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Reconciliation of experimental results on H₂O speciation in rhyolitic glass using in-situ and quenching techniques

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Abstract

In order to resolve the controversy over how to interpret experimental H₂O speciation results using in-situ and quenching techniques, we have carried out an infrared spectroscopic study to determine whether the molecular H₂O (5230 cm⁻¹) and OH (4520 cm⁻¹) band intensity variation with measurement temperature below glass transition is owing to species interconversion or to the temperature dependence of molar absorptivities. By comparing rhyolitic glasses with different total H₂O content from 0.18 to 0.76 wt.%, we show that the peak height of the 4520 cm⁻¹ band increases by a similar relative amount (about 2% if the baseline is fit with a flexicurve and 10% if the baseline is fit by a straight line) from 25 to 400°C, independent of the total H₂O content. The results show that (1) the molar absorptivities do indeed change with temperature, and (2) in our experiments below the glass transition temperature, species concentrations do not change noticeably with temperature, and the band intensity variations are caused mainly by changes in the shape of the absorbance bands with temperature. The absence of unquenchable species reaction in the glass state (on our experimental time scale) confirms that speciation data can be obtained using the quench technique from 400 to 600°C. On the other hand, the temperature dependence of the molar absorptivities must be quantified for the full potential of the in-situ technique to be realised. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Water is the most abundant volatile component of terrestrial magmas. Glass inclusions in minerals and phase equilibrium considerations indicate that rhyolitic and dacitic melts in magma chambers below active volcanoes may have water contents of up to

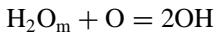
7 wt.% [1–7]. The presence of dissolved water has an overwhelming effect on the physical properties of the melt, decreasing viscosity and increasing the potential for explosive volcanism.

It is known from infrared spectroscopy that water is present in silicate glasses in the form of at least two species: H₂O molecules (referred to as H₂O_m hereafter) and hydroxyl groups (henceforth referred to as OH), characterised by the combination bands centred around 5230 cm⁻¹ and 4520 cm⁻¹, respectively, in the near infrared spectrum. The two species inter-convert through the following homogeneous re-

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action in the melt phase:



where O is an anhydrous oxygen. Assuming ideal mixing of the H_2O_m , O, and OH species, the equilibrium constant for the above reaction is:

$$K = \frac{[\text{OH}]^2}{[\text{H}_2\text{O}_m][\text{O}]}$$

where square brackets signify mole fractions calculated on a single oxygen basis [8]. Quantitative knowledge of species concentrations as a function of temperature, pressure and total water content is prerequisite for understanding and modelling the thermodynamics of hydrous silicate melt. Furthermore, the speciation plays an important role in H_2O diffusion [9,10] and solubility [11,12], thermal effect of degassing [13], and hydrogen isotope fractionation between the melt phase and another phase [14].

Two experimental methods have been used to investigate how hydrous species concentrations vary with temperature and total H_2O concentration (referred to as H_2O_t). In one approach, which we will refer to as the quenching technique, rhyolitic glasses are heated to a temperature of 400–600°C for the species reaction to reach equilibrium and quenched to room temperature for infrared analysis [7,9,15,16]². In quench studies, it is assumed that the speciation did not change during quenching. In a second approach, referred to as the in-situ technique, hydrous aluminosilicate glasses are heated to temperatures of 50–800°C and the sample analysed in situ, using infrared spectroscopy [18,19]. In order to interpret the spectra, molar absorptivities for the combination bands are assumed to be independent of measurement temperature. Concentrations of OH derived from the in-situ measurements are significantly higher than those measured in quenched samples (Fig. 1). Furthermore, the in-situ experiments show that infrared band intensities for the 5230 cm^{-1} and 4500 cm^{-1} bands vary even below the glass transition temperature (T_g). The initial interpretation of these results suggested that some hydrous species

