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AMORPHOUS MATERIALS: PROPERTIES, STRUCTURE, AND DURABILITY

The nearly complete dissociation of water in glasses with strong aluminum avoidance†

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ABSTRACT

Water is dissolved in silicate glasses and melts as hydroxyl groups and molecular water, with mostly hydroxyl groups at low water contents and mostly molecular water at high water contents. However, we recently predicted that water will be dissociated nearly completely in potassium aluminosilicate glasses with more alumina than silica because of the strong aluminum avoidance and the strong tendency for Al-O-Al linkages to hydrolyze in such glasses. In the present study, I test this prediction on hydrous $K_2Al_2SiO_6$ glasses: the Raman and infrared absorption spectra show that water is indeed predominantly present as hydroxyl groups, even for glasses with more than 7 wt% water. This observation validates the previously proposed speciation reactions, demonstrates that variations in water speciation are related to the nature of the cations to which the hydroxyl groups are bonded, and indicates that the classical picture of water dissolution, with predominantly molecular water at high water contents, may not apply near compositional extremes.

Keywords: Potassium aluminosilicate glasses; Raman spectroscopy; infrared absorption spectroscopy; water speciation; aluminum avoidance

INTRODUCTION

It has been known for nearly half a century that water is dissolved in silicate melts and glasses as hydroxyl groups (OH) and molecular water (H_2O_{mol}) (Eq. 1) (Scholze 1966; Stolper 1982a, 1982b).

$$O^{2-} + H_2O_{mol} = 2\ OH^- \text{ with } K_1 = [OH^-]^2/([O^{2-}]\cdot[H_2O_{mol}]) \quad (1)$$

Since these pioneering studies, a large experimental effort has been devoted to quantify the OH/H_2O_{mol} speciation as a function of composition and temperature with Fourier transform infrared (FTIR) spectroscopy (Behrens and Muller 1995; Behrens and Nowak 2003; Behrens et al. 1996; Behrens and Yamashita 2008; Malfait 2009; Nowak and Behrens 1995, 2001; Shen and Keppler 1995; Silver and Stolper 1989; Silver et al. 1990; Stolper 1982a, 1982b) and nuclear magnetic resonance (NMR) spectroscopy (Schmidt et al. 2001). As a result, the OH/H_2O_{mol} speciation of magmatic glasses and melts is now relatively well known.

The nature of the hydroxyl groups has also been investigated. In Al-free silicate glasses, hydroxyl groups are mostly present as silanol groups (Si-OH), with additional free hydroxide (M-OH), i.e., hydroxyls that are ionically bonded to network modifiers (M, e.g. Mg, Ca), for highly depolymerized compositions (Farnan et al. 1987; Kummerlen et al. 1992; Xue and Kanzaki 2004; Zotov and Keppler 1998). The amount of free hydroxide decreases with increasing degree of polymerization and decreasing cationic field strength of the network-modifying or charge-balancing cations (Xue and Kanzaki 2004, 2008). Thus, no significant amounts of free hydroxyls are expected for metaluminous alkali aluminosilicate glasses. For Al-bearing glasses, initial NMR data were interpreted to indicate the absence of significant Si-OH and Al-OH groups (Kohn et al. 1989, 1994). However, subsequent NMR and infrared spectroscopic studies demonstrated that water is dissolved in aluminosilicate glasses as Si-OH and Al-OH, in addition to M-OH for more depolymerized compositions (Malfait and Xue 2010a, 2010b; Sykes and Kubicki 1993, 1994; Xue 2009; Xue and Kanzaki 2006, 2007, 2008, 2009; Zeng et al. 1999, 2000).

Recently, we have quantified the Si-OH and Al-OH abundances of nominally fully polymerized sodium and potassium aluminosilicate glasses with ^{1}H, ^{27}Al-^{1}H, and ^{1}H-^{29}Si-^{1}H NMR spectroscopy (Malfait and Xue 2010a, 2010b, 2014). The derived concentrations enabled us to constrain the equilibrium constants (K_2-K_5) for the aluminum avoidance reaction (Eq. 2) (Loewenstein 1954; Tossel 1993) and the different hydrolysis reactions (Eqs. 3–5).

$$\text{Si-O-Si} + \text{Al-O-Al} = 2\ \text{Si-O-Al}$$
$$\text{with } K_2 = [\text{Si-O-Al}]^2/[\text{Si-O-Si}]\cdot[\text{Al-O-Al}] \quad (2)$$
$$\text{Si-O-Si} + H_2O = 2\ \text{Si-OH}$$
$$\text{with } K_3 = [\text{Si-OH}]^2/[\text{Si-O-Si}]\cdot[H_2O] \quad (3)$$
$$\text{Si-O-Al} + H_2O = \text{Si-OH} + \text{Al-OH}$$
$$\text{with } K_4 = [\text{Si-OH}].[\text{Al-OH}]/[\text{Si-O-Al}]\cdot[H_2O] \quad (4)$$
$$\text{Al-O-Al} + H_2O = 2\ \text{Al-OH}$$
$$\text{with } K_5 = [\text{Al-OH}]^2/[\text{Al-O-Al}]\cdot[H_2O] \quad (5)$$

