

## LETTERS

### Infrared spectroscopy of hydrous silicate melts to 1000 °C and 10 kbar: Direct observation of H<sub>2</sub>O speciation in a diamond-anvil cell

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#### ABSTRACT

Near-infrared spectra of hydrous silicate melts are reported up to 10 kbar and 1000 °C. Measurements were performed using an externally heated diamond-anvil cell that allows precise control of pressure and temperature. In hydrous glasses, changes in H<sub>2</sub>O speciation occur below the glass-transformation temperature; however, the standard enthalpy of the speciation reaction  $\text{H}_2\text{O} + \text{O} = 2\text{OH}$  is very different for the melt and glass phases. For a peraluminous sodium aluminosilicate glass containing 8.1 wt% total H<sub>2</sub>O, the temperature dependence of the H<sub>2</sub>O speciation equilibrium can be described by two equations:  $\ln K = -2.65 - 1.91 \times 10^2 \text{ K } T^{-1}$  (glass phase,  $\Delta H = 1.6 \text{ kJ/mol}$ ) and  $\ln K = 3.04 - 3.64 \times 10^3 \text{ K } T^{-1}$  (melt phase,  $\Delta H = 30.3 \text{ kJ/mol}$ ). The intersection of these two equilibrium curves defines a glass-transformation temperature of 335 °C. The near-infrared spectrum of a peraluminous sodium silicate melt with 30–40 wt% H<sub>2</sub>O at 10 kbar and 1000 °C shows the presence of both OH and H<sub>2</sub>O; however, exceptionally strong speciation changes occur upon quenching. From visual observation, it appears that at 10 kbar and 1000 °C there is complete miscibility between this melt and water. Therefore, these data constitute the first infrared spectra of a phase beyond the critical point in a system of silicate melt and H<sub>2</sub>O.

#### INTRODUCTION

H<sub>2</sub>O is the most important volatile component in the Earth's crust and mantle and has a dramatic effect on the physical and chemical properties of silicate melts (Burnham, 1979). Because it is well established that H<sub>2</sub>O dissolves both as OH and as molecular H<sub>2</sub>O in silicate melts (Bartholomew et al., 1980; Stolper, 1982a, 1982b), the speciation of H<sub>2</sub>O in silicate melts has attracted considerable attention over the last decades (McMillan, 1994). However, very little spectroscopic data are available for hydrous silicate melts above the glass-transformation temperature ( $T_g$ ) (Aines et al., 1983; Keppler and Bagdassarov, 1993; Nowak and Behrens, 1995). Originally, it was suggested that the speciation of H<sub>2</sub>O in quenched glasses is rather similar to the speciation in the melt at the temperature from which the glasses were quenched (Stolper, 1982a). Dingwell and Webb (1990), however, pointed out that the relaxation rate in silicate melts above  $T_g$  is so fast that H<sub>2</sub>O speciation cannot be quenched at temperatures above  $T_g$ . They suggested that the H<sub>2</sub>O speciation in a glass represents the equilibrium at the bulk  $T_g$  of the glass. Keppler and Bagdassarov measured infrared spectra of a rhyolite containing 300 ppm H<sub>2</sub>O to 1300 °C. They observed changes in the type of OH groups present below bulk  $T_g$ , suggesting that direct measurements

of speciation below and above  $T_g$  are necessary to study the equilibrium between OH and H<sub>2</sub>O. Very recently, Nowak and Behrens (1995) reported first measurements of this equilibrium in hydrous melts using an optical cell based on the piston-cylinder principle. This cell is limited to 800 °C and 3 kbar. In the present paper, we report direct FTIR measurements of H<sub>2</sub>O speciation in hydrous silicate melts to 1000 °C and 10 kbar. These measurements were made with a diamond cell specially designed for FTIR studies.