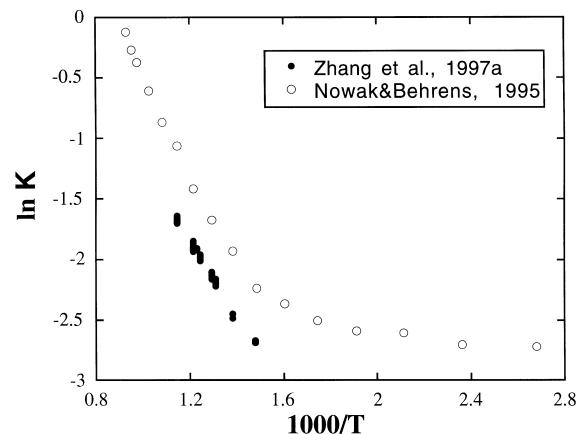


Fig. 1. A comparison of equilibrium coefficient K from two studies [7,18]. The data are as reported in literature without any reinterpretation. The data of Shen and Keppler [19] are similar to those of Nowak and Behrens [18] and are not shown for clarity.

interconversion occurs in the glass state, at temperatures close to room temperature and below T_g . The possibility of such reaction called into doubt the validity of quench studies, as measurements of hydrous species concentrations would not reflect their true, equilibrium values. Since the first in-situ measurements were published, the questions of whether molar absorptivities are temperature-dependent and whether species interconversion occurs in the glass state have remained controversial [19–21]. The disagreement over this basic issue limits many applications, such as thermodynamic modelling of hydrous silicate melts, H_2O diffusivity and solubility in silicate melts (which, in turn, are essential for understanding violent volcanic eruptions) and the thermal effect of degassing.

In order to resolve this controversy, we determined the effect of temperature on the infrared spectra of natural, rhyolitic glasses containing 0.18–0.76 wt.% water, at temperatures up to 500°C. The rationale behind our experiments was as follows. It is known that species concentration ratio ($\text{H}_2\text{O}_m/\text{OH}$) increases with H_2O_t . At very low H_2O_t , H_2O_m concentration is negligible and OH is the dominant species, meaning that the interconversion between H_2O_m and OH would not significantly affect the OH concentration. The variation of the 4520 cm^{-1} band intensity with temperature indicates, therefore, the dependence of the molar absorptivity on tem-

² Earlier experimental investigations of speciation involved experiments quenched from $\geq 700^\circ\text{C}$ to room temperature. It was shown that cooling rates were not high enough to preserve speciation at the experimental temperature [15,17]. These experimental results are not considered here.

perature. As H_2O_t increases, H_2O_m concentration becomes significant, and interconversion between H_2O_m and OH would significantly affect the OH concentration. Hence, we used two rhyolitic glasses with very low H_2O_t to examine whether molar absorptivity of the 4520 cm^{-1} band depends on temperature. We then studied another rhyolitic glass with higher H_2O_t to determine whether the entire intensity variation of the 4520 cm^{-1} band can be attributed to the temperature dependence of the molar absorptivities, or part of the band intensity variation is owing to species interconversion in the glass state.

2. Analytical methods

Infrared spectroscopic measurements were performed on three rhyolitic glasses with similar anhydrous compositions but different H_2O_t (Table 1). The samples were from Mono Craters, California, USA (PD and KS), and Dry Fountain flow, Erevan, Armenia (EDF).

Doubly polished cylindrical glass pieces were prepared for infrared analysis. The thickness of each sample was measured using a digital micrometer (Mitutoyo; precision = $2 \mu\text{m}$) to be $1.0\text{--}2.0 \text{ mm}$. Infrared measurements were made at variable temperatures using a modified Linkam THM600 heating/cooling stage under an IR microscope attached to a Bruker IFS88 infrared spectrometer.

