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In situ spectroscopic study of water speciation in the depolymerized $Na_2Si_2O_5$ melt

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ABSTRACT

Water speciation in the sodium disilicate melts containing 1.3–8.1 wt.% of total water was studied by near-infrared spectroscopy at 900 °C and pressures from 0.2 to 1.7 GPa using externally heated diamond anvil cell. Hydrous sodium disilicate melt served both as a sample and as a pressure medium in the experiments, which allowed to keep the total water content of the melt constant and thereby to perform an internally consistent calibration of molar absorption coefficients for the near-infrared bands of water species. No pressure dependence of water speciation was observed in the studied pressure range, indicating that formation of structurally bound OH groups at the expense of H_2O molecules in the melt is accompanied by a negligible volume change. At 900 °C, compositional dependence of water speciation was found to be much weaker than that expected from the previously reported data for low-temperature range near the glass transition. This can be explained by significant weakening of hydrogen bonding in the sodium silicate melts at high temperatures.

1. Introduction

Incorporation of water into the network structure of silicate melt changes its physical properties and has a substantial effect on melt viscosity, density and liquidus temperature. For instance, with the addition of 5 wt.% water viscosity of rhyolitic melt at 1200 °C and 200 MPa drops from 10^5 to 10^2 Pa s (Giordano et al., 2008), a decrease of ~10% is expected for its density (Ochs and Lange, 1997; 1999) and its liquidus temperature gains >250 °C depression (Holtz et al., 2001).

According to Stolper (1982b), interaction between water and melt can be described by a speciation reaction between the molecular water (H_2O_m), the bridging oxygen of silicate network structure (O) and the structurally bound hydroxyl groups (OH) in the melt:

$$H_2O_m(\text{melt}) + O(\text{melt}) = 2OH(\text{melt}) \quad (1)$$

and a heterogeneous reaction between the melt and the vapor phases:

$$H_2O(\text{vapor}) = H_2O_m(\text{melt}). \quad (2)$$

Dingwell and Webb (1990) first quantitatively demonstrated based on the structural relaxation theory that the product of the speciation reaction (1) is strongly favored by increasing temperature in the melt state. This prediction was later confirmed for the well-polymerized aluminosilicate melts by a number of experimental studies (e.g., Romano et al., 1995; Shen and Keppler, 1995; Sowerby and Keppler, 1999; Nowak and Behrens, 2001). Romano et al. (1995) raised the question about the compositional dependence of water speciation equilibrium and showed that exchange of K for Na has little influence on water speciation in the melt. On the other hand, Behrens and Yamashita (2008) have found ~3 ln units higher values of equilibrium constant K_1 for the speciation reaction (1) at temperatures 200–320 °C for the more depolymerized $Na_2Si_4O_9$ and $Na_2Si_6O_{13}$ compositions (number of non-bridging oxygens per silica tetrahedron, NBO/T, is 0.50 and 0.33 respectively on the anhydrous basis) than those reported for the haplogranitic composition (NBO/T ≈ 0) by Behrens and Nowak (2003). Though such difference of equilibrium constants was reported at the temperature near the glass transition, dependence of K_1 on the degree of melt depolymerization has never been evaluated at magmatic temperatures and pressures.

The primary task of this work was to determine the effects of pressure and temperature on water speciation equilibrium in the depolymerized silicate melts. In order to fulfill this task, we performed a series of quantitative spectroscopic measurements for the depolymerized $Na_2Si_2O_5$ melt, a structural analog of basaltic melt in terms of the number of non-bridging oxygens per silica tetrahedron (NBO/T ≈ 1.0), at 900 °C and pressures to 1.7 GPa using externally heated diamond anvil cell technique.