#### EXPERIMENTAL METHODS

An anhydrous, peraluminous sodium aluminosilicate glass was prepared by slowly heating a mixture of analytical grade Na<sub>2</sub>CO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> in a Pt crucible to 1600 °C. The glass was quenched in water and crushed. Chemical analysis by ICP-AES yielded a composition of 82.5 wt% SiO<sub>2</sub>, 11.6 wt% Al<sub>2</sub>O<sub>3</sub>, and 5.2 wt% Na<sub>2</sub>O. Hydrous glasses of defined H<sub>2</sub>O content were prepared by weighing appropriate amounts of doubly distilled water and anhydrous glass powder into Pt capsules, sealing the capsules in an electrical arc, and annealing them for 7 d at 2.5 kbar and 1000–1100 °C in rapid-quench TZM autoclaves.

High-pressure FTIR spectroscopic measurements were

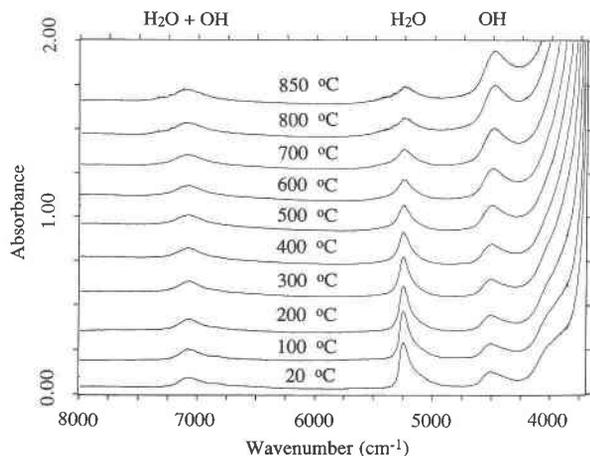


Fig. 1. Near-infrared spectra of a hydrous sodium aluminosilicate glass (8.1 wt% H<sub>2</sub>O) from room temperature to 850 °C. Experiments were conducted under isochoric conditions in an externally heated diamond-anvil cell. Hydrostatic pressure was generated by a hydrous fluid phase of about 0.5 g/cm<sup>3</sup> density, which yields a pressure of 2.5 kbar at 850 °C. Sample thickness was 210 μm. Spectra are raw data without any smoothing or background correction.

performed using an externally heated diamond cell similar in design to that described by Bassett et al. (1993). The tungsten carbide seats in this cell as well as the supporting steel plates were modified to allow optical access with an opening angle of 60° on both sides of the sample. During the high-temperature experiments, the cell was purged with a gas mixture of 99% Ar and 1% H<sub>2</sub> to avoid oxidation of the diamonds (Type I) and Mo heaters. The mica windows in the original design by Bassett et al. (1993) were replaced by single-crystal CaF<sub>2</sub> plates.

Infrared spectra were measured using a Bruker IFS 120 HR Fourier-transform spectrometer coupled with a Bruker IR microscope. A tungsten light source, a CaF<sub>2</sub> beam-splitter, and a narrow-band MCT detector were used in all experiments. The IR beam was focused to a spot size of 60 μm, and 200 scans were accumulated for each spectrum.

High-pressure experiments in the diamond cell were conducted using Re gaskets of 250 μm initial thickness and a hole of 500 μm diameter. The culet size of the diamonds was 1 mm. The principle of these experiments is based on the observation by Bassett et al. (1993) that after a first heating cycle, the sample chamber in this cell behaves as an isochoric system. Therefore, if one uses water as pressure medium and determines the homogenization or ice-dissolution temperature, one can determine the bulk density of water in the cell. Together with the equation of state of water, this allows an accurate determination of pressure at any temperature. Temperature was measured by type-K thermocouples touching the diamond anvils. The temperature in the sample chamber was calibrated against the thermocouple reading by observing the melting of NaNO<sub>3</sub> and NaCl in the cell at zero pressure.

