

# Water in rhyolitic magmas: getting a grip on a slippery problem

Marcus Nowak\*, Harald Behrens

*Institut für Mineralogie, Universität Hannover, Am Welfengarten 1, D-30167 Hannover, Germany*

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## Abstract

Molecular water and hydroxyl groups are stable species in hydrous rhyolitic melts. To quantify the species concentrations we have used in situ IR spectroscopic measurements at 773–1073 K and 100–300 MPa in combination with an internally consistent calibration. The derived reaction enthalpy and entropy values for the homogeneous species reaction ( $\text{H}_2\text{O}_{\text{melt}} + \text{O}_{\text{melt}} = 2 \text{OH}_{\text{melt}}$ ) are  $35.0 \pm 1.2 \text{ kJ mol}^{-1}$  and  $27.7 \pm 1.3 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively and are independent of water content in the range 1.27–5.15 wt% water. Both values are significantly higher than extrapolated data based on species measurements of hydrous glasses at room temperature. The reaction entropy and enthalpy of hydroxyl formation are fundamental quantities for understanding and modeling hydrous magma properties. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* infrared spectroscopy; water; chemical fractionation; rhyolites; melts

## 1. Introduction

Water is the most abundant volatile component in Earth's crust, mantle and in magmatic liquids. Dissolved water contents in rhyolitic melts range up to 10 wt% at 500 MPa water pressure and 1073 K [1]. The dissolved water has a dramatic effect on physicochemical and kinetic properties of aluminosilicate melts [2,3]. The knowledge of the structural incorporation and the thermodynamic properties of water in silicate melts is fundamental for understanding melt rheology, diffusivities of chemical components in the melt,

volcanic hazards related to magma degassing, and petrogenesis. Thus, the quantification of thermodynamic properties of dissolved water in silicate melts is still challenging.

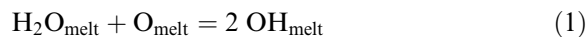
Burnham [4] developed a thermodynamic model for water dissolution in aluminosilicate melts based on  $P$ - $V$ - $T$  measurements and water solubility data, assuming a quantitative reaction of molecular water ( $\text{H}_2\text{O}$ ) with the aluminosilicate network and charge-balancing alkalis to produce hydroxyl groups (OH). In contradiction to this model, numerous spectroscopic studies at ambient pressure and temperature have shown that water is incorporated into quenched silicate melts (glasses) both as  $\text{H}_2\text{O}$  and as OH [5]. However, there is a fundamental limitation of these indirect studies for determination of water speciation in the melt: the relaxation time in silicate melts is

\* Corresponding author. Tel.: +49-511-7622564; Fax.: +49-511-7623045; E-mail: m.nowak@mineralogie.uni-hannover.de

so fast that water speciation cannot be quenched at temperatures above the glass transition temperature ( $T_g$ ) [6–8]. Thus, the water speciation in silicate glasses measured at room temperature represents at best the speciation near  $T_g$ . Above  $T_g$  the reaction rate is too high to quench in water speciation by normal laboratory methods whereas far below  $T_g$  the rate is too low to achieve equilibrium. Thus only a small range of about 150 K is suitable for the quench technique at a given water content.

The first high-temperature, high-pressure in situ IR spectroscopic studies of hydrous aluminosilicate melts confirmed that indeed both  $H_2O$  and OH are stable species in silicate melts [9,10]. However, there is still no consensus regarding the concentration of molecular water and hydroxyl in melt at high  $P$  and  $T$ . In the case of rhyolitic melt at 1073 K and 6 wt% total water, the OH/ $H_2O$  ratios derived from room temperature measurements on glasses, thermodynamic modeling of water solubility data, and in situ measurements on the corresponding melts cover a wide range from 0.58 [11] to 2.16 [9].

