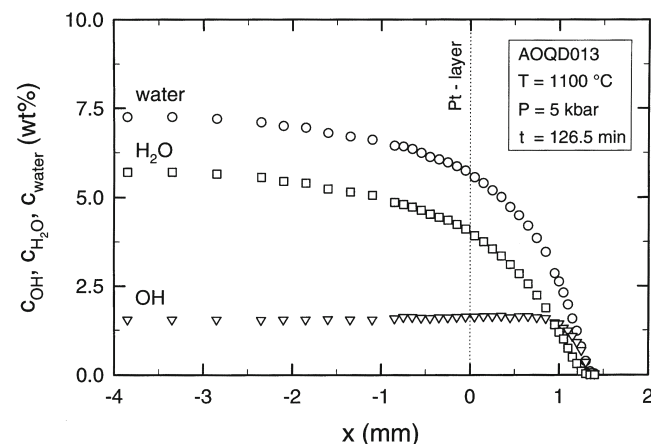
Typical OH, H₂O and total water concentration-distance profiles of a diffusion couple experiment (AOQD013) are presented in Fig. 2. The profile shapes of the total water concentration-distance profiles of all diffusion couple experiments deviate from the error function shape, indicating a strong concentration dependence of the effective water diffusion coefficients.

Coupling to alkali

Concentration-distance profiles of Na and K were measured by electron microprobe analysis parallel to the diffusion direction of water for the samples AOQD04 and AOQD09. In agreement with previous studies (Lapham et al. 1984; Zhang et al. 1991a) concentrations of alkalis normalized to anhydrous glass composition show no variations outside the analytical error along the diffusion profile of water.

Effect of quenching on water speciation

As noted by Silver et al. (1990) the concentration of OH measured in a glass depends on the cooling rate. This

**Fig. 2** Concentration-distance profile of water dissolved as OH and H₂O and total water concentration for the diffusion sample AOQD013. The interface of the water rich and the dry glass block was marked with some grains of platinum powder

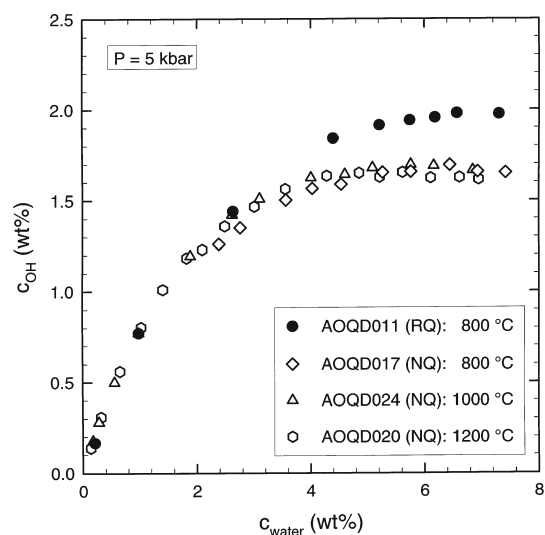


Fig. 3 Concentrations of OH groups versus total water content obtained from diffusion couple experiments cooled down from run temperature isobarically in a few seconds (RQ) and in a few minutes (NQ). The water speciation of the glass at room temperature depends on the quench rate but is independent of run temperature

effect is confirmed by species concentrations obtained from diffusion experiments at 800°C and 5 kbar with different quench rates (Fig. 3). For 6 wt% water, the OH content is 15% higher for the rapidly cooled sample (RQ: 800 to 100°C in 13 s) than for samples cooled with standard quench rates (NQ: 800 to 100°C in 300 s). Species concentrations are identical for runs at various temperatures but with the same quench rate. As shown recently by *in situ* measurements, the speciation of the melt state can not be frozen in during cooling (Nowak 1995; Nowak and Behrens 1995; Shen and Keppler 1995). Therefore, the OH and H₂O concentration-distance profiles could not be used to calculate diffusivities of these species as done by Zhang et al. (1991a, b) for water diffusion in rhyolitic glasses. Thus effective diffusion coefficients of water were calculated from total water concentration-distance profiles.

Calculation of effective water diffusion coefficients from diffusion couple experiments

The basis for calculating the diffusion coefficients is Fick's second law that represents a relation between the local and temporal concentration changes. For one dimensional diffusion Fick's second law is given by:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) \quad (1)$$

where c denotes the concentration, x the distance, t the run time and D the chemical diffusion coefficient.

Boltzmann (1894) and Matano (1933) substituted $y = x/\sqrt{t}$ in Eq. (1). A single integration and substitution of $dy = dx/\sqrt{t}$ leads to Eq. (2) and enables to calculate concentration dependent diffusion coefficients:

$$D(c) = \frac{1}{2t} \left(\frac{dx}{dc} \right)_c \int_c^1 x dc \quad (2)$$

Equation (2) is valid for one dimensional molar volume independent diffusion in two semi-infinite spaces if at $t = 0$ a concentration step exists within the diffusion couple. For analytical evaluation of Eq. (2) the total water concentration-distance profiles are normalized by the maximum and minimum water concentrations and, thus, $c [= (C_{\text{water}} - C_{\text{water, min}}) / (C_{\text{water, max}} - C_{\text{water, min}})]$ varies between 0 and 1. Polynomials $x(c)$ of 7th order were used to fit the normalized concentration-distance profiles of the samples AOQD02 and AOQD013 for calculating the slopes at c and the integrals from c to 1. In Fig. 4a the normalized concentration-distance profile of the sample AOQD013 is shown as an example.

