High-temperature FTIR spectra of H$_2$O in rhyolite melt to 1300 °C

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Abstract

A rhyolite glass containing about 300 ppm by weight of H$_2$O was heated in a microscope heating stage to 1300 °C, and true infrared absorbance spectra were obtained in situ at various temperatures using an FTIR spectrometer, together with the focusing optics of an IR microscope. Virtually all H$_2$O dissolved as OH at all temperatures. However, large changes both in band shape and integral extinction coefficient suggest that the type of OH species present changes with temperature. At 20 °C, the OH stretching band with a maximum at 3570 cm^{-1} was asymmetric with a broad shoulder extending to lower frequencies, which is due to strongly H-bonded OH groups. By 500 °C, still well below the bulk glass transformation temperature (T$_g$ about 800 °C) a large part of the strongly H-bonded species had disappeared, causing the OH stretching band to become more symmetrical and decreasing the integral extinction coefficient. This trend continues to higher temperatures. At 1300 °C, the spectrum in the OH stretching region consisted of a rather sharp, symmetrical band at 3570 cm^{-1}, superimposed on a broad absorption feature, which is probably due to a highly mobile type of proton. The high mobility of protons means that a distinction between OH groups and molecular H$_2$O in a H$_2$O-rich melt is probably impossible at these temperatures. All changes observed in the spectra are completely reversible upon cooling to room temperature, and no significant amount of H$_2$O was lost from the sample during the entire experiment. Our results show that the speciation and integral extinction coefficients of OH in silicate melts and glasses are strongly temperature dependent and that significant structural changes occur well below the bulk glass transformation temperature.

Introduction

The structural role of H$_2$O in silicate melts has attracted considerable attention because of the pronounced effect it has on the physical and chemical properties of melts and on phase equilibria (e.g., Burnham, 1979). Various types of spectroscopic investigations (by IR, Raman, NMR, and other methods) have been carried out on quenched melts (glasses) in order to understand melt structure. Nevertheless, there is still no general consensus on the structure of the geologically most important hydrous aluminosilicate melts. Bartholomew et al. (1980) and Stolper (1982a, 1982b) demonstrated that dissolved H$_2$O is present in glasses, both as OH groups and in molecular form, the ratio of OH/H$_2$O being a function of H$_2$O content. The nature of the OH-bearing species, however, is still controversial. The existence of a band in the near infrared at 4500 cm^{-1}, interpreted as being due to a combination of the stretching vibrations of O-H and (Al,Si)-OH suggests the presence of Si-OH or Al-OH groups in the glass. This contrasts somewhat with the observation that none of the Raman bands in the Si-O or Al-O stretching region shows a significant isotopic shift upon deuteration, as expected for Si-OH or Al-OH groups. However, McMillan et al. (1993) recently attributed this effect to strong vibronic coupling within the silicate framework and pointed out that this observation does not preclude the presence of Si-OH or Al-OH groups. Recent NMR studies (Kohn et al., 1989), however, suggested that all H$_2$O in aluminosilicate glasses is present either as molecular H$_2$O or as NaOH groups and that the silicate framework is not depolymerized by H$_2$O. In contrast to the situation with aluminosilicate glasses, recent NMR studies in the system Na$_2$Si$_4$O$_9$-H$_2$O provided conclusive evidence for the depolymerization of the silicate framework by H$_2$O (Kümmerlen et al., 1992).

Virtually all previous studies of glass structure have been motivated by the assumption that a glass somehow preserves the structural state of the melt, probably at the bulk glass transformation temperature (Dingwell and Webb, 1990). In order to test this assumption, direct infrared spectroscopic measurements of H$_2$O in silicate melts at high temperature are necessary. With the exception of one study by Aines et al. (1983), such data have not yet been available. In this paper we present true infrared absorbance spectra of a rhyolite melt containing about 300 ppm of H$_2$O from room temperature to 1300 °C. These measurements show that glasses at room temperature are not necessarily a good model for the behavior of H$_2$O in silicate melts at high temperature, as significant structural changes are observed upon heating. This observation might help to partially resolve the controversy on the structure of hydrous aluminosilicate melts.