In principle, in situ near-IR spectroscopic studies of hydrous silicate melts allow the quantitative determination of the water species concentrations using combination bands of  $H_2O$  at  $5220\text{ cm}^{-1}$  ( $1.92\text{ }\mu\text{m}$ ) and OH at  $4500\text{ cm}^{-1}$  ( $2.22\text{ }\mu\text{m}$ ). The temperature-dependent equilibrium constant  $K$  of the homogeneous reaction:



can be derived from these speciation data. The prerequisite for this determination is the knowledge of thickness and density of the sample, and molar absorptivities of the combination bands ( $\epsilon_{H_2O}$  and  $\epsilon_{OH}$ ) [12,13]. Previous in situ studies were hampered by an insufficient knowledge of the density and molar absorptivities for hydrous melts [9,10,14]. Thus, simplifying assumptions were made such as temperature-independent molar absorptivities [10,14] or constant density of the melt in combination with a constant ratio of the linear molar absorptivities [9]. However, as shown recently, both density and molar absorptivities in fact vary with temperature [15,16]. The recently

published density model for hydrous silicate melts from Ochs and Lange [16] in combination with the complete set of in situ data allows us to resolve this controversy and to improve the thermodynamic data basis. With this model, the required absorption bands of a haplogranitic melt (76.14  $SiO_2$ , 13.53  $Al_2O_3$ , 4.65  $Na_2O$ , 5.68  $K_2O$ , in wt%)<sup>1</sup> containing 1.27–5.15 wt% water were calibrated directly and internally consistently in order to determine reliable temperature-dependent species concentrations of water in the haplogranitic melts above  $T_g$ .

## 2. Experimental and analytical methods

Near-IR spectra at  $3800\text{--}8000\text{ cm}^{-1}$  were measured with a Bruker IFS88 FTIR spectrometer with a spectral resolution of  $4\text{ cm}^{-1}$ , using a tungsten lamp as the light source, a  $CaF_2$  beam splitter, and an InSb detector. The intensity of the emitted light of the spectrometer is a periodic function of time, and the high-temperature spectra were calculated only with the modulated portion of the near-IR signal. Unmodulated light like heat radiation did not influence the measurements. In the experiments, a sapphire window cell was used up to 1073 K and 300 MPa [18]. In this externally heated cell, a hydrous glass disk of 4 mm diameter was compressed between a tungsten carbide piston and a cylindrical sapphire window. A platinum gasket surrounding the sample prevented loss of melt or water during the experiments. At 1073 K the accuracy in the temperature determination of the melt is smaller than  $\pm 10\text{ K}$ , the accuracy in the pressure determination is better than  $\pm 50\text{ MPa}$ . The relatively large error in pressure determination is not crucial for this study because pressure variation of a sample with 4.14 wt% water between 100 and 300 MPa at 1073 K had no effect on the absorptivities of the combination bands. The spectra measured after mechanical relaxation and temperature equilibra-

<sup>1</sup> Besides speciation measurements, the haplogranitic melt composition (labelled AOQ) has been used to investigate water solubility [17], water diffusivity [27] and melt viscosity [28].

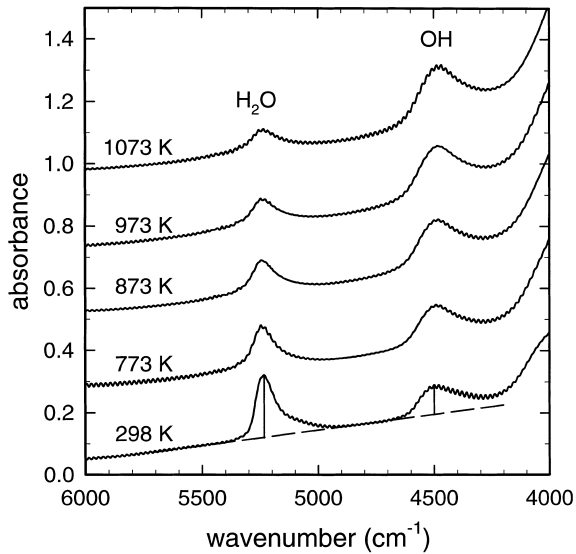


Fig. 1. Intensity-corrected near-IR absorption spectra of a haplogranitic melt/glass at 150 MPa pressure containing 4.14 wt% water, collected during the cooling period. Spectra are offset for clarity. The absorption band at  $5220\text{ cm}^{-1}$  is due to molecular water ( $\text{H}_2\text{O}$ ) and that at  $4500\text{ cm}^{-1}$  to hydroxyl groups (OH). The high-frequency modulations are due to interference fringes. Peak heights of the absorption bands were determined after subtraction of a linear baseline as shown in the spectrum at the bottom. For a more detailed discussion see [9,18].