For the Boltzmann-Matano analysis, the Matano-interface must be the origin of the coordinate system, which is defined by mass balance consideration. The amount of water that diffuses out of the water rich part of the melt must be equal to the amount of water that diffuses into the water poor part of the melt. This means that the integral in Eq. (2) in the integration boundaries 0 to 1 is zero. The Matano-interface is not necessarily equal to the platinum powder marked contact plane of the diffusion couple. For instance the Kirkendall-effect (interdiffusion between particles and vacancies) can cause a shift of the Matano-interface. The shift x_m of the Matano-interface relative to the marked contact plane can be calculated by the following condition:

$$\int_0^1 (x - x_m) dc = 0 \quad (3)$$

The function $x(c)$ is inserted in Eq. (3) and solved to x_m . The calculated shift is subtracted from the function $x(c)$ so that the origin of the new coordinate system and the Matano-interface becomes identical.

Sauer and Freise (1962) derived from the Boltzmann-Matano equation a common equation that is independent of the position of the Matano-interface and that can be applied to systems with changes in molar volume. Equation (4) is a special case for molar volume independent diffusion. The boundary conditions of the Boltzmann-Matano equation (one dimensional diffusion in two semi-infinite spaces with a concentration step at $t = 0$) are also valid for the equation of Sauer and Freise (1962).

$$D(x) = \frac{1}{-2t(\partial c / \partial x)_x} \left[(1 - c(x)) \int_x^{+\infty} c dx + c(x) \int_{-\infty}^x (1 - c) dx \right] \quad (4)$$

For calculating diffusion coefficients with this equation polynomials $c(x)$ of 5th to 7th order were used to describe the normalized water concentration-distance profiles. A fit of run AOQD13 by a 5th order polynomial is shown in Fig. 4b. For the Boltzmann-Matano analysis as well as for the Sauer-Freise analysis the molar volume and thus the density of the silicate melts must be in-

dependent from the water concentration. Burnham and Davis (1971) determined the difference in density for a dry albite melt to an albite melt with 5 wt% water at 950°C and 5 kbar to be only 6%. In the glassy state at 1 bar and room temperature the difference in density is only 4%. Thus in first approximation the density of aluminosilicate melts can be considered as independent from the water concentration.

A schematic illustration of both methods and a comparison of the obtained diffusivities for the sample AOQD013 are presented in Fig. 4. Both methods supply nearly identical diffusion coefficients for a given water content. For both samples AOQD02 and AOQD13 diffusivities obtained by the Boltzmann-Matano analysis show a larger scatter than those obtained by the Sauer-Freise analysis. This is an artefact of the polynomial fitting procedure. The fitted polynomial $x(c)$ has a maximum relative deviation of 15% to the measured concentration profile whereas the fitted polynomial $c(x)$ only has a maximum deviation of 2% to the measured

profile. Because of its higher precision the Sauer-Freise method was chosen for determination of the diffusion coefficients of all diffusion couple runs. Reliable data can be obtained by this method for water concentrations between $c_{min} + 0.2$ wt% and $c_{max} - 1$ wt%. Otherwise the products of the normalized concentrations and the integrals are composed of very small and very large values. Errors in determination of the small values have large effects on the calculated diffusion coefficients. For instance the decrease of the diffusion coefficients at > 6.5 wt% water content shown in Fig. 4c as an example is due to systematic errors resulting from the fit of the concentration-distance profile.

Positions of the Matano-interfaces determined graphically from the intersections of the two solved integrals in Eq. (4) for the runs AOQD002 and AOQD013 are identical to those determined by the method of Boltzmann-Matano. The shift of the Matano-interface for all runs is presented in Table 1. In agreement with results of Lapham et al. (1984) a shift of the Matano-