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One of the striking results of the study on potassium aluminosilicate glasses was the strong aluminum avoidance (K_2 = 1340) compared to sodium aluminosilicate glasses (K_2 = 50). Please note that this observation is not incompatible with the possible occurrence of Al rich regions in orthoclase melts (Le Losq and Neuville 2013; Rammensee and Fraser 1982), because the proposed Al/(Al+Si) ratio of these regions (~0.33) is low enough to easily accommodate a strong Al avoidance through the rearrangement of the next-nearest-neighbors. The strong aluminum avoidance for potassium aluminosilicate glasses drives the hydrolysis of Al-O-Al linkages (K_5 = 27) upon the addition of water. For dry glasses with Al/(Al+Si) < 0.5, Al-O-Al linkages can be avoided through rearrangement of the next-nearest-neighbors of Al, but for samples with higher Al contents, significant amounts of Al-O-Al must be present. As a result, most of the water added to such glasses will be consumed to hydrolyze the Al-O-Al bridges. Indeed, even at high water contents, little H_2O_{mol} is predicted to be present in these glasses (Fig. 1), resulting in very large OH/H_2O_{mol} ratios and values for $K_1 = [OH^-]^2/([O^{2-}]\cdot[H_2O_{mol}])$.

In this study, I test the predictions made by the speciation model derived from ^1H and ^{27}Al-^1H NMR data (Eqs. 2–5) by verifying one of its most striking predictions: the nearly full dissociation of water in glasses for Al/(Al + Si) > 0.5, even at high water content. For this, I synthesized $K_2Al_2SiO_6$ glasses [Al/(Al+Si) = 0.67] with nominally 5 and 8 wt% water and determined the water speciation by Raman and FTIR spectroscopy. The spectra of the hydrous $K_2Al_2SiO_6$ glasses indicate that the concentration of H_2O_{mol} is indeed much lower compared to conventional compositions. This observation validates the results and methodology by Malfait and Xue (2010a, 2010b, 2014) and illustrates the strong effect of aluminum avoidance on water speciation.

EXPERIMENTAL METHODS

The synthesis of a dry $K_2Al_2SiO_6$ glass as starting material is extremely challenging due to the excessively high, still unknown, liquidus temperature (>2000 K) for this composition (Schairer and Bowen 1947). To synthesize the hydrous glasses, mixtures of K_2CO_3, Al_2O_3, and SiO_2 were decarbonated and sintered overnight at 1073 K and welded in Pt capsules with de-ionized water. Synthesis experiments were performed in an end-loaded piston-cylinder apparatus (Boyd and England 1960) with a talc-silica glass-MgO assembly at 0.7 GPa and 1923 K for 30 and 60 min for nominal water contents of 5 and 8 wt%, respectively. The melts were quenched to glasses by switching of the power to the graphite furnace (quench rate ~150 K/s). The composition and homogeneity of the glasses was verified by electron microprobe analysis (JEOL, JXA-8200) with an acceleration voltage of 15 kV, using a large spot size (30 μm) and low beam current (2 nA) to avoid the migration of potassium under the electron beam (Table 1). Natural orthoclase was used as a standard for all elements. Within analytical uncertainty, the compositions were found to be identical to the target composition. The $K_2Al_2SiO_6$-5 sample contains euhedral crystals (~20–50 μm) of $K_2Al_2SiO_6$, indicating that the liquidus temperature is above 1923 K for 5 wt% water, but the glass phase was otherwise homogenous. The $K_2Al_2SiO_6$-8 sample was completely glassy and homogenous. The difficulty of preparing carbonate free glasses with very high K_2O content has been reported before (Bourgue and Richet 2001; Malfait et al. 2007). Indeed, the Raman spectra contain a strong, relatively sharp band near 1050 cm^{-1} and a very weak, broad band near 1420 cm^{-1} (Fig. 2). Similar bands at the same positions were observed for carbonate-bearing potassium silicate glasses (Bourgue and Richet 2001). The carbonate content cannot be robustly quantified from the Raman spectra because the unusual glass composition lies far outside the calibration ranges for existing quantification models (Morizet et al. 2013). Nevertheless, a comparison of the intensity of the 1050 cm^{-1} band in the Raman spectra our glasses to the spectra of Bourgue and Richet (2001) indicates a carbonate content on the order of 2.1 and 0.8 wt% (CO_2 equivalents) in the $K_2Al_2SiO_6$-5 and the $K_2Al_2SiO_6$-8 glass, respectively. Note that these estimates may be off by as much as a factor of two due to differences in glass composition between our potassium aluminosilicate glasses and the aluminum-free glasses studied by Bourgue and Richet.