tion of the cell at 1073 K and during the following cooling with a rate of  $5\text{ K min}^{-1}$  were not affected by a change in thickness of the melt. This is proven by the temperature-independent high-frequency sinusoidal oscillations (Fig. 1) caused by interference fringes that are very sensitive to the sample thickness [19]. Thus the error in thickness of the sample is defined by the precision of the micrometer ( $\pm 1\text{ }\mu\text{m}$ ) that was used to determine the thickness of the quenched melts (glasses) after the experiments. A loss of water during the in situ measurements was not observed. This was tested by measuring the water contents of the glass disks before and after the experiments using a Bruker A590 IR microscope.

Absorption spectra of the samples were calculated using reference spectra of water-free Infracil glass measured at the same temperatures. The room temperature spectra measured in the sapphire window cell gave slightly smaller intensities

of the absorption bands in comparison to spectra of the same sample measured by standard techniques. This effect is attributed to a small portion of the light beam of 6–16% that was reflected from parts of the cell and reached the detector without passing through the sample. During the individual cooling periods of the experiments, the portion of light that passed the sample and reached the detector was constant. Thus, the original spectra could be corrected very easily [9,18]. The peak heights of the combination bands (Table 1) were determined after subtraction of a linear baseline as shown in Fig. 1 and after filtering the sinusoidal oscillations. The error in peak height is  $\pm 0.003$  absorbance units.

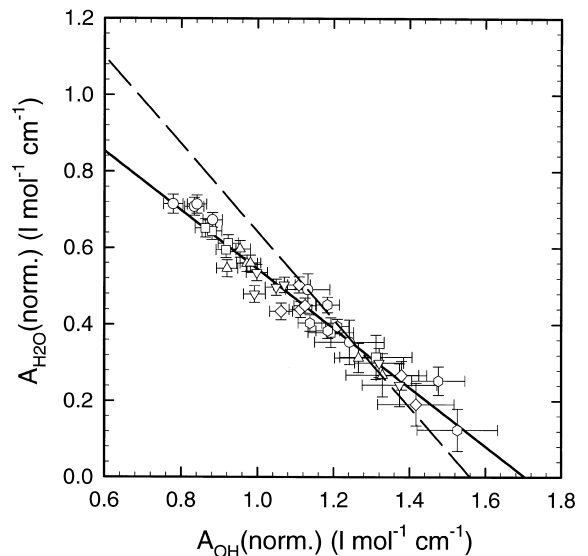


Fig. 2. Plot of normalized absorbances  $A_{\text{H}_2\text{O}}(\text{norm.})$  vs.  $A_{\text{OH}}(\text{norm.})$  for the hydrous haplogranitic melts. Water contents range from 1.27 to 5.15 wt%, and pressures from 100 to 250 MPa. Temperatures are 823 K (circles), 873 K (squares), 923 K (triangles up), 973 K (triangles down), 1023 K (diamonds), 1073 K (hexagons). Error bars are calculated from uncertainties of water analyses, thickness measurements, and determinations of the peak heights. The solid straight line was obtained by a linear least-squares regression analysis of the in situ data. The dashed line represents the molar absorptivities of the corresponding hydrous glasses at 298 K and 0.1 MPa.