EXPERIMENTAL

Measurements of infrared absorbance spectra at high temperature are complicated by black body radiation emitted from the sample and the heater. Measurements above 500 °C are difficult and those above 900–1000 °C nearly impossible using conventional, dispersive IR spectrometers (e.g., Aines et al., 1983; Gable and Shankland, 1984). These problems can be overcome by Fourier transform infrared (FTIR) spectroscopy. In an FTIR spectrometer, the beam passes through an interferometer that imposes a modulation on the IR signal, i.e., the intensity of the IR beam is a periodic function of time. The spectra are calculated from the modulated part of the IR signal only; any nonmodulated radiation does not affect the measurements. Therefore, the nonmodulated IR radiation emitted from the furnace and the sample does not interfere with the measurement, provided two conditions are met: (1) Only a small amount of unmodulated thermal radiation reaches the detector, so that the detector response function does not become nonlinear because of excessively strong IR irradiation. (2) Thermal radiation from the sample does not enter the interferometer and is reflected back into the detector. Were the thermal radiation to enter the interferometer, it would become modulated and therefore pose a severe experimental problem.

In our experiments, the first condition was met by focusing the IR beam on a very small sample held in a microscope heating stage. The small size of the sample and, therefore, the small amount of remitted thermal radiation also helped to meet the second condition. This was checked by switching off the IR light source and observing the interferogram during a high-temperature measurement. With the source turned off, the modulated IR signal always disappeared entirely. Therefore, the spectra recorded are true absorbance spectra, and no correction for emission was necessary (compare Aines and Rossman, 1984).

All measurements were carried out with a Bruker IFS 120 high-resolution FTIR spectrometer. This instrument contains a permanently aligned, Michelson-type interferometer with a 30° angle of incidence. A W source and a Si-coated CaF$_2$ beam splitter were used for all experiments. The modulated IR beam was passed into a Bruker IR microscope equipped with all-reflecting, cassegranian optics and a high-sensitivity, narrow-band mercury cadmium telluride (MCT) detector.

The sample was a doubly polished disk (0.77-mm thickness, 1-mm diameter) of rhyolite glass prepared by the melting of obsidian from the Dry Fountain lava flow, Erevan, Armenia. The chemical composition of this obsidian was given by Bagdassarov and Dingwell (1993). According to room-temperature FTIR measurements and the extinction coefficients by Stolper (1982b; rhyolite sample GML), the rhyolite samples used contain about 300 ppm by weight of H$_2$O.

The rhyolite disk was mounted in a heating stage designed by A. Slutsky (Vernadsky Institute of Geochemistry, Moscow) and brought into the focal plane of the
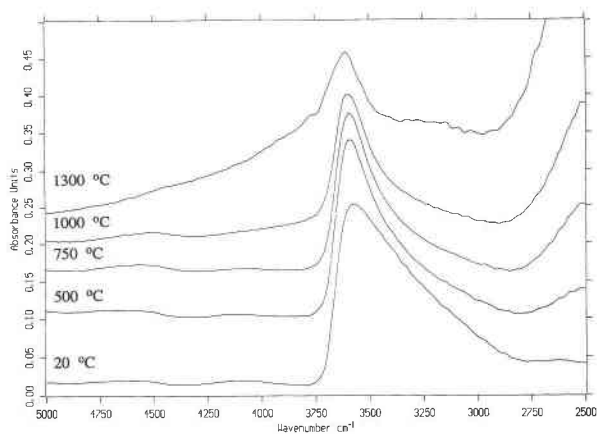

Fig. 1. FTIR spectra of H$_2$O in rhyolite glass and melt at various temperatures. Sample thickness 0.77 mm, H$_2$O$_{tot}$ content approximately 300 ppm by weight (estimated using extinction coefficients of Stolper, 1982b).