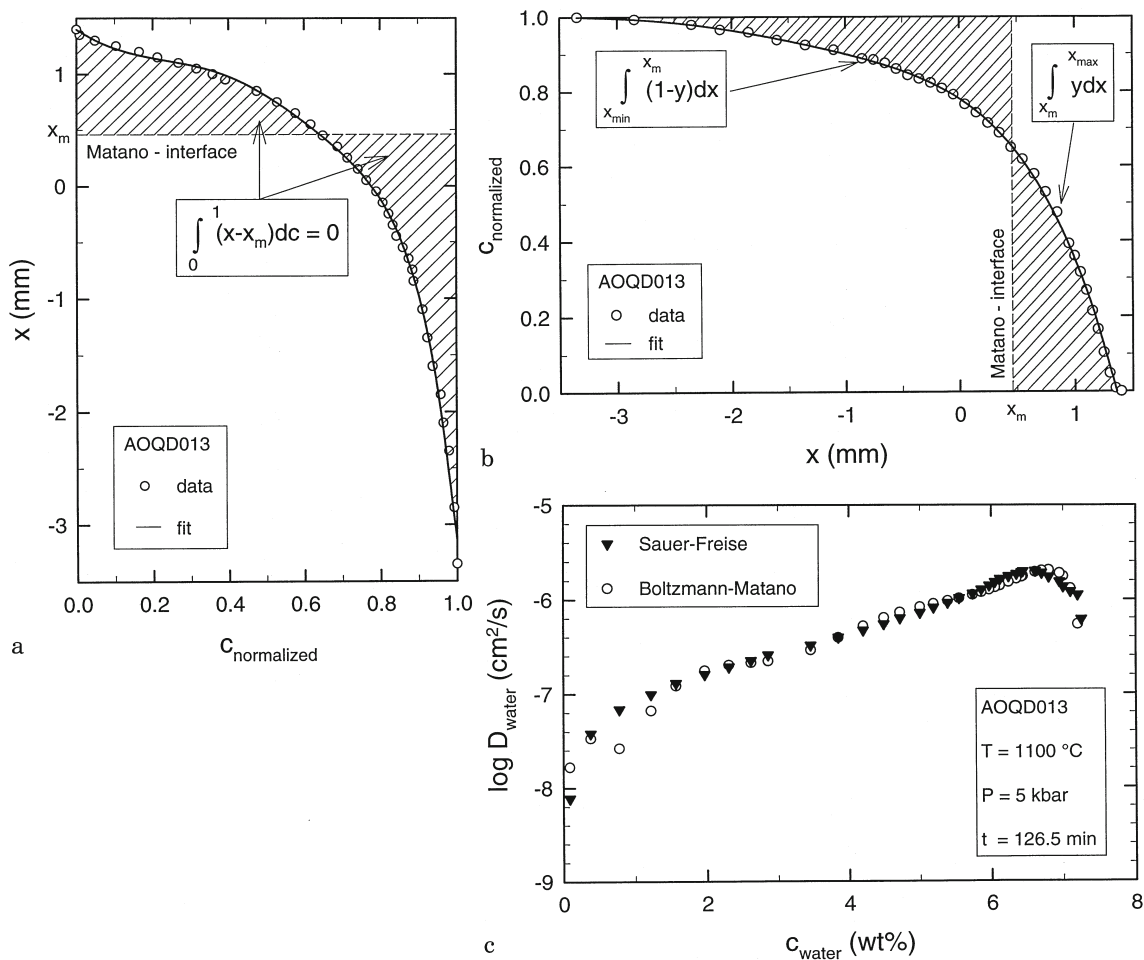


Fig. 4 **a** Normalized water concentration-distance profile (x vs $c_{normalized}$) used for data analysis by the original Boltzmann-Matano method. **b** Normalized water concentration-distance profile ($c_{normalized}$ vs x) used for data analysis by the method modified by Sauer and Freise (1962). A 7th order (in **a**) and a 5th order (in **b**) polynomial were fitted to the profiles for evaluation. Note the shift of the Matano

interface by 0.460 mm into the dry part of the diffusion sample. **c** $\log D_{water}$ versus total water content for the diffusion couple sample AOQD013 calculated by Boltzmann-Matano and Sauer-Freise. The decrease of diffusivity at > 6.5 wt% water content is due to systematic errors resulting from the polynomial fit of the concentration profile

interface in the direction to the melt with lower water content was observed.

Since the activation energy of water diffusion is small (see below), diffusion of water already takes place during heating to run temperature and continues during cooling after the experiment. Thus, the effective diffusion time t_e is larger than the nominal time t_n at which the sample is at run conditions. The effective run time was obtained by an iterative procedure in which the heating and cooling periods are divided in temperature intervals of 100°C. For each interval an average diffusivity is calculated. Summing up the product of the average diffusivities and run dwells for each interval divided by the diffusivity at run conditions is added to t_n for correction. The deviation of the corrected and uncorrected diffusion coefficients was not larger than 18% relative for runs of ≥ 30 min duration. For the short run with 6 min nominal run time (AOQD012) the deviation of the corrected and uncorrected diffusion coefficients is about 50% relative.

H/D interdiffusion experiments

In the case of the H/D interdiffusion experiments concentration-distance profiles of H₂O, OH and HOD were obtained using also NIR microspectroscopy. Concentrations are given in wt% of water in the form of these species. Summing up ($C_{H_2O} + C_{OH} + 0.47 C_{HOD}$) leads to the total water concentration-distance profiles. In first approximation the diffusion coefficient can be considered as concentration independent because pieces with nearly the same molar concentrations of water (either H₂O or D₂O) were used (Table 2). Thus, the chemical gradients are nearly zero in these experiments. The solution of Fick's second law for this situation is given by

$$c(x, t) = \frac{c_0}{2} \left[1 - \operatorname{erf} \frac{x}{2\sqrt{Dt}} \right] \quad (5)$$

where erf denotes the error function (Crank 1975).