Table 1  
Experimental data

$c_{\text{water}}$ (wt%)	$T_g$ (K)	$P$ (MPa)	$T$ (K)	$\rho$ (g l <sup>-1</sup> )	$d$ (cm)	$A_{\text{OH}}$	$A_{\text{H}_2\text{O}}$	$K$	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$K_{\text{calc}}$	Residual (%)
1.27	766	100	823	2311	0.0340	0.069	0.020	0.193 (34)	33.0 (3.2)	26.0 (3.5)	0.168	15
			873	2306		0.073	0.017	0.242 (47)			0.225	7.6
			923	2301		0.073	0.015	0.291 (64)			0.293	-0.7
			973	2296		0.076	0.013	0.345 (83)			0.370	-6.8
			1023	2291		0.078	0.011	0.464 (138)			0.457	1.5
			1048	2288		0.082	0.009	0.577 (190)			0.504	15
			1073	2286		0.084	0.007	0.83 (37) <sup>a</sup>			0.553	50
1.90	732	100	823	2292	0.095	0.041	0.176 (17)	0.168	4.8			
			873	2286	0.100	0.032	0.252 (29)	0.225	12			
			923	2280	0.106	0.026	0.343 (45)	0.293	17			
			973	2274	0.110	0.025	0.390 (52)	0.370	5.4			
			1023	2268	0.115	0.022	0.479 (71)	0.457	4.8			
			1048	2265	0.119	0.021	0.560 (88)	0.504	11			
			1073	2262	0.123	0.021	0.579 (89)	0.553	4.7			
4.14 <sup>b</sup>	667	150	773	2242	0.0330	0.130	0.132	0.118 (7)	35.8 (1.1)	28.1 (1.2)	0.121	-2.5
			823	2234		0.141	0.120	0.153 (9)			0.168	-8.9
			873	2225		0.156	0.103	0.216 (12)			0.225	-4.0
			923	2217		0.163	0.094	0.262 (15)			0.293	-11
			973	2208		0.176	0.083	0.343 (19)			0.370	-7.3
			1023	2200		0.186	0.073	0.436 (26)			0.457	-4.6
			1048	2196		0.191	0.069	0.485 (29)			0.504	-3.8
			1073	2192		0.197	0.064	0.565 (35)			0.553	2.2
4.14	667	200	773	2252	0.0330	0.130	0.142	0.109 (6)	32.9 (1.4)	24.1 (1.6)	0.121	-9.9
			823	2243		0.143	0.121	0.155 (9)			0.168	-7.7
			873	2235		0.149	0.109	0.187 (10)			0.225	-17
			923	2226		0.161	0.101	0.237 (13)			0.293	-19
			973	2218		0.168	0.090	0.288 (16)			0.370	-22
			1023	2209		0.186	0.084	0.380 (21)			0.457	-17
			1048	2205		-	-	-			0.504	-
			1073	2201		0.198	0.075	0.482 (27)			0.553	-13
4.14	667	250	773	2262	0.0344	0.142	0.133	0.132 (7)	32.7 (1.7)	25.2 (1.8)	0.121	9.1
			823	2253		0.157	0.120	0.180 (9)			0.168	7.1
			873	2245		0.163	0.106	0.219 (12)			0.225	-2.7
			923	2236		0.173	0.099	0.266 (14)			0.293	-9.2
			973	2227		0.188	0.089	0.353 (19)			0.370	-4.6
			1023	2219		0.197	0.079	0.437 (24)			0.457	-4.4
			1048	2215		-	-	-			0.504	-
			1073	2211		0.211	0.069	0.573 (33)			0.553	3.6
5.15	649	200	773	2224	0.0248	0.118	0.126	0.139 (9)	36.2 (1.3)	29.6 (1.4)	0.121	15
			823	2215		0.122	0.112	0.168 (11)			0.168	0.0
			873	2205		0.135	0.102	0.226 (15)			0.225	0.4
			923	2195		0.143	0.085	0.305 (20)			0.293	4.1
			973	2186		0.154	0.074	0.403 (27)			0.370	8.9
			1023	2176		0.164	0.067	0.511 (35)			0.457	12
			1048	2172		0.169	0.065	0.556 (38)			0.504	10
			1073	2167		0.175	0.062	0.631 (44)			0.553	14
<b>1.27–5.15</b>		<b>100–250</b>	<b>773–1073</b>						<b>35.0 (1.2)</b>	<b>27.7 (1.3)</b>		

Total water content  $c_{\text{water}}$  determined with near-IR spectroscopy at room temperature; glass transition temperature corrected to a quench rate of 5 K min<sup>-1</sup>:  $T_g = 786 - 83.47 \ln(c_{\text{water}})$  [21];  $\rho$  calculated with the model of Ochs and Lange [16];  $A_{\text{OH}}$  and  $A_{\text{H}_2\text{O}}$  are corrected absorbance values [9,18]; concentrations of H<sub>2</sub>O and OH (wt%) can be calculated by:  $c_{\text{H}_2\text{O}, \text{OH}} = 1802 A_{\text{H}_2\text{O}, \text{OH}} / (d \rho \epsilon_{\text{H}_2\text{O}, \text{OH}})$  using  $\epsilon_{\text{H}_2\text{O}} = 1.32 \text{ l mol}^{-1} \text{ cm}^{-1}$  and  $\epsilon_{\text{OH}} = 1.68 \text{ l mol}^{-1} \text{ cm}^{-1}$ ; equilibrium constant  $K$  calculated from Eq. 3;  $K_{\text{calc}}$  calculated from Eq. 5.