Table 1
Composition of rhyolitic glasses used in this study (wt.%)

	PD	EDF	KS
SiO_2	77.00	76.69	76.52
TiO_2	0.06	0.11	0.06
Al_2O_3	12.68	12.70	12.61
FeO	0.91	0.67	1.00
MgO	0.03	0.08	0.03
CaO	0.54	0.57	0.54
Na_2O	3.87	4.05	4.03
K_2O	4.71	4.77	4.79
H_2O_t	0.182	0.215	0.761
Sum	99.97	99.86	100.34

Major oxide contents were determined by electron microprobe (KS from [7], PD and EDF from this work). H_2O_t contents were determined from room temperature IR spectra using the calibration of Zhang et al. [7].

Spectral resolution was better than or equal to 4 cm^{-1} . Further details of the analytical set-up are given elsewhere [21]. Background spectra were measured using the same experimental arrangement but without a sample. It was found that the background spectrum shape was unaffected by temperature changes within the range of this study. Hence a single, room temperature background spectrum was collected at the start of a series of analyses (meaning all spectra obtained for one spot on a sample during a heating–cooling cycle) and used for each of the subsequent measurements. Each series of spectra was collected within 60 min, and was terminated with a room temperature measurement to check that no water loss had occurred during the measurements. The sample was not moved between measurements, thus ensuring that exactly the same spot was analysed with each measurement. In this way, changes due to small inhomogeneity of the sample were avoided within the series of measurements. The infrared beam was focused to a spot diameter of $50 \mu\text{m}$, and 256 scans were accumulated for each spectrum.

We used two different ways to fit the baseline in order to examine the effect of the baseline shape. One type is a flexicurve baseline [15,16,22], and the other is a linear fit to the baseline for the 5230 cm^{-1} band and extended to the 4520 cm^{-1} band [18,21,23]. The peak heights of the combination bands were used as a measure of absorption intensity. The uncertainty in peak height determination was obtained from the noise of the spectra. The absolute uncertainty is 0.0005 to 0.0008 absorbance unit. The relative uncertainty is about 0.5% (KS), 1.3% (EDF), and 1% (PD) for the 4520 cm^{-1} band and 1.5% (KS), 13% (EDF), and 20% (PD) for the 5230 cm^{-1} band.

3. Results

Our experimental results show that below T_g (the exact temperature depends on H_2O_t and time scale), the shape and peak height of the combination bands of rhyolitic glasses vary systematically with temperature. Two spectra (one taken at room temperature and one taken at 400°C) for the KS sample are shown in Fig. 2A. The peak position of the OH combination band shifts to lower frequency from 4513 cm^{-1} at 25°C to 4503 cm^{-1} at 400°C for the KS sample, and

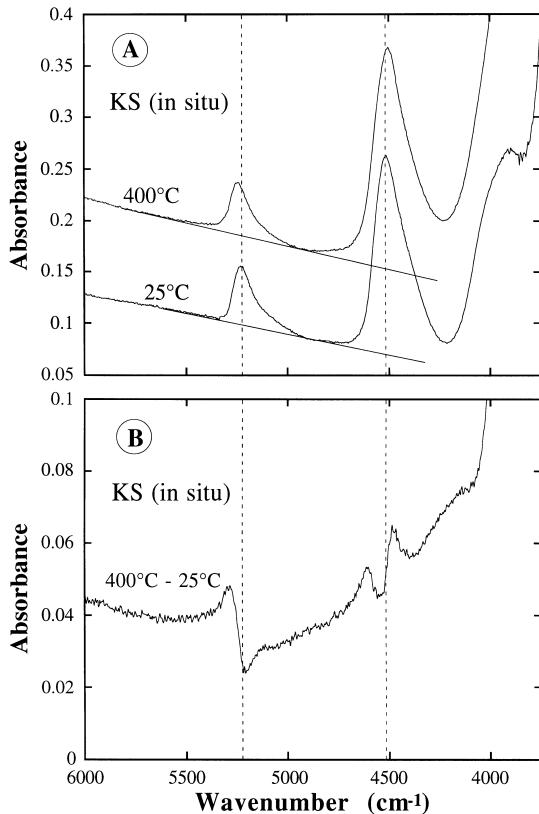


Fig. 2. (A) Two in-situ spectra for sample KS (1.5 mm thick) at 25°C and 400°C. Linear fits of the base line of each of the two spectra are shown. (B) The difference between the two spectra.