microscope. In this heating stage, the sample is held in a loop of Pt wire with a type S thermocouple closely attached to it. The sample is surrounded by a cylindrical piece of Pt foil which serves as a heater. Temperatures of about 1500 °C can be reached with this stage. The maximum temperature gradient across the sample is about 5 °C (Zapunnyy et al., 1989). During the experiment, a stream of pure N$_2$ is passed through the heating stage. Infrared measurements were done through two quartz glass windows, and background spectra were also measured through these windows. An external aperture in the rear focal plane of the objective was used to limit the spot sizes of the measurements to about 200 μm in diameter. About 100–250 scans with 4-cm^{-1} resolution were accumulated for each measurement, which took only a few minutes. Spectra were measured up to 1300 °C. Above this temperature, deformation of the rhyolite sample due to high surface tension creates a lens effect, causing the intensity of IR radiation that reaches the detector to drop off rapidly. Without this effect, measurements at even higher temperatures would have been possible.

RESULTS AND DISCUSSION

Infrared spectra at various temperatures in the OH stretching region are shown in Figure 1. It is well established that rhyolite glasses with very little H$_2$O contain dominantly OH groups, with almost no molecular H$_2$O (Stolper, 1982a, 1982b). This is probably true at high temperature as well, because available data on the temperature dependence of H$_2$O speciation from quench-rate and diffusion experiments (Dingwell and Webb, 1990; Zhang et al., 1991) suggest that at high temperature the equilibrium favors the formation of OH by means of the reaction H$_2$O + O = 2OH. Therefore, it is reasonable to assume that all the features seen in Figure 1 are due to OH groups and not to molecular H$_2$O.

All spectral changes seen in Figure 1 are completely reversible, and no significant loss of H$_2$O occurred during
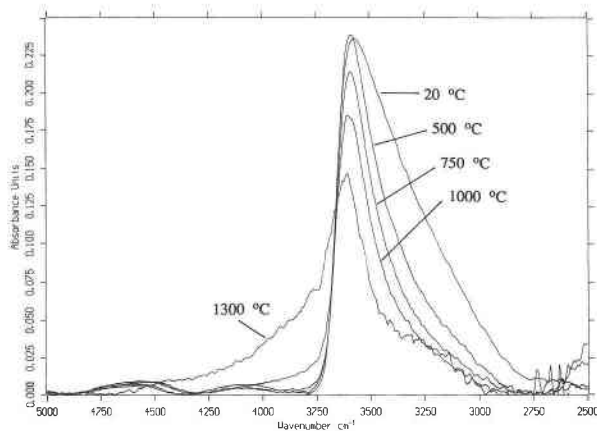
Fig. 2. FTIR spectra of H_2O in rhyolite glass and melt at various temperatures, after background correction.
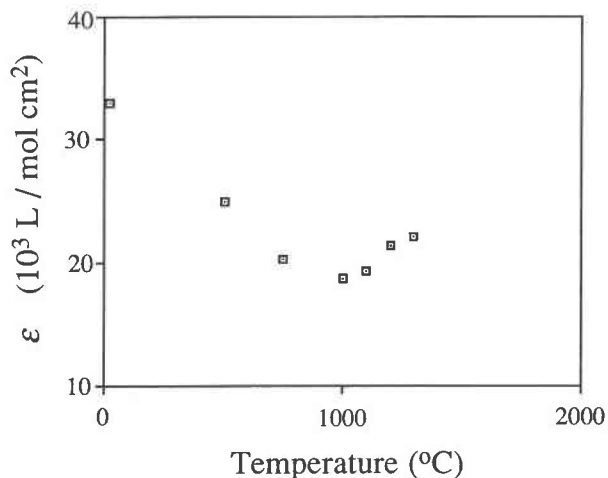

Fig. 3. Integral extinction coefficient of the OH stretching vibration in rhyolite glass and melt as a function of temperature.

the entire experiment. This was shown by cooling the sample to room temperature after each high-temperature experiment and collecting a spectrum. All such spectra were indistinguishable from the original spectrum observed at 20 °C. After heating to 1300 °C, the sample was recovered and repolished; the IR spectrum collected after that was identical in shape to the original spectrum and yielded an unchanged H_2O content. No bubbles were formed during the experiment. This result is not surprising when one considers the small diffusion coefficient of OH as compared with molecular H_2O in silicate melts (Zhang et al., 1991) and that each high-temperature measurement took only a few minutes.