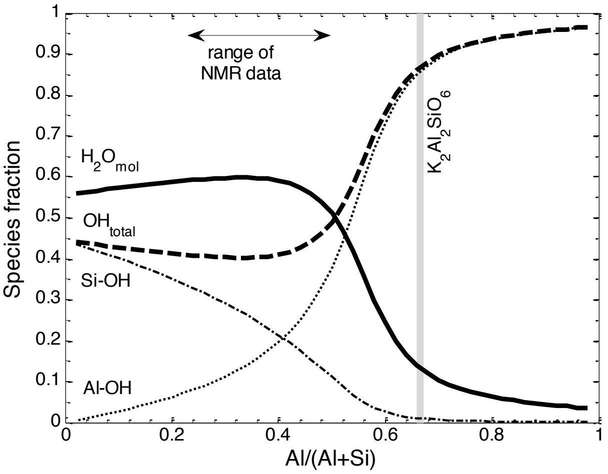

FIGURE 1. Predicted abundances of H_2O_{mol}, OH_{total}, Si-OH, and Al-OH for metaluminous potassium aluminosilicate glasses with ca. 8 wt% water (Eqs. 2–5) (Malfait and Xue 2014). Molecular water is the most abundant species for Al/(Al + Si) < 0.5, but hydroxyl groups are predicted to be more abundant at higher Al contents. The model is calibrated for Al/(Al + Si) ratios between 0.25 and 0.50, but its extrapolation predicts that water will be predominantly present as Al-OH for the $K_2Al_2SiO_6$ composition investigated in this study (gray line).

TABLE 1. Electron microprobe results, IR absorbances, and predicted OH/H_2O_{mol} ratio

		$K_2Al_2SiO_6$-5	$K_2Al_2SiO_6$-8
SiO_2	(wt%)	22.2 ± 0.2	21.4 ± 0.2
Al_2O_3	(wt%)	36.5 ± 0.3	35.2 ± 0.1
K_2O	(wt%)	34.2 ± 0.4	32.5 ± 0.2
Total[a]	(wt%)	92.9 ± 0.5	89.0 ± 0.2
H_2O[b]	(wt%)	5.3	8.5
H_2O[c]	(wt%)	n.d.[e]	7.2
Formula		$K_{2.00}Al_{1.97}Si_{1.02}O_6$	$K_{1.98}Al_{1.98}Si_{1.02}O_6$
A_{4500}	(cm^{-1})	3.0 ± 0.5	4.9 ± 0.5
A_{5200}	(cm^{-1})	0.19 ± 0.04	1.7 ± 0.2
A_{4500}/A_{5200}		15.8 ± 4.2	2.9 ± 0.4
OH/H_2O_{mol}[d]		$18.9^{+87.0}_{-16.5}$	$9.1^{+40.8}_{-7.5}$

[a] Low totals are related to dissolved H_2O and CO_2.
[b] Nominal water content.
[c] Determined by Karl Fischer Titration (KFT).
[d] Predicted by Malfait and Xue (2014).
[e] No homogenous fraction of the heterogeneous sample (glass and crystals) could be measured by KFT.

The Raman spectra were collected with a LabRam Raman spectrometer, equipped with an external Argon laser (514 nm, 6 mW measured at the sample surface). The infrared absorption spectra were collected on double polished sections (540 μm thick) with a Bruker Hyperion 3000 microscope connected to a Vertex 70 interferometer. Spectra were collected on three spots per section with a spectral resolution of 4 cm^{-1}. To compare the Raman and infrared absorption spectra of the $K_2Al_2SiO_6$ glasses to those of a sample with a more typical OH/H_2O_{mol} speciation, the infrared and Raman spectra of a hydrous haplogranitic sample with similar water content (Malfait et al. 2014) were also measured.