from 4522 cm^{-1} to 4509 cm^{-1} for the PD sample. On the other hand, the peak position of the H_2O_m combination band, which only can be properly located for the KS sample, shifts to higher frequency from 5230 cm^{-1} at 25°C to 5241 cm^{-1} at 400°C. Due to broadening of the fundamental O–H absorption band centred at $\sim 3550 \text{ cm}^{-1}$, the intensity below the 5200 cm^{-1} and 4520 cm^{-1} bands increases with temperature (Fig. 2A). This effect is responsible for the relatively large increase in the 4520 cm^{-1} band intensity when a linear baseline is used (see Fig. 3B).

The difference obtained by subtracting the 25°C spectrum from the 400°C spectrum shows that the 5230 cm^{-1} band changes with increasing absorbance at lower and decreasing at higher wavenumbers, thereby becoming more symmetric (Fig. 2B). The changes of the 4520 cm^{-1} band are more complex, with increasing absorbance at higher and lower

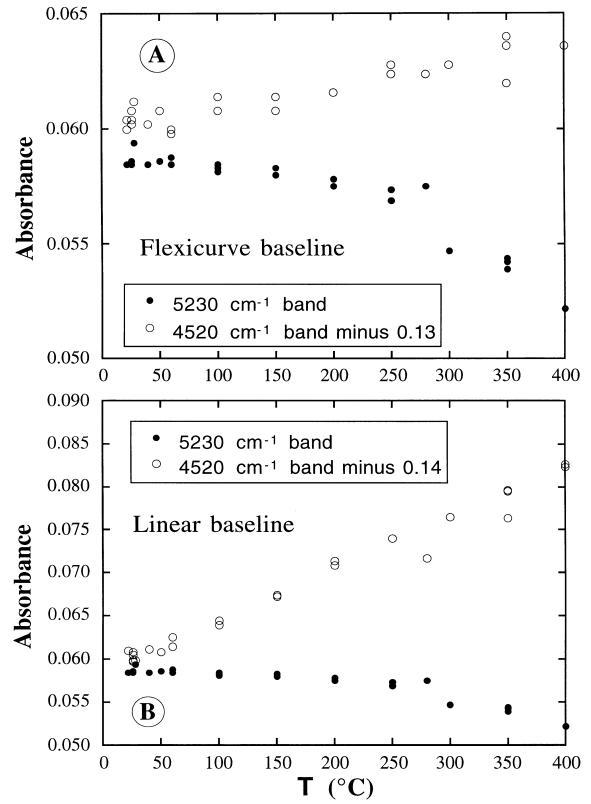


Fig. 3. Band intensity plot for the KS sample (1.5 mm thick). For better comparison, 0.13 or 0.14 is subtracted from the absorbance of the 4520 cm^{-1} band. With the linear baseline, the increase in the OH band intensity is not compensated by the decrease of H_2O_m band intensity. Note the difference in the vertical scale.

wavenumbers and decreasing absorbance at intermediate wavenumbers.

Fig. 3 shows how the absolute absorbances of the 4520 cm^{-1} (OH) and 5230 cm^{-1} (H_2O_m) bands vary with temperature for the KS sample. Using the flexicurve baseline, the intensity increase of the 4520 cm^{-1} band with temperature is small and is similar in magnitude to the intensity decrease of the 5230 cm^{-1} band. With the linear baseline (as used in the in-situ investigation of Nowak and Behrens [18]), the intensity of the 5230 cm^{-1} band is similar to that with the flexicurve baseline, but that of the 4520 cm^{-1} band is greater, especially at high temperatures. The intensity increase in the 4520 cm^{-1} band with temperature is much greater than the intensity decrease in the 5230 cm^{-1} band. Therefore, using the linear baseline, the variations of the two bands do not compensate each

other, which is inconsistent with the explanation that the band intensity variation in the glass state is owing to interconversion of the two species.