With increasing temperature, there is an increase in absorption below 3000 cm⁻¹ (Fig. 1) due to (Al,Si)-O stretching vibrations of the silicate matrix and their overtones. At the highest temperature investigated, a tail of this band extends into the OH-stretching region. To facilitate comparison of spectra recorded at different temperatures, a background correction was carried out that removed the contribution of the silicate matrix. This was done by a spline fit through points of the spectra outside of the OH absorption region. The results are shown in Figure 2.

At room temperature, the OH stretching band is strongly asymmetric, with a maximum near 3570 cm⁻¹ and a broad shoulder extending down to <3000 cm⁻¹. This broad shoulder is due to strongly H-bonded OH groups, since the OH stretching frequency generally decreases with increasing H bond strength (Nakamoto et al., 1955). With increasing temperature, the strongly H-bonded species disappear, and the band becomes narrower and more symmetrical. At the same time, the integrated extinction coefficient in the OH stretching region decreases dramatically (Fig. 3). This observation is consistent with the assumption that strongly H-bonded species are being converted into OH groups with weaker H bonding, as the extinction coefficient of OH is known to increase with H bond strength (Paterson, 1982). By 1000 °C most of the strongly H-bonded species have disap-

peared, and the integral extinction coefficient remains almost constant during continued heating. The sharpening of the OH band with temperature up to 1000 °C is very unusual, as in crystalline materials OH bands tend to broaden upon heating (Aines and Rossman, 1984).

It is interesting to note that changes in band shape and extinction coefficient are already seen at 500 °C, well below the bulk glass transformation temperature (T_g about 800 °C for dry rhyolite: Dingwell and Webb, 1990). This means that there must be some mechanism for the reorganization of OH bonds that is decoupled from the bulk relaxation of the glass structure (compare Zhang and Stolper, 1993). Such a mechanism could be of the type $X - OH\cdots O - Y \rightarrow X - O\cdots HO - Y$, which is a simple jumping of a proton from one O atom to another within a H bridge, converting a strongly H-bonded OH group into one with weak H bonding. This type of repolarization of H bonds is known to contribute to the anomalous mobility of protons in liquid H_2O (Moore, 1983).

At 1300 °C, the spectrum in the OH stretching region consists of a rather sharp, symmetrical peak, superimposed on a broad background feature. Such broad bands have been observed at high temperatures during the dehydration of minerals; they have been attributed to highly mobile, gaslike species (Aines and Rossman, 1984). As pointed out above, all our present knowledge about the temperature dependence of the reaction $H_2O + O = 2OH$ in silicate melts makes it very unlikely that this band is due to molecular H_2O. More likely, it is caused by protons jumping rapidly from one O atom to another one, by a mechanism similar to that suggested above. The broadness of this band is partially due to the range of bond strengths involved and partially due to true lifetime broadening. This interpretation is supported by the observation that the integral extinction coefficient remains almost constant above 1000 °C, within the potential errors introduced by background correction (Fig. 3), sug-

gesting an almost constant average H bond strength. Therefore, the appearance of the broad band at high temperature must be due to some dynamic effect. If the line width of this band (about 500 cm^{-1}) were exclusively due to lifetime broadening, the lifetime τ of the bonded species could be estimated using the Heisenberg uncertainty relation $\delta E \cdot \tau = h/2\pi$, where E is energy and h is the Planck constant. This yields a lifetime of the bonded state on the order of 10^{-14} s, i.e., a lifetime comparable with one vibrational period of the OH group. This would mean that on the average each proton jumps from one O atom to another one within the time required for one OH stretching vibration. In reality, the true lifetime of the bonded state is probably somewhat longer, because lifetime broadening is probably not the only reason for the width of the OH band observed at high temperature.