2. Experimental methods

2.1. Preparation of starting glasses

Anhydrous sodium disilicate glass was prepared from the mixture of reagent grade SiO_2 and Na_2CO_3 powders in the ratio corresponding to

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Table 1
Compositions of the synthesized anhydrous glass (NS2) and the reference soda-lime glass (SRM 621).

wt.%	NS2	[SRM 621]	
SiO_2	65.47 (0.33)	70.68 (0.48)	[71.13][a]
Al_2O_3	0.04 (0.05)	3.06 (0.17)	[2.76]
CaO	0.03 (0.04)	11.21 (0.49)	[10.71]
Na_2O	34.09 (0.60)	12.89 (0.50)	[12.74]
K_2O	0.04 (0.06)	2.04 (0.25)	[2.01]
Total	99.68 (0.39)	99.87 (0.51)	
	$n = 9$[b]	$n = 9$	

1σ standard deviation is shown in parentheses.
[a] Concentration of each oxide component for the reference soda-lime container glass certified by the National Institute of Standard and Technology, USA, is shown in brackets.
[b] n — number of analyses.

$Na_2O{\cdot}2SiO_2$ molar composition after decarbonation. This mixture was melted in a Pt crucible for several hours at 1400 °C and 1 atm in air, quenched to the glass, then grinded and re-melted to ensure the homogeneity. Obtained glass composition was checked by electron microprobe analysis (JEOL JXA-8800) with a defocused beam of 50 μm, beam current of 1.0 nA, and an acceleration voltage of 15 kV (Table 1).

Hydrous glasses (1.3 to 8.1 wt.% total water) were synthesized from the anhydrous $Na_2Si_2O_5$ glass grinded to 0.5–1 mm pieces and the appropriate amount of deionized water in the sealed 5 mm-diameter Pt capsules. Synthesis was carried out in a Kobelco internally heated pressure vessel (IHPV) (Yamashita, 1999) at 1200 °C and ~200 MPa for 24 h. This technique provides nearly isobaric quenching by letting the capsule fall into the cold bottom of the vessel.

Recovered hydrous glasses were transparent, free from crystals and bubbles, indicating that melts were saturated with water during synthesis. Relatively big pieces (25–180 mg) were picked up for the determination of glass density using Archimedes' principle in toluene. Several doubly polished thin sections (0.2–0.7 mm thick) were prepared from the each synthesis product for the measurement of its total water content by near-infrared (NIR) spectroscopy following the method of Yamashita et al. (2008) (Table 2). Obtained total water contents were in agreement with the loaded amount of water within 0.2 wt.%, except for the run product with 1.3 wt.% total water (loaded amount was 0.9 wt.% H_2O), probably due to a hydroscopic behavior of the dry $Na_2Si_2O_5$ glass. In order to minimize hydration by atmospheric moisture the synthesis products were stored in a desiccator with P_2O_5 drying agent.

2.2. NIR and Raman spectroscopy

NIR spectroscopy was carried out using a Jasco FTIR-6200 Fourier-transform spectrometer with a CaF_2/Si beam splitter and a halogen light source. The NIR light was aimed at 50 × 50 μm sample spot by a Jasco IRT-7000 microscope with Cassegrain optics (10X/0.45N.A.) in the transmission mode. The transmitted light was received by a LN_2-cooled InSb detector, and 100 to 256 scans were accumulated for each spectrum with a spectral resolution of 4 cm^{-1}. The light path was continuously purged with nitrogen gas to minimize atmospheric background in the spectra.

Raman spectroscopy was carried out using a Jasco RMP-330 confocal micro-Raman system equipped with a 532 nm (Nd-YAG double frequency) laser operated at 8.4 mW for excitation, a 2400 g/mm grating, a 300 mm focal length mirror, and a Peltier cooled CCD array detector (1024 × 256 pixels). This system was fitted to IRT-7000 microscope (shared with NIR spectroscopy) with an Olympus infinity-corrected objective (50X/0.35N.A./3.6 mm focal length), an imaging lens (20 mm focal length) and confocal optics with a 100 μm pinhole aperture, which yields an excitation volume of 20 μm in diameter and ~50 μm in depth in the 180° scattering geometry. The Raman scattering light was transmitted from the confocal optics to the spectrometer by a 100 μm diameter optical fiber with a 50 μm-wide slit at the exit. The spectra were collected during 2 acquisitions of 30 s exposure and corrected to the Ne 585 nm line measured simultaneously.