The relative change in 4520 cm^{-1} band intensity with temperature is similar for all three glasses (Fig. 4). Between 25 and 400°C , a small but systematic increase of up to 2% is visible if a flexicurve baseline is used (Fig. 4A). Using a linear baseline, the intensity increase over the same temperature range varies from 8 to 15% (Fig. 4B). Below 400°C the relative change in intensity for the haplogranitic AOQ sample studied by Nowak and Behrens [18] is very close to that of the rhyolitic samples (Fig. 4B). The small deviations between the trends shown in

Fig. 4B may be related to differences in composition (including H_2O_t) and the uncertainty arising from extrapolation of the linear fit to the 4520 cm^{-1} band. Above 400°C , the trends for the rhyolitic and haplogranitic samples diverge owing to the onset of species interconversion in the haplogranitic sample which has a high H_2O_t of 4.14 wt.% and hence a low T_g of $\sim 400^\circ\text{C}$ for the experimental time scale [18].

4. Discussion

The intensity ratio of the 5230 cm^{-1} band to the 4520 cm^{-1} band (roughly the species concentration ratio of $\text{H}_2\text{O}_m/\text{OH}$) is 0.31 for the KS sample, 0.10 for the EDF sample, and 0.059 for the PD sample (flexicurve fitting). If there were unquenchable equilibrium species interconversion owing to temperature variation, it would cause a relatively large variation of the 4520 cm^{-1} band intensity of the KS sample (there is more H_2O_m to be converted to OH) than that of the EDF and PD samples. On the other hand, if the band intensity variation were caused by the temperature dependence of the molar absorptivities, the 4520 cm^{-1} band intensity would vary the same relative amount for all the three samples. Fig. 4A shows that the relative intensity variation of the 4520 cm^{-1} band for the three samples is the same within error, indicating that all the band intensity variation is owing to the temperature dependence of the molar absorptivities, rather than temperature-induced species interconversion. Therefore, there is no noticeable interconversion between H_2O_m and OH below T_g . With baselines fit by a flexicurve, the molar absorptivity depends weakly on temperature. When the baseline is fit by a straight line (Fig. 4B), our data show similarly that there is no interconversion between H_2O_m and OH below T_g , but the molar absorptivity depends much more strongly on temperature³.

Two recent studies have discussed variations in the shape of the 5230 cm^{-1} and 4520 cm^{-1} bands. Behrens et al. [24] investigated an albitic glass with 6.58 wt.% H_2O_t , and showed that the peak height

