

## *In situ* IR spectroscopy on hydrous albitic and rhyolitic glasses and its implications for water speciation and water species reactions in silicate glasses and melts

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The interpretation of spectroscopic and experimental data on speciation of water in silicate melts and glasses has been controversial. There are two experimental approaches using IR absorption spectroscopy for studying the equilibrium speciation of H<sub>2</sub>O as a function of temperature (and pressure) and total water content. One method is by holding the silicate glass at high temperature to reach equilibrium, then rapidly quenching it to room temperature and measuring IR spectra at room temperature (e.g. Zhang *et al.*, 1991). In the other method IR spectra are measured *in situ* as the sample is held at high temperature and pressure (Nowak and Behrens, 1995; Shen and Keppler, 1995). The *in situ* spectra show systematic changes in band intensities with temperature even in the glass state. Assuming that the molar extinction coefficients do not depend on temperature the authors of the *in situ* studies have inferred that (i) the speciation varied in the glass state (25-400°C), and (ii) the equilibrium constant for the speciation reaction depends more strongly on temperature than inferred from data using the quench technique. It is important to resolve whether the difference of the results from the two techniques is owing to the inability to quench species concentrations even from 400°C for the quench technique, or to the temperature dependence of extinction coefficients or other physical properties of the glass (e.g. density) for the *in situ* technique.

In order to resolve the apparent contradictions of the two experimental approaches we have measured near-infrared spectra of hydrous albitic glass (0.5–9.2 wt.% total water) and rhyolitic glasses (0.2–6.0) *in situ* in a wide temperature range (–192 to +600°C, depending on water content) as well as after quenching from high temperature. Because different baseline corrections have been applied to determine the concentrations of OH groups and molecular H<sub>2</sub>O from the combination bands at 4500

and 5220 cm<sup>-1</sup>, respectively, we have tested the equivalence of these methods for the albitic composition (9 samples). The baselines chosen are (i) a linear baseline for the band at 5220 cm<sup>-1</sup>, extension of this line to low frequency combined with a gaussian fitted to the band at 4000 cm<sup>-1</sup> as the baseline for the band at 4500 cm<sup>-1</sup> (Behrens *et al.*, 1996), (ii) linear baselines for both bands (Shen and Keppler, 1995) and (iii) flexicurve baselines for both bands (Newman *et al.*, 1986). If the molar extinction coefficients were independent on total water, OH and H<sub>2</sub>O concentrations differ by at most 3 % relative if absorbances (peak heights) are evaluated (for baselines i, ii and iii) or if integrated intensities (peak areas) are evaluated (for baselines i and ii). However, integrated intensities gives systematically lower OH and higher H<sub>2</sub>O (up to 10% relative) at low total water and higher OH and lower H<sub>2</sub>O (up to 7 % relative) at high total water. We suggest that the systematic differences may be due to the variation of the linear molar extinction coefficient with water content in accordance with results of Zhang *et al.* (1997).

IR spectra were measured *in situ* using a heating/cooling stage fitted to an IR microscope. Fig.1 display an example which is typical for the albitic and rhyolitic glasses. Systematic variation with temperature even close to liquid nitrogen temperature are observed for both absorbances and integrated intensities. For the H<sub>2</sub>O band the absorbance has a maximum close to room temperature whereas the integrated intensity is continuously decreasing with temperature. For the OH band both the absorbances and the integrated intensities are continuously increasing with temperature. For albitic glasses the T-dependence of the integrated intensity of the H<sub>2</sub>O band is almost independent on water content (about 3% per 100K) and only is weakly effected by the type of baseline correction. In contrast, the OH band is

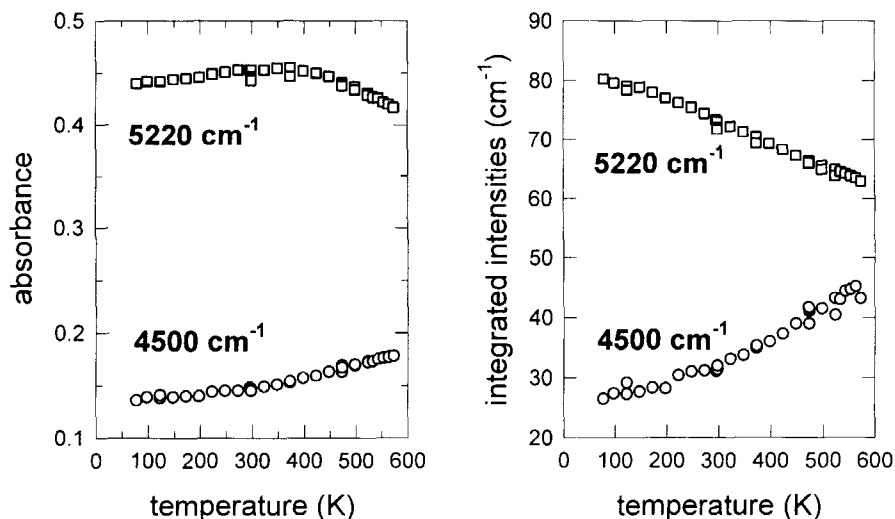


FIG. 1. Absorbances and integrated intensities of the OH combination band at  $4500\text{ cm}^{-1}$  and the  $\text{H}_2\text{O}$  combination band at  $5200\text{ cm}^{-1}$  determined from *in situ* IR spectra of an albitic glass with 6.58 wt.% total water (sample thickness: 0.0501 cm, baseline type i).

strongly effected by the baseline correction. For an albitic glass containing 6.0 wt.% total water the integrated intensity decrease by 16% per 100 K if baseline i is used but only by 2% per 100 K if baseline ii is used. The effect of temperature typically is smaller for rhyolitic than for the albitic glasses. Direct evidence for a temperature dependence of the extinction coefficients is given for the OH band by *in situ* measurements with a rhyolitic glass containing 0.2 wt.% total water. For this glass the OH concentration-change with temperature is negligible because the molecular  $\text{H}_2\text{O}$  content is very low and its conversion into OH does not affect the OH content significantly. Heating to  $500^\circ\text{C}$  increases the peak height of the  $4520\text{ cm}^{-1}$  band by a similar relative amount (about 2% after baseline correction iii) than for a glass containing 0.8 wt.% total water which contains some  $\text{H}_2\text{O}$ .

From our results there are two possible ways for determination of water species in glasses and melts at elevated temperature using *in situ* IR spectra (a) extrapolation of data from low temperatures at which no species reactions are expected and (b) determination of extinction coefficients at high temperature using a set of sample with known water contents. For the albitic glass we have determined the integral molar extinction coefficients separately for various

temperatures using plots of normalized integrated intensities (see Behrens *et al.*, 1996). Using these values we found that the species concentrations do not vary noticeably with temperature in the glass state. Indication for an interconversion of water species is given by both *in situ* measurements and room temperature measurements on the rapidly quenched glasses only for temperatures close to or above the glass transition (e.g. at about  $550^\circ\text{C}$  for an albitic glass with 2.0 wt.% water and at about  $400^\circ\text{C}$  for an albitic glass with 6.0 wt.% water.).

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