<sup>a</sup>This data point was not used for calculating  $\Delta H^\circ$  and  $\Delta S^\circ$  because of the large relative error of  $A_{\text{H}_2\text{O}}$ .

<sup>b</sup>The raw data of the melt with 4.14 wt% water at 150 MPa were published in [9].

### 3. Results

The Beer–Lambert law was used, as rewritten below to allow the determination of linear molar absorptivities:

$$1802 \cdot A_{\text{H}_2\text{O}} / (d \cdot \rho \cdot c_{\text{water}}) = \varepsilon_{\text{H}_2\text{O}} - \varepsilon_{\text{H}_2\text{O}} / \varepsilon_{\text{OH}} \cdot 1802 \cdot A_{\text{OH}} / (d \cdot \rho \cdot c_{\text{water}}) \quad (2)$$

where the peak heights of the absorption bands at  $4500 \text{ cm}^{-1}$  ( $A_{\text{OH}}$ ) and  $5220 \text{ cm}^{-1}$  ( $A_{\text{H}_2\text{O}}$ ) are normalized by the molecular weight of water, the total water content ( $c_{\text{water}}$ , in wt%), the sample thickness ( $d$ , in cm), and the density of the melts ( $\rho$ , in  $\text{g l}^{-1}$ ). The density model of Ochs and Lange [16] was used to calculate  $\rho$  as a function of  $T$ ,  $P$  and  $c_{\text{water}}$  (Table 1). The normalized absorbances  $A_{\text{H}_2\text{O}}(\text{norm.})$  vs.  $A_{\text{OH}}(\text{norm.})$  ( $\text{l mol}^{-1} \text{ cm}^{-1}$ ) of the in situ data are plotted in Fig. 2. A linear regression through the data yields  $\varepsilon_{\text{H}_2\text{O}}$  and  $\varepsilon_{\text{OH}}$  as the intercepts on the  $y$ -axis at  $x=0$  and the  $x$ -axis at  $y=0$ , respectively. It turned out that at temperatures above  $T_g$  between 823 and 1073 K the fitted straight line differs clearly from the regression line representing room temperature data for the same hydrous glasses [9]. The linear molar absorptivities and their ratios change dramatically from glass at room temperature to melt but are within error constant in the melt up to 1073 K:  $\varepsilon_{\text{H}_2\text{O}}$  ( $\pm 1\sigma$ ) decreases from 1.79 ( $\pm 0.02$ ) to 1.32 ( $\pm 0.03$ )  $\text{l mol}^{-1} \text{ cm}^{-1}$  and  $\varepsilon_{\text{OH}}$  ( $\pm 1\sigma$ ) increases from 1.56 ( $\pm 0.02$ ) to 1.68 ( $\pm 0.02$ )  $\text{l mol}^{-1} \text{ cm}^{-1}$ .

The species concentrations  $c_{\text{H}_2\text{O}}$  and  $c_{\text{OH}}$  were calculated with the properly determined high-temperature molar absorptivities for the melt. Assuming ideal mixing, these speciation data allow the calculation of an equilibrium constant:

$$K = [\text{OH}_{\text{melt}}]^2 / ([\text{O}_{\text{melt}}] [\text{H}_2\text{O}_{\text{melt}}]) \quad (3)$$

where  $[\text{OH}_{\text{melt}}]$ ,  $[\text{O}_{\text{melt}}]$ , and  $[\text{H}_2\text{O}_{\text{melt}}]$  are the molar fractions of OH, bridging oxygens, and molecular  $\text{H}_2\text{O}$  in the melt, respectively, based on a single-oxygen basis (Table 1). The  $1\sigma$  error of  $K$  is based on errors of  $d$ ,  $A_{\text{OH}}$ , and  $A_{\text{H}_2\text{O}}$ .