The H/D interdiffusion coefficients were determined from the slope in plots of $\operatorname{erf}^{-1}[1 - (2c(x, t))/c_0]$ versus x . Figure 5a shows as an example for the H/D interdiffusion experiment IAOQD01 at 800°C and 5 kbar the measured concentration-distance profile in comparison to the profile calculated by Eq. (5) using the obtained diffusion coefficient. It can be seen that the calculated diffusion profile fits the measured profile very well. The obtained H/D interdiffusion coefficients for 3.61 and 6.10 wt% water, 800°C and 5 kbar agree within experimental error with the diffusion coefficients calculated from diffusion couple experiments at the same $P - T$ conditions (Fig. 5b).

Uncertainty of the diffusion coefficients

The accuracy of the obtained diffusion data is determined by the precision and the accuracy of determination of the experimental parameters as well as by the

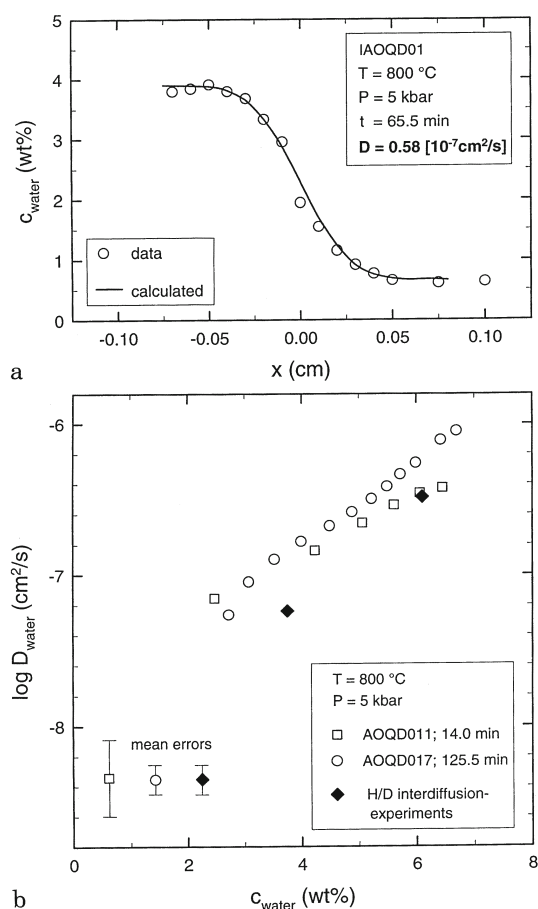


Fig. 5 **a** Total water concentration-distance profile of the H/D interdiffusion sample IAOQD01. **b** $\log D_{\text{water}}$ versus total water content determined from diffusion couple experiments in comparison with water diffusion coefficients determined by H/D interdiffusion experiments at 800°C and 5 kbars

measurements of the concentration-distance profiles and the following evaluation procedure. The error of run duration is assumed to be less than 5% after correction for the heating and cooling period in the IHPV except for runs with short duration (AOQD004 and AOQD012). The uncertainty of the run temperature ($\pm 10^\circ\text{C}$) causes a maximum error in the diffusion coefficients of $\pm 5\%$ relative as indicated by the temperature dependence of the D values. The pressure dependence of the D values is small and deviations of actual pressure from nominal pressure can be neglected (see below).

Another important source of error for the short time runs AOQD004, AOQD011 and AOQD012 is the measurements of the water concentration-distance profiles. The relatively steep profiles in these experiments are broadened due to the local resolution of the NIR microscope.

Deviation of the diffusion direction from the direction of the measured profile is estimated to be less than 10 degrees resulting in a maximum overestimation of the D values of 3% relative. The uncertainties of extinction coefficients and of measurements of sample thickness

($\pm 2 \mu\text{m}$) are systematic errors in each experiment because each of these errors influences the resulting data points in the same direction. The maximum influence on the diffusion coefficients is estimated to be less than 1%. The reproducibility of determination of peak heights of the absorption bands (possible error: 0.003 absorbance units) and of distances (possible error: $\pm 10 \mu\text{m}$) has been tested by measuring one concentration-distance profile twice. Species concentrations from both measurements are identical within 2% relative for a given distance.

As an approximation we assume that the length of the concentration-distance profile in the melt is the same as that measured in the quenched glass since the thermal expansivity is not known for our composition. Density data of Burnham and Davis (1971) for albite glasses suggest that the diffusion coefficients might be 6% higher than determined for the glass.