Optical access to sample position could be switched in the IRT-7000 microscope from the Cassegrain optics to the objective lens — confocal optics at any time, which made it possible to probe the sample by both NIR spectroscopy and Raman spectroscopy without interruption during high temperature experiments.

2.3. High-temperature experiments in the externally heated diamond anvil cell

High-temperature spectroscopic measurements were performed using an externally heated hydrothermal diamond anvil cell (Bassett et al., 1993) with 1 mm diamond culets. Small ^{13}C diamond aggregates (20–40 μm in size) synthesized according to the procedure described in Chertkova et al. (2014) were used as pressure sensors during the experiments. ^{13}C diamond was loaded into the 400 μm hole of 250 μm thick Ir gasket together with a piece of hydrous $Na_2Si_2O_5$ glass thin section, polished down to 150–200 μm, without any additional pressure medium. Background NIR spectrum of the empty diamond anvil cell was recorded prior to each high-temperature experiment. At the beginning of each experiment the sample was pressurized by driving the screws along the guide posts of the diamond anvil cell, then the sample assembly was heated to 900 °C at a rate of 1 °C/s. Temperature was controlled to ± 1 °C using the alumel–chromel thermocouples attached near the culet surfaces of the upper and lower anvils and calibrated to the melting points of NH_4NO_3 (169.6 °C), $NaNO_3$ (306.8 °C) and CsCl (645 °C). Pressures were calculated based on the measured Raman shift of ^{13}C diamond using the calibration of Schiferl et al. (1997). Reproducibility of the ^{13}C diamond Raman shift measurement is estimated to be better than ± 0.5 cm^{-1}, which translates into pressure uncertainty of less than ± 0.2 GPa in the calibration of Schiferl et al. (1997).

Typically, a NIR spectrum of the melt was collected immediately after the cell reached desired temperature and pressure, and then Raman spectrum of the ^{13}C diamond pressure sensor was acquired. In several experiments NIR spectra were repeatedly collected from 5 to 20 min after the first measurement and no detectable change of the spectra was observed, which implies a fast equilibration for the water

Table 2
Representative NIR data for the six products of hydrous $Na_2Si_2O_5$ glass synthesis in an internally heated pressure vessel.

Total water content (wt.%)	Density (g l^{-1})	Thickness (cm)	A_{4500}[a]	A_{5200}	C_{OH} calib A (wt.%)	$C_{H_2O_m}$ calib A (wt.%)	C_{OH} calib B (wt.%)	$C_{H_2O_m}$ calib B (wt.%)
1.34 (0.08)[b]	2490	0.0725	0.0216	0.0113	1.03	0.31	0.99 (0.07)[c]	0.30 (0.03)[c]
2.09 (0.12)	2469	0.0478	0.0216	0.0123	1.57	0.52	1.55 (0.11)	0.49 (0.05)
4.12 (0.18)	2448	0.0352	0.0245	0.0289	2.44	1.68	2.61 (0.16)	1.53 (0.08)
5.69 (0.19)	2415	0.0598	0.0452	0.0865	2.69	3.00	3.07 (0.15)	2.66 (0.11)
6.15 (0.21)	2415	0.0520	0.0433	0.0800	2.96	3.19	3.46 (0.17)	2.81 (0.12)
8.07 (0.25)	2374	0.0633	0.0550	0.148	3.14	4.93	4.01 (0.17)	4.23 (0.18)

Estimated uncertainties are: ± 50 g l^{-1} for density, ± 0.0002 cm for thickness, ± 0.001 for peak heights.
Errors shown in parentheses were estimated by propagating these uncertainties into the calculated values.
[a] A_{4500} and A_{5200} denote peak heights of the respective bands, C_{OH} and $C_{H_2O_m}$ denote water as OH groups and water as H_2O molecules.
[b] Molar absorption coefficients $\varepsilon_{4500} = 0.21$ (0.01) and $\varepsilon_{5200} = 0.36$ (0.01) (calibration A in Yamashita et al., 2008) were used for the calculation of total water content.
[c] Total water content-dependent molar absorption coefficients (calibration B in Yamashita et al., 2008) were employed for the precise determination of water species abundances.