At the beginning of a high-pressure experiment, an irregular chip of hydrous glass was loaded into the cell together with pure water and an air bubble. The thickness of the glass chip was slightly thinner than the initial thickness of the gasket. Upon heating, the bubble disappeared and the fluid phase homogenized. At higher temperature, the glass chip rounded at the edges while the gasket deformed slightly. Around 600–800 °C, this process caused the silicate melt to make contact with both the upper and the lower diamond anvil while being laterally surrounded by fluid. This geometry allows FTIR measurements through the melt phase under perfectly hydrostatic conditions without spectroscopic interference by the fluid. Measurements were then taken starting from the maximum temperature and decreasing in steps of 50 °C. During cooling, the silicate melt remained in contact with both anvil faces. Each measurement took about 2 min. The homogenization temperature of the fluid was observed during cooling and allows a precise estimate of pressure for each temperature during the experiment. After the experiment, the thickness of the Re gasket was measured and was used as the effective sample thickness for the evaluation of the spectroscopic data. During the cooling cycle, the H<sub>2</sub>O content in the glass sample did not change significantly. This was shown by heating the sample after the first measurement cycle to the maximum initial temperature and immediately taking a spectrum, which was indistinguishable from the original.

## RESULTS

Figure 1 shows the near-infrared spectra of a peraluminous sodium aluminosilicate glass containing 8.1 wt% total H<sub>2</sub>O from room temperature to 850 °C. The water medium used to generate pressure in this experiment had a density of 0.5 g/cm<sup>3</sup>, which yields a pressure of 2.5 kbar at 850 °C. We conducted similar experiments at pressures up to 7 kbar and did not observe a significant effect on the spectra, suggesting that the pressure dependence of the speciation equilibrium is rather small, in agreement with Zhang (1993). The following observations can be made from the spectra in Figure 1, using generally accepted band assignments (McMillan, 1994): (1) The overtone band at 7000 cm<sup>-1</sup>, due to both OH and molecular H<sub>2</sub>O, shows little change in integrated intensity over the temperature range studied. This is consistent with a constant total H<sub>2</sub>O content in the sample. (2) The band due to the combination mode of molecular H<sub>2</sub>O at 5200 cm<sup>-1</sup> decreases in intensity with temperature. (3) The combination band of OH groups at 4500 cm<sup>-1</sup> increases with temperature. (4) There are major changes in band shape at 5200 and 7000 cm<sup>-1</sup>. Observations 2 and 3 suggest that with increasing temperature, the H<sub>2</sub>O speciation equilibrium in the melt, H<sub>2</sub>O + O = 2OH, is shifted to the right side.

Figure 2 shows the result of another type of experiment. In this experiment, the sample was heated to 800 °C and then cooled down. Upon cooling, a fluid density of 0.79 g/cm<sup>3</sup> was determined. The sample temperature

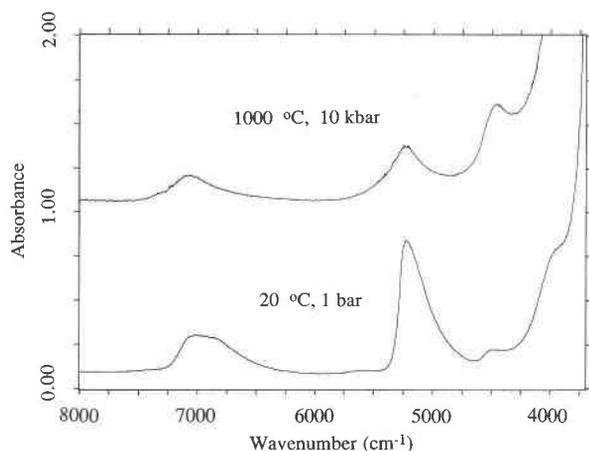


Fig. 2. Near-infrared spectra of a hydrous sodium aluminosilicate melt containing about 30–40 wt% H<sub>2</sub>O at 1000 °C and an estimated pressure of 10 kbar, and of the glassy phase obtained by quenching this melt to ambient conditions. Sample thickness was 195  $\mu\text{m}$ .