Diffusion studies on melts might be affected by non diffusive mass transport such as convection, especially, if horizontally oriented diffusion couples (see e.g. Hofmann and Margaritz 1977) are used. A negligible influence of convection in our experiments is proved in three ways: (1) Diffusion experiments under the same $P - T$ conditions but with different run durations supply nearly identical water diffusivities (Fig. 6a, b). Hence, the diffusivity of water is time independent. (2) After the runs layers of platinum powder used as markers have been not broader than $5 \mu\text{m}$. Melt convection should give a large broadening of the layer. (3) A sharp colour contrast at the platinum layer was observed in experiments AOQD011 and AOQD012, in which the diffusion couple consisted of an intensive blue coloured water rich glass block [a diluted $\text{Co}(\text{NO}_3)_2$ solution was added for synthesis] and a colourless dry glass block. Cobalt in aluminosilicate melts is mainly present as divalent cation in distorted tetrahedral coordination (Keppler 1992) and thus its diffusivity is probably as slow as that of network formers as shown for other di- and trivalent cations (e.g. Baker 1991). The sharp colour contrast at the platinum layer after the run demonstrates the absence of melt mixing by convection.

The shift of the Matano-interface towards the water poor part of the diffusion couple shows no systematic dependence on run conditions (Table 1). This implies that this shift is not related to the diffusion of water in the melt. A rapid transport of water at the beginning of the experiments is indicated by the zero time experiment AOQD004 (see Table 1) in which the sample was cooled directly after reaching the run temperature. The diffusivities calculated by using an effective run duration are one order of magnitude higher than data obtained from long time runs. A shift of the Matano-interface of 0.025 mm was observed for the zero time experiment (Table 1).

A possible explanation for the shift of the Matano-interface can be transport of water through gas phase at the beginning of the experiments. Water already is set free from hydrous glasses significantly below the glass

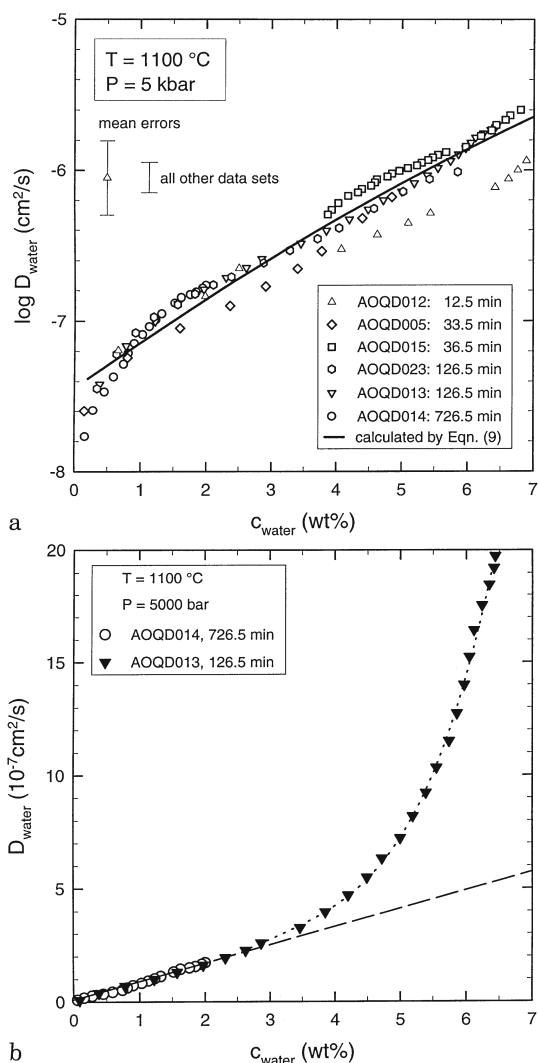


Fig. 6 a $\log D_{\text{water}}$ versus total water content for six diffusion couple experiments at same $P - T$ conditions and various run times. This comparison indicates that the diffusion of water in AOQ melts is time independent. The diffusion coefficients obtained from the short time experiment AOQD012 have the largest error because of the uncertainty in the calculation of the effective run duration during heating and cooling of the sample. **b** D_{water} versus total water content for two diffusion couple experiments carried out using the same preparation technique and the same IHPV furnace. The *dashed straight line* is fitted to diffusion coefficients $< 3 \text{ wt}\%$ water showing the linear dependency at low water contents, the *dotted line* is fitted to diffusion coefficients $> 3 \text{ wt}\%$ water representing the exponential increase of water diffusivity at higher water contents. For error bars see Fig. 6a

transition as shown by water determination (e.g. Behrens 1995; Behrens et al. 1996) and by diffusion experiments (e.g. Zhang et al. 1991a). The released water can migrate from the water rich glass to the water poor glass if pores or cracks are present between the glass pieces or between glasses and capsule walls. Such paths for gas phase transport may result from sample preparation or from stress during pressurization. They are preserved until the glasses become soft enough to fill the free volume above the glass transition.

It might be expected that the preparation technique has a large influence on the initial process. However, rectangular pieces and cylinders as starting materials gave similar results. The mechanical stress during preparation which can produce microcracks was larger for the cylinders obtained by diamond coring than for the rectangular pieces carefully cut by a diamond saw. Furthermore, the use of the glass cylinders coated on the walls with platinum as described by Lapham et al. (1984) gives no difference to the use of uncoated samples. Coating seals the surfaces and, thus, prevents dehydration at these parts of the samples. Probably, stress on the assemblage during pressure load is more critical for the experiments than preparation of glasses before the experiment.