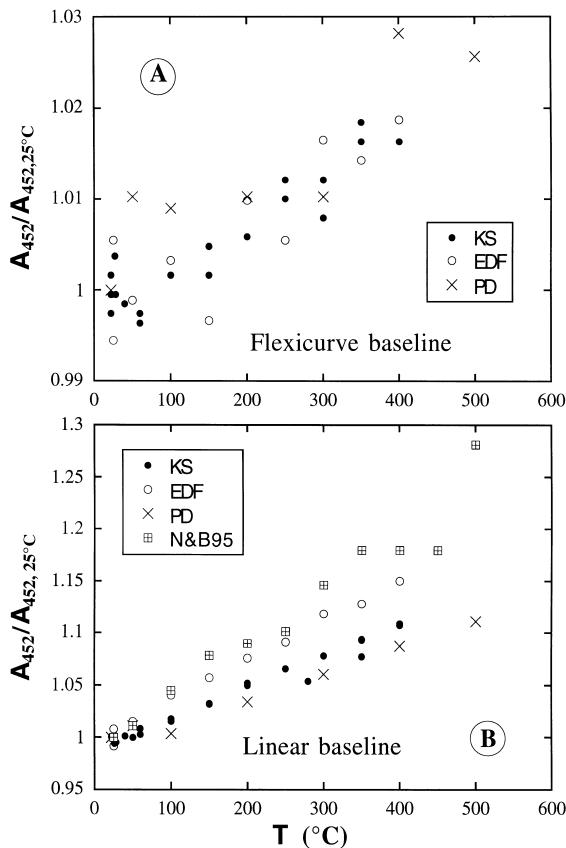


Fig. 4. The relative peak height change of the 4520 cm^{-1} band (sample thickness was 1.95 mm for PD, 0.999 mm for EDF and 1.5 mm for KS) with temperature using (A) flexicurve baseline, and (B) a linear baseline. Data of N and B95 are from [18]. The vertical axis is the peak height at a given temperature divided by that at room temperature. Note the vertical scale difference.

³ It may even be possible to choose some baseline such that the molar absorptivity (in particular, the integrated molar absorptivity) is independent of temperature. Reproducibly fitting such a baseline to a measured spectrum, however, may be problematic.

of the 5230 cm^{-1} band increases with temperature from -190°C to 70°C and then decreases, while that of the 4520 cm^{-1} band increases almost linearly with temperature from -190 to 300°C . They also showed that the integrated peak area of the 5230 cm^{-1} band decreases linearly, and that of the 4520 cm^{-1} band increases almost linearly with temperature from -190 to 300°C . In a recent study by Withers and Behrens [21], natural and synthetic glasses were hydrated to varying degrees, and used to determine quantitatively the temperature dependence of molar absorptivity at -173 to 27°C . The authors demonstrated temperature-dependent variations in the shape of the infrared spectra of hydrous silicate glasses. These studies interpreted the variations as reflecting the temperature-dependence of the effective molar absorptivities of the combination bands. Hence, our conclusion that the molar absorptivities depend on temperature is consistent with these studies. In addition, and in contrast to the previous studies using glasses with high H_2O_t , our new study comparing low and intermediate H_2O_t demonstrates unequivocally that species interconversion in the glass state is negligible.

The observed changes in band shapes and molar absorptivities for the near infrared combination bands with temperature are not surprising when we consider previously documented changes in the mid-infrared spectra of hydrous silicate glasses and melts. The near infrared absorption bands are stretching and bending combination modes. The 5230 cm^{-1} band combines the H_2O bending vibration (1630 cm^{-1}) and the OH stretching vibrations ($\sim 3550\text{ cm}^{-1}$). The 4520 cm^{-1} band is a combination of OH stretching vibrations and a band at around 1000 cm^{-1} . In polymerised silicate glasses, the peak area of the OH stretching vibration band typically decreases strongly with temperature while the peak height decreases only slightly [25–28]. On the other hand, for the H_2O bending vibration, both peak height and area decrease strongly with temperature [27].

5. Conclusions

Our new data demonstrate that hydrous species interconversion is negligible in the glass state. Hence quench studies can be used to measure very pre-

cisely equilibrium species concentrations, provided that care is taken to circumvent problems related to diffusive water loss and to excessive heating. The in-situ technique is promising and may represent the future of IR study of hydrous silicate melts, especially because these measurements can be made over a wide range of temperatures, well above glass transition. However, interpretation of hydrous melt spectra measured at high temperature requires prior knowledge of the molar absorptivities and the physical properties of the melt (e.g. the density) at the temperature of measurement. A method of determining high temperature molar absorptivities for hydrous species in silicate melts is therefore required for accurate interpretation of in-situ studies. We are optimistic that this may be achieved, either by in-situ, high pressure analysis of glasses with low H_2O_t , or by performing a calibration under specific pressure and temperature conditions.

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