was then raised to 1000 °C. At this temperature, it was observed that the contrast between the melt and the fluid phase diminished and that a homogeneous phase formed. This suggests that the experiment had reached conditions above the critical curve in the system silicate melt–water (Paillat et al., 1992). The spectrum of the very H<sub>2</sub>O-rich silicate melt or fluid phase (30–40 wt% total H<sub>2</sub>O) is shown in the upper part of Figure 2. The pressure estimate of 10 kbar is based on an extrapolation of the fluid isochore into the supercritical field; because the excess mixing volumes of the H<sub>2</sub>O and silicate component are not known, the uncertainty in this estimate is high, probably on the order of  $\pm 3$  kbar.

Figure 2 shows that even at very high H<sub>2</sub>O contents and extreme  $P$  and  $T$  conditions, OH and molecular H<sub>2</sub>O species are present that are similar to those in the silicate melts containing <10 wt% H<sub>2</sub>O. However, enormous changes in speciation occur upon quenching. During cooling of the supercritical phase to room temperature within 1–2 min, melt droplets precipitated and finally the entire phase solidified to an aggregate of glass droplets without interstitial fluid. The glass was milky and birefringent, but no discrete crystals could be observed under the microscope. The lower spectrum in Figure 2 shows that upon quenching almost the entire hydrous component was converted to molecular H<sub>2</sub>O.

### DISCUSSION

To evaluate quantitatively the speciation changes apparent in Figure 1, the integral extinction coefficients of the OH and H<sub>2</sub>O species at high temperature must be known. At room temperature, these coefficients were calibrated using glasses of known H<sub>2</sub>O content, yielding  $\epsilon_{\text{H}_2\text{O}} = 214 \text{ L}/(\text{mol}\cdot\text{cm}^2)$  (5200  $\text{cm}^{-1}$  band) and  $\epsilon_{\text{OH}} = 208 \text{ L}/(\text{mol}\cdot\text{cm}^2)$  (4500  $\text{cm}^{-1}$  band). Infrared extinction coefficients essentially depend on two factors, the transition

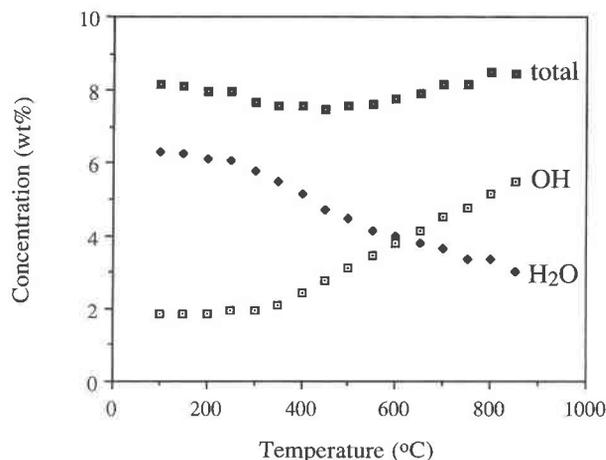


Fig. 3. Water speciation in a hydrous sodium aluminosilicate glass (8.1 wt% total H<sub>2</sub>O) as a function of temperature. OH values are the amounts of H<sub>2</sub>O in weight percent that are dissociated into OH groups.

dipole momentum and the population density of the vibrational states involved (e.g., McQuarrie, 1983). The transition dipole momentum is a function only of molecular geometry, which may or may not significantly change with temperature. The population density of vibrational states, however, is governed by a simple Boltzmann distribution and therefore always changes with temperature. However, one can easily calculate that, because of the high energy of the 4500 and 5200  $\text{cm}^{-1}$  bands, a temperature change of 800 °C would affect the population of these excited states by only about 2%. Therefore, in the