The rapid transport process at the beginning modifies the starting conditions for diffusion and, thus, the boundary conditions for evaluation are not strictly valid. However, because the diffusion data are time independent (except of the zero time experiment) and because no correlation exists between the shift of the Matano-interface and diffusion coefficients we suggest that the initial process is of minor importance for our results.

All discussed errors including the possible effect of a rapid transport process at the beginning of the experiments result in a maximum uncertainty of the diffusivities of 25% relative for run durations longer than 30 min.

Discussion

Effect of water content on water diffusivity

The diffusivity of water in the haplogranitic melt strongly increases with total water content of the melt. A similar behaviour has been observed in previous studies for diffusion of Si (Baker 1991), Zr (Harrison and Watson 1983), P (Harrison and Watson 1984) and REEs (Rapp and Watson 1986) in silicate melts. The increase of the mobility of melt components can be attributed to the depolymerization of the network by reaction of water molecules with bridging oxygens (Nowak 1995; Nowak and Behrens 1995).

The shape of plots of wt% water versus $\log D$ is almost identical in the whole investigated temperature and pressure range for haplogranitic melts at which the dependence is clearly different for low and for high water contents (Fig. 6a, b). Below 3 wt% water the diffusion coefficient of water increases linearly with water content whereas it increases exponentially above 3 wt% water.

Zhang et al. (1991b) have predicted a linear dependence of water diffusivity for rhyolitic glasses for the case that D_{OH} (diffusivity of hydroxyl groups) is negligible and D_{H_2O} (diffusivity of water molecules) and K (equilibrium constant of the reaction $H_2O + O = 2 OH$) are independent of water concentration. Furthermore, a linear dependence of water diffusivity has been proposed

by Doremus (1995) to fit concentration-distance profiles measured by Roberts and coworkers (Drury et al. 1962; Roberts and Roberts 1964; Burn and Roberts 1970) after sorption of water in fused silica. The change of the dependence of water diffusivity observed for haplogranitic melt at about 3 wt% water content may indicate a change in diffusion mechanisms at this water concentration (Behrens and Nowak, this issue).

Pressure dependence of water diffusivity

At three different temperatures from 900 to 1100°C we found the diffusivity of water in haplogranitic melts systematically decreasing with pressure (see Table 1 and Fig. 7). This is in contrast to results of Lapham et al. (1984) for rhyolitic composition. These authors did not observe any pressure dependence of water diffusivity. Possibly, the differences are due to the less precise determination of water concentration-distance profiles with the ion microprobe by Lapham et al. (1984) because the effect of pressure on diffusivity is relatively small.

The dependence of diffusivity on pressure can be caused by enlargement of the network during jump of the diffusing species and/or by changes of the melt structure or concentrations of hydrous species with pressure. Polymerized melts such as jadeite or albite melts show negative pressure dependencies of the viscosity (Kushiro 1976, 1978; Brearley et al. 1986). This has been variously attributed to coordination change of aluminum (Kushiro 1976), disruption of the structure (Brearley et al. 1986) and weakening of bridging T-O-T bonds (Scarfe et al. 1987). Since the viscosity of a haplogranitic melt containing 6 wt% water was found to be constant in the range from 3–10 kbar (Schulze et al. in press) we take this as an indication that pressure induced structural changes are small in this pressure range. *In*

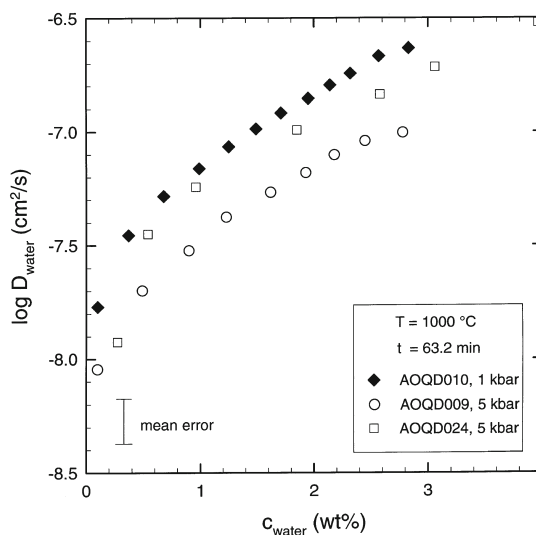


Fig. 7 Effect of pressure on water diffusivity in haplogranitic melts

situ NIR spectroscopic measurements have shown that the water species in haplogranitic melt containing 4 wt% water are independent of pressure in the range 1.5 to 3.0 kbar (Nowak 1995; Nowak and Behrens 1995). Therefore, we suggest that the negative pressure dependence of water diffusion in haplogranitic melts is not related to changes in concentration of the hydrous species, but is attributable to the activation volume during the transition state of the diffusive jump. The activation volume V can be obtained by an Arrhenius equation