In the investigated pressure range of 100–300

MPa within error the in situ determined equilibrium constants are independent of pressure. This is consistent with previous studies [8] and implies that the volume change for the homogeneous species reaction in rhyolitic melt is negligible in the pressure range of the experiments [16,20].

The reaction enthalpy  $\Delta H^\circ$  and reaction entropy  $\Delta S^\circ$  of Eq. 1 were determined by linear least-squares regression of:

$$\ln K = -\Delta H^\circ / (RT) + \Delta S^\circ / R \quad (4)$$

for the temperature range 773–1073 K (Fig. 3). For the individual experiments  $\Delta H^\circ$  ( $\pm 1\sigma$ ) range from 32.7 ( $\pm 1.7$ ) to 36.2 ( $\pm 1.3$ )  $\text{kJ mol}^{-1}$  and

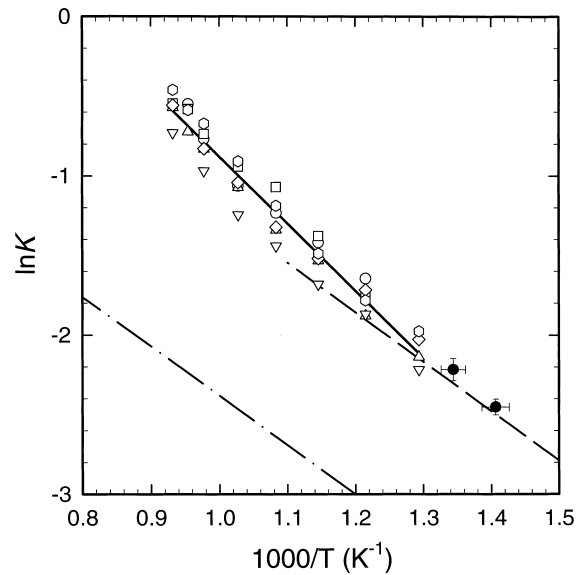


Fig. 3. Comparison of the temperature dependence of the equilibrium constant  $K$  of the homogeneous reaction  $\text{H}_2\text{O}_{\text{melt}} + \text{O}_{\text{melt}} = 2 \text{OH}_{\text{melt}}$  derived from three different methods. The solid line represents a linear least-squares regression through the newly calibrated in situ data of the hydrous haplogranitic melts containing 1.27 (circles, 100 MPa), 1.90 (squares, 100 MPa), 4.14 (triangles up, 150 MPa; triangles down, 200 MPa; diamonds, 250 MPa) and 5.15 wt% water (hexagons, 200 MPa) ( $\ln K_{\text{calc}} = -4210/T + 3.33$ ). The dashed line represents data of rapidly quenched rhyolitic glasses containing  $\leq 2.4$  wt% water which were annealed near  $T_g$  [8]. The dashed-dotted line is based on thermodynamic modeling of water solubility data for rhyolites [11]. Note the good agreement of isothermal annealing–rapid quench experiments (dots) and in situ data for haplogranitic melts. For errors of in situ data see Table 1.

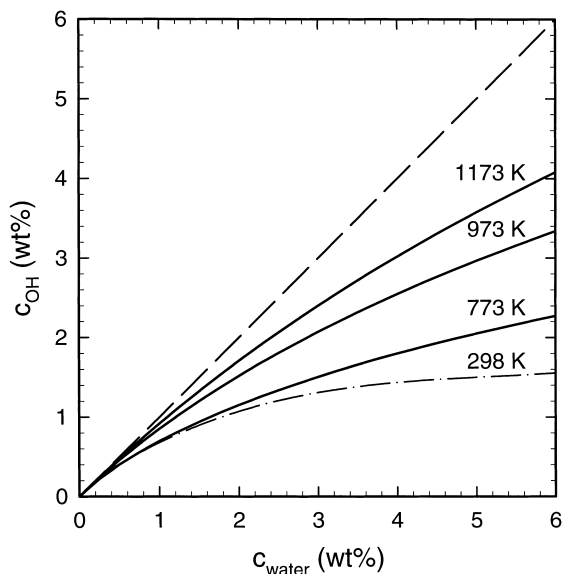


Fig. 4. Dependence of hydroxyl groups ( $c_{\text{OH}}$ ) on total water ( $c_{\text{water}}$ ) for the haplogranitic composition. Solid lines:  $c_{\text{OH}}$  vs.  $c_{\text{water}}$  based on  $K_{\text{calc}}$  (Eq. 5) derived from the internally calibrated in situ IR spectroscopic measurements. Dashed line: Prediction based on the assumption of a complete dissociation of water in the melt [4]. Dashed-dotted line: Speciation in the glasses at room temperature after quenching at 200 K  $\text{min}^{-1}$  [9].