The previous considerations suggest that hydrous silicate melts are proton conductors at high temperature. Additionally, at very high temperature, OH groups might contribute significantly to the mobility of H_2O in silicate melts, whereas at lower temperatures, the diffusion rate is essentially determined by the mobility of molecular H_2O. Because of the high jumping frequency of protons at 1300 °C, probably no distinction between OH groups and molecular H_2O can be made anymore in an H_2O-rich melt at these temperatures. This will hold true if the observed motility of the protons is not just local but occurs throughout the entire melt structure. In order to distinguish molecular H_2O and OH spectroscopically, the two combination bands in the IR spectrum at 5200 cm^{-1} (H_2O) and 4500 cm^{-1} (OH) have to be resolved. If the line width of the OH fundamental vibration at 3750 cm^{-1} is on the order of 500 cm^{-1}, the same holds for the combination bands. This means that the peaks at 5200 and 4500 cm^{-1} cannot be resolved anymore.

ACKNOWLEDGMENTS

REFERENCES CITED

Aines, R.D., and Rossman, G.R. (1984) The high temperature behavior of water and carbon dioxide in cordierite and beryl. American Mineralogist, 69, 319–327.

Aines, R.D., Silver, L.A., Rossman, G.R., Stolper, E.M., and Holloway, J.R. (1983) Direct observation of water speciation in rhyolite at temperatures up to 850 °C. Geological Society of America Abstracts with Program, 15, 512.

Bagdassarov, N.S., and Dingwell, D.B. (1993) Frequency dependent rheology of vesicular rhyolite. Journal of Geophysical Research, 98, 6477–6487.

Bartholomew, R.F., Butler, B.L., Hoover, H.L., and Wu, C.K. (1980) Infrared spectra of a water-containing glass. Journal of the American Ceramic Society, 63, 481–485.

Burnham, C.W. (1979) The importance of volatile constituents. In H.S. Yoder, Ed., The evolution of the igneous rocks, p. 439–482. Princeton University Press, Princeton, New Jersey.

Dingwell, D.B., and Webb, S.L. (1990) Relaxation in silicate melts. European Journal of Mineralogy, 2, 427–449.

Gable, C.W., and Shankland, T.J. (1984) Radiative heat transfer in molten and glassy obsidian. Journal of Geophysical Research, B89, 7107–7110.

Kohn, S.C., Dupree, R., and Smith, M.E. (1989) A multinuclear magnetic resonance study of the structure of hydrous albite glasses. Geochimica et Cosmochimica Acta, 53, 2925–2935.

Kümmerlen, J., Merwin, L.H., Sebald, A., and Keppler, H. (1992) Structural role of H_2O in sodium silicate glasses: Results from ²⁹Si and ¹H NMR spectroscopy. The Journal of Physical Chemistry, 96, 6405–6410.

McMillan, P.F., Poe, B.T., Stanton, T.R., and Remmele, R.L. (1993) A Raman spectroscopic study of H/D isotopically substituted hydrous aluminosilicate glasses. Physics and Chemistry of Minerals, 19, 454–459.

Moore, W.J. (1983) Physikalische Chemie (3rd edition), 1236 p. De Gruyter, Berlin.

Nakamoto, K., Margoshes, M., and Rundle, R.E. (1955) Stretching frequencies as a function of distances in hydrogen bonds. Journal of the American Chemical Society, 77, 6480–6488.

Paterson, M. (1982) The determination of hydroxyl by infrared absorption in quartz, silicate glasses and similar materials. Bulletin de Minéralogie, 105, 20–29.

Stolper, E. (1982a) The speciation of water in silicate melts. Geochimica et Cosmochimica Acta, 46, 2609–2620.

——— (1982b) Water in silicate glasses: An infrared spectroscopic study. Contributions to Mineralogy and Petrology, 81, 1–17.

Zapunnyy, S.A., Sobolev, A.V., Bogdanov, A.A., Slutsky, A.B., Dmitriev, L.V., and Kunin, L.L. (1989) An apparatus for high-temperature optical research with controlled oxygen fugacity. Geochemistry International, 26, 2, 120–128.

Zhang, Y., and Stolper, E.M. (1993) Reaction kinetics, fictive temperature, cooling rates, and glass relaxation. Eos, 74 (Spring meeting suppl.), 351.

Zhang, Y., Stolper, E.M., and Wasserburg, G.J. (1991) Diffusion of water in rhyolitic glasses. Geochimica et Cosmochimica Acta, 55, 441–456.