$$D = D_0 \cdot e^{-\left(\frac{P}{RT}\right)} \quad (6)$$

where D_0 denotes the pre-exponential factor and R the gas constant. A precise determination of the activation volume is not possible from our experiments because the effect of pressure is relatively small if compared to the uncertainty of the diffusion coefficients. Activation volumes calculated for water contents of 0.5, 1 and 1.5 wt% and temperatures of 900, 1000 and 1100°C using the low pressure data and the averages of the 5 kbar data vary from 5 to 11 cm³/mole. Assuming that the activation volume is independent of temperature a mean value of 9 cm³/mole is obtained. Because the shape of the $\log D$ versus C_{water} curves is similar for low and high pressure (Fig. 7) we suggest that the activation volume is almost independent of water content up to 3 wt%.

Temperature dependence of water diffusivity

The Arrhenius plot for water diffusion in haplogranitic melts at 5 kbar is presented in Fig. 8a. All diffusion coefficients obtained at 5 kbar except those from short time runs AOQD004, AOQD011 and AOQD012 which have relatively large uncertainties were used to evaluate the temperature dependence of the water diffusivity. In the investigated temperature range the diffusivity can be described for given water content by an Arrhenius equation:

$$D = D_0 \cdot e^{-\left(\frac{E_a}{RT}\right)} \quad (7)$$

where E_a denotes the activation energy. The logarithm of D_0 increases continuously with water content from -4.9 ± 0.4 cm²/s at 0.5 wt% water to -4.1 ± 0.06 cm²/s at 6 wt% water (Fig. 8b). The E_a decreases from 64 ± 10 kJ/mole at 0.5 wt% water to 46 ± 5 kJ/mole at 4 wt% water and remains almost constant from 4 to 6 wt% (Fig. 8c). Extrapolation to 0 wt% water gives a value of 70 kJ/mole for E_a . This value is comparable to the activation energy for trace water diffusion data in silica glass (Moulton and Roberts 1961).

A decrease of activation energy with water content also was observed for diffusion of Zr, P, and REEs in granitic melts (Harrison and Watson 1983, 1984; Rapp and Watson 1986) in which the decrease is larger at low than at high water content. It should be noted that for viscous flow in haplogranitic melts a similar dependence on water content was found to be similar to the dependence of water diffusion on water content even if the

absolute values of E_a differ strongly (Dingwell et al. 1996; Schulze et al. in press). This supports that the effect of water on the melt structure is more pronounced at low than at high water content.

General equation for calculation of water diffusivity in haplogranitic melts

In order to interpolate diffusion coefficients over the range of our measurements and to extrapolate our data for comparison to data given in literature we present a general equation describing $\log D_{\text{water}}$ as a function of T , P and C_{water} . Considering both temperature and pressure the Arrhenius equations can be written as

$$\log D_{\text{water}} = \log D_0 - \frac{E_a}{2.303 RT} - \frac{PV}{2.303 RT} \quad (8)$$

$\log D_0$ and E_a were fitted in dependence on C_{water} for the 5 kbar experiments by second order polynomials using weighted least square regressions (see Table 3 and Fig. 8b, c). The term V is taken as the mean activation volume determined from the pressure dependence. By doing so we obtained

$$\log D_{\text{water}} = (-4.81 - 0.045 \cdot C_{\text{water}} + 0.027 \cdot C_{\text{water}}^2) - (3378 - 483 \cdot C_{\text{water}} + 46.9 \cdot C_{\text{water}}^2 + 47.5 \cdot P)/T \quad (9)$$

where C_{water} is given in wt%, T in K and P in kbar. This equation is suitable to calculate water diffusivity for haplogranitic melts in the ranges $1073 \text{ K} \leq T \leq 1473 \text{ K}$; $0.5 \text{ kbar} \leq P \leq 5 \text{ kbar}$; $0.5 \text{ wt}\% \leq C_{\text{water}} \leq 6 \text{ wt}\%$. The deviation of measured diffusivities from those calculated by Eq. (9) is below 25% for 81% of the data given in Table 1 and below 40% for 98% of the data. Only the two values for high water content of run AOQD012 fall out of this range, both values are highly uncertain because of the short run duration (see Fig. 6a).