$\Delta S^\circ$  ( $\pm 1\sigma$ ) from 24.1 ( $\pm 1.6$ ) to 29.6 ( $\pm 1.4$ ) J  $\text{mol}^{-1} \text{K}^{-1}$  (Table 1). A water concentration dependence and a pressure dependence are not indicated. Use of the complete set of in situ speciation data provides a  $\Delta H^\circ$  of 35.0 ( $\pm 1.2$ ) kJ  $\text{mol}^{-1}$  and a  $\Delta S^\circ$  of 27.7 ( $\pm 1.3$ ) J  $\text{mol}^{-1} \text{K}^{-1}$ . The resulting equilibrium constant  $K_{\text{calc}}$  in hydrous haplogranitic melts can be expressed as:

$$K_{\text{calc}} = 27.98e^{-4210/T} \quad (5)$$

The residuals of  $K_{\text{calc}}$  (measured minus calculated  $K_{\text{calc}}$ ) are within  $\pm 15\%$  in 38 of 44 cases and the average residual is  $\pm 9\%$ . Concentrations of  $\text{OH}_{\text{melt}}$  for the haplogranitic melt with total water contents up to 6 wt% were calculated with the newly determined  $\Delta H^\circ$  and  $\Delta S^\circ$  values (Fig. 4). The data show that the OH concentration strongly increases with temperature, for instance by 80% when heating a melt with 6 wt% water from 773 to 1173 K.

#### 4. Discussion

The equilibrium constants  $K_{\text{calc}}$  of the species reaction in the investigated temperature range found in this study are significantly lower, by a factor of about 2, than previously published in situ data for the haplogranitic melt with 4.14 wt% water at 150 MPa [9], bringing the new in situ data into excellent agreement with the data based on species concentrations determined in quenched rhyolitic glasses [8]. The consistency of both experimental approaches (in situ and quench technique) close to  $T_g$  was tested for the haplogranitic composition by two long-term annealing experiments in an externally heated pressure vessel at 500 MPa. Glasses containing 3.78 and 1.98 wt% water were processed for 4 days at 711 K and 12 days at 744 K, respectively. The samples were quenched to room temperature within a few seconds to preserve the water speciation at run conditions. The  $T_g$  for the two glasses were calculated with an estimated quench rate of 100 K  $\text{s}^{-1}$  to be 788 K for the glass with 3.78 wt% water and 868 K for the glass with 1.98 wt% water [21,22]. The  $K$  values measured on the quenched samples are in excellent agreement with the in situ data demonstrating equivalence of the two methods at these temperatures (Fig. 3). On the other hand,  $\Delta H^\circ$  of 25.8 kJ  $\text{mol}^{-1}$  and  $\Delta S^\circ$  of 15.6 J  $\text{mol}^{-1} \text{K}^{-1}$  obtained from quenched rhyolitic glasses [8] are significantly lower than our in situ data. Thus, extrapolating to magmatic temperatures the  $K$  values predicted by the two studies differ by a factor of 1.5 (Fig. 3). The scatter in the in situ data may partially contribute to this discrepancy. The  $2\sigma$  uncertainty for  $\ln K$  is 0.2, obtained from our data at the same temperatures but different water contents. This is an order of magnitude higher than for the quenched speciation data [8]. Another contribution to the differences between the in situ data and the quench data may be the use different background corrections of the near-IR spectra. Furthermore, physicochemical properties of hydrous silicate melts can be non-Arrhenian as shown by viscosity data for hydrous haplogranitic melts [21,22]. Thus, the discrepancy of the  $\Delta H^\circ$  and  $\Delta S^\circ$  values can be due to the different temperature ranges of

the quench experiments and in situ measurements. As a consequence, extrapolation of the quenched speciation data far beyond the range of determination may have a large error.