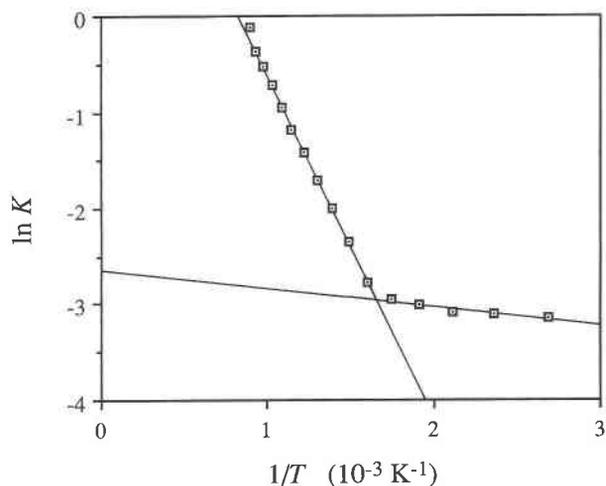


Fig. 4. Temperature dependence of the equilibrium constant  $K$  of the reaction  $\text{O} + \text{H}_2\text{O} = 2\text{OH}$ . The steep line applies to the melt phase, the shallow line to the glass. The intersection defines the glass-transition temperature of 335 °C. The equations for the two regression lines are (glass phase)  $\ln K = -2.65 - 1.91 \times 10^2 \text{ K } T^{-1}$  and (melt phase)  $\ln K = 3.04 - 3.64 \times 10^3 \text{ K } T^{-1}$ . This corresponds to a standard reaction enthalpy of 1.6 kJ/mol in the glass and of 30.3 kJ/mol in the melt phase.

following discussion, it is assumed that the temperature dependence of these extinction coefficients is negligible over the temperature range studied. This assumption is justified by the following observations: (1) The band at 7000 cm<sup>-1</sup>, which is proportional to the total H<sub>2</sub>O content, barely changes in integrated intensity. (2) If the amounts of OH and H<sub>2</sub>O in the sample are calculated using the assumption of constant extinction coefficients, the data very closely add up to the nominal total H<sub>2</sub>O content (Fig. 3). Small deviations may be due to a slight temperature dependence of  $\epsilon$  or to density variations. (3) Studies of hydrous solutions at high  $P$  and  $T$  have shown that the extinction coefficients of overtones and combination bands are much less affected by hydrogen-bonding interactions than the fundamental modes (Buback et al., 1987). This means that the intensities of the overtone and combination bands are rather insensitive to temperature.

From the data shown in Figure 3, the equilibrium constant of the water speciation reaction,  $K = c_{\text{OH}}^2/c_{\text{O}} \cdot c_{\text{H}_2\text{O}}$ , can be calculated assuming ideal mixing. A plot of the logarithm of this equilibrium constant vs. reciprocal temperature is shown in Figure 4. Apparently, water speciation changes in the glassy state, but the reaction enthalpy is very different in the glass and melt phases. The temperature dependence of  $K$  can be described by two equations:  $\ln K = -2.65 - 1.91 \times 10^2 \text{ K } T^{-1}$  (glass phase,  $\Delta H = 1.6 \text{ kJ/mol}$ ) and  $\ln K = 3.04 - 3.64 \times 10^3 \text{ K } T^{-1}$  (melt phase,  $\Delta H = 30.3 \text{ kJ/mol}$ ). The intersection of these two equilibrium curves defines a glass-transformation temperature for H<sub>2</sub>O speciation of 335 °C. Very similar values for  $\Delta H$  in both the glass and melt phases were recently reported by Nowak and Behrens (1995) for a haplogranitic composition containing 4.1 wt% H<sub>2</sub>O. This suggests that the temperature dependence of H<sub>2</sub>O speciation is rather similar for a variety of melt compositions and total H<sub>2</sub>O contents.

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