As a first approximation Eq. (9) also can be used to calculate water diffusivity in granitic melts because variation of water diffusivity with anhydrous composition is small for polymerized melts (Behrens and Nowak, this issue). However, it is emphasized that the lowest water content for which this equation gives a good approximation is about 0.5 wt% because at lower water contents the experimental curves are not well reproduced by the fit and the calculation strongly overestimates D_{water}

Table 3 $\log D_0$ and the activation energy E_a for water contents 0.5–6 wt% obtained from the linear regressions in the Arrhenius plot (fig. 8a)

c_{water} [wt%]	$\log D_0$ [cm ² /s]	E_a [kJ/mole]
0.5	-4.93 ± 0.40	63.6 ± 10.1
1.0	-4.78 ± 0.48	60.9 ± 12.3
1.5	-4.68 ± 0.54	59.2 ± 14.0
2.0	-4.74 ± 0.32	54.4 ± 8.0
3.0	-4.72 ± 0.24	48.8 ± 5.7
4.0	-4.60 ± 0.20	46.1 ± 5.0
5.0	-4.36 ± 0.19	45.8 ± 4.6
6.0	-4.10 ± 0.06	45.6 ± 1.3

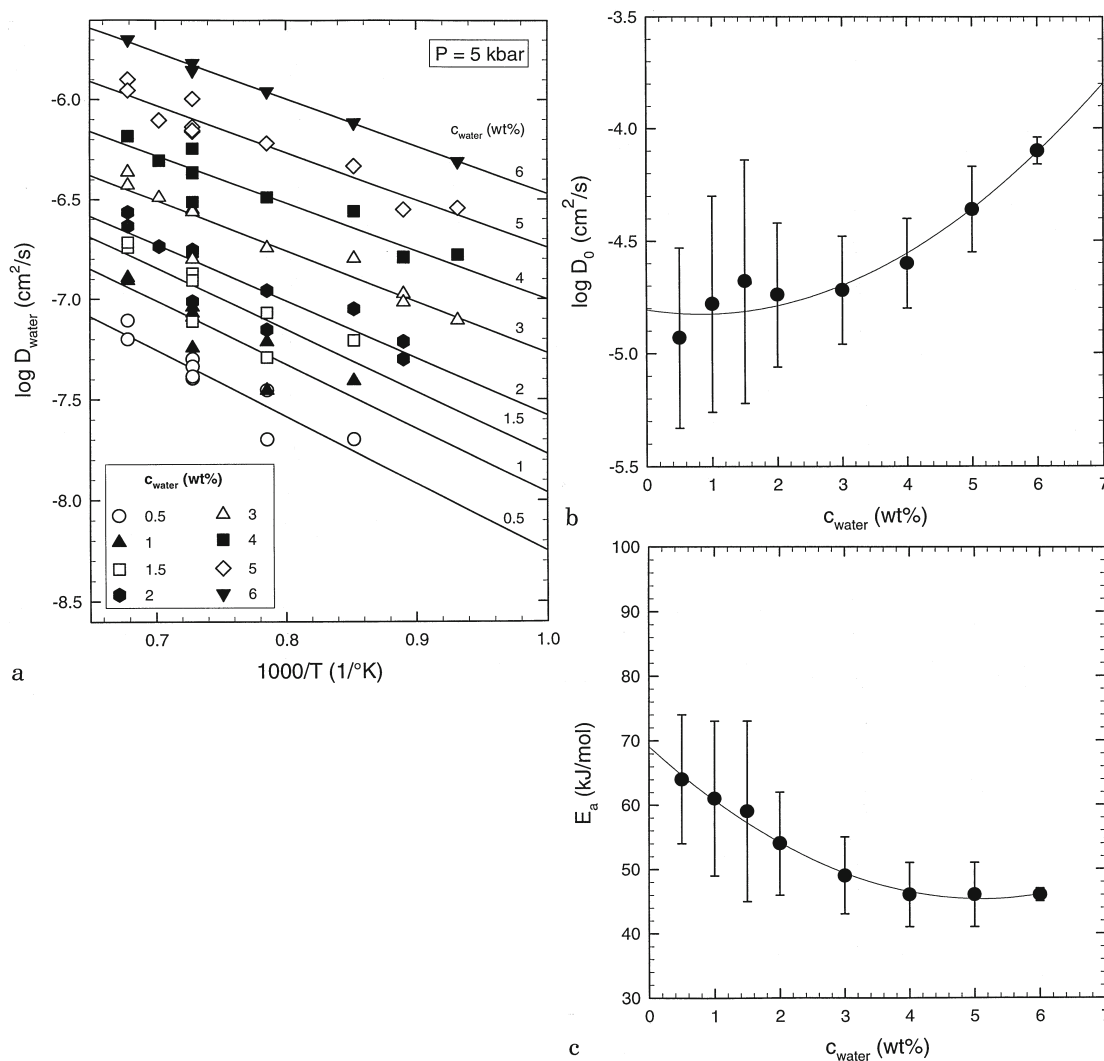


Fig. 8 a Temperature dependence of water diffusivity in haplogranitic melts. The slope of the fitted *straight lines* decreases systematically with increasing water content. **b** $\log D_0$ versus total water content

(see Fig. 6a). Diffusivities for low water contents may be estimated by using the linear relationship of D_{water} and C_{water} and extrapolating experimental data determined in the range 0.5 to 3 wt%. Furthermore it is important to note that the determined exponential dependence can not be extrapolated to very high water contents. An upper limit of D_{water} will be the diffusivity in supercritical H_2O .

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derived from the axis intersection of the linear fits of the Arrhenius plot. **c** Activation energy versus total water content derived from the slopes of the linear regression lines of the Arrhenius plot

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