Another approach which has been used to determine  $\Delta H^\circ$  and  $\Delta S^\circ$  for the homogeneous species reaction is based on thermodynamic modeling of the effect of temperature on water solubility in rhyolitic melt [11]. Compared to our in situ determination, values derived from the solubility data are significantly smaller and the errors are very high ( $\Delta H^\circ = 25.8 (\pm 11.8) \text{ kJ mol}^{-1}$  and  $\Delta S^\circ = 6.0 (\pm 8.7) \text{ J mol}^{-1} \text{ K}^{-1}$ ). It is evident that the accuracy of water solubility measurements is not high enough to extract reliable speciation data without further constraints. Evidently in situ spectroscopic measurements at high pressures and temperatures in combination with an internally consistent calibration provide reliable values of  $\Delta H^\circ$  and  $\Delta S^\circ$ . Excitingly, brand new molecular dynamic (MD) simulations performed by Spera [23] on melts in the systems  $\text{NaAlO}_2\text{-SiO}_2$  and  $\text{CaAl}_2\text{Si}_2\text{O}_8$  yield a  $\Delta H^\circ \approx 35 \text{ kJ mol}^{-1}$  and a  $\Delta S^\circ \approx 20\text{--}25 \text{ J mol}^{-1} \text{ K}^{-1}$  for the homogeneous reaction:



where  ${}^{[0]}\text{O}$  represents an oxygen with no nearest T neighbors,  ${}^{[2]}\text{O}$  represents a bridging oxygen with two nearest T neighbors and  ${}^{[1]}\text{O}$  represents a non-bridging oxygen bonded to only a single T (Si or Al). The computed reaction enthalpies and the entropies are very similar to the in situ data although the bulk composition of our model rhyolite is not the same used in the MD simulations and the simulations are on liquids at much higher temperature. The agreement may indicate that the thermodynamic quantities  $\Delta H^\circ$  and  $\Delta S^\circ$  for the depolymerization reaction between the silicate network and network modifiers are not sensitive to the nature of the network modifier, i.e. these quantities are not affected by hydrogen bonding at least for highly polymerized melts (the ratio of non-bridging oxygens to tetrahedrally coordinated cations in dry glass is zero).

Eq. 6 is an alternative formulation of Eq. 1

implying that hydrogen is a network modifier. However, in highly polymerized aluminosilicate melts, the interpretation of NMR and IR structural data leads to contrasting structural models for OH incorporation [5]. NMR measurements support protons that are attached to bridging oxygens and OH connected to charge-balancing cations without depolymerizing the melt structure [24,25]. On the other hand, IR measurements support depolymerization of the melt structure with formation of OH connected to the network-forming cations, Si and Al. Although the structural interpretations are different, the quantifications of  $\text{H}_2\text{O}$  and OH by NMR and IR spectroscopy in the same aluminosilicate glasses are nevertheless in excellent agreement [26]. Thus, the quantities  $\Delta H^\circ$  and  $\Delta S^\circ$  based on the in situ determined water speciation data do not depend on the model for the structural incorporation of OH on the atomic scale.

## 5. Conclusions

Besides volumetric properties of hydrous silicate melts [16,20], the derived values of  $\Delta H^\circ$  and  $\Delta S^\circ$  of the water species reaction are of broad interest because these data are essential input data needed to develop and improve thermodynamic and kinetic models for hydrous magmas, e.g. water solubilities, melt rheologies, diffusivities of chemical components, bubble formation, and phase relations. These models will improve the understanding of hydrous magma properties which are essential to volcanic hazard mitigation and petrogenetic studies. Another application of the speciation data is the quantification of volatile partitioning between melts and hydrous minerals. For example,  $\text{H}_2\text{O}/\text{CO}_2$  ratios of cordierite equilibrated with a magma depend on the concentration of molecular  $\text{H}_2\text{O}$  and  $\text{CO}_2$  in the melt. Further, the fluorine content of amphiboles and biotites is not only affected by the fluorine concentration of the melt but also by the OH concentration. It seems that we now have more of a grip on the slippery problem of water in silicate melts.

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