RESULTS AND DISCUSSION

The Raman spectrum of the haplogranitic glass (Fig. 2) displays two major bands related to vibrations of hydrous species: a

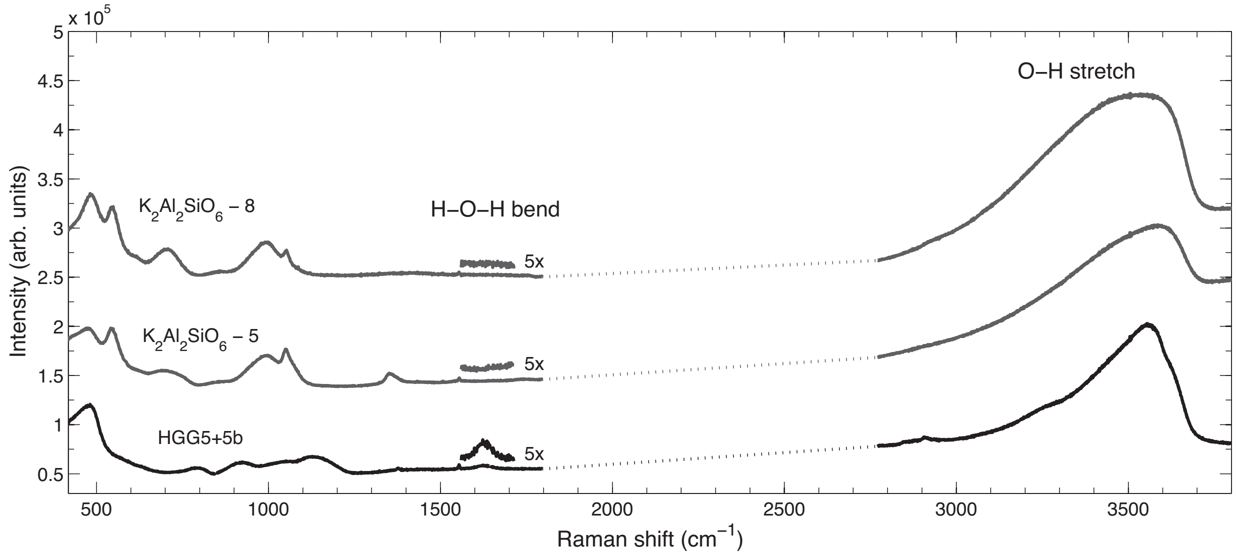

FIGURE 2. Raman spectra of a hydrous haplogranitic (HGG5+5b, 7.7 wt% water) and two hydrous $K_2Al_2SiO_6$ glasses (nominally 5 and 8 wt% water). A band for the H-O-H bending mode near 1600 cm^{-1} is present for the haplogranitic glasses, but absent for the $K_2Al_2SiO_6$ glasses. The sharp band near 1050 cm^{-1} is related to dissolved carbonate groups.

strong, broad band for the fundamental O-H stretching vibration near 3600 cm^{-1} and a weaker, narrower band for the fundamental H-O-H bending vibration near 1600 cm^{-1}. The former band contains signal from both OH and H_2O_{mol}, the latter from H_2O_{mol} only. The band near 1600 cm^{-1} is within the noise for the spectra of the $K_2Al_2SiO_6$ glasses. This suggests, at least qualitatively, that the concentration of H_2O_{mol} is low in these glasses. The contrasting behavior between the haplogranitic and $K_2Al_2SiO_6$ glasses is confirmed by the FTIR spectra (Fig. 3): the overtone related to H_2O_{mol} near 5200 cm^{-1} is much stronger than the overtone related to OH near 4500 cm^{-1} in the haplogranitic glass, but this is reversed for the $K_2Al_2SiO_6$ glasses. Unfortunately, the range in water content for which $K_2Al_2SiO_6$ glasses can be synthesized is relatively narrow: at water contents up to at least 5 wt%, the liquidus temperature exceeds the melting temperature of the Pt capsules and at water contents above 8 wt%, the melts cannot be quenched to a glass. As a result, it was not possible to synthesize a set of samples with a range of OH/H_2O_{mol} ratios and to determine the molar absorption coefficients for the 4500 and 5200 cm^{-1} bands from an internally consistent calibration.

The band near 3600 cm^{-1} has a more pronounced tail to lower wavenumbers for the $K_2Al_2SiO_6$ glasses compared to the haplogranitic glass (Fig. 2). In a seminal paper, Libowitzky (1999) demonstrated that the frequency of the O-H stretching vibrations correlates with the hydrogen bond strength. Thus, Raman and infrared absorption bands at lower wavenumbers indicate strong hydrogen bonding and short OH···O lengths. Because water-rich glasses typically display both high degrees of hydrogen bonding and high H_2O_{mol} contents, the correlation between hydrogen bonding and O-H stretching frequency (Libowitzky 1999) produces a secondary correlation between the O-H stretching frequency and water speciation. Several studies tried to use this secondary correlation to derive OH/H_2O_{mol} speciation data from the Raman spectra of hydrous glasses, with variable success (Behrens et al. 2006; Chabiron et al. 2004; Le Losq et al. 2013; Zajacz et al. 2005). It is important to note that, despite the secondary correlation between the O-H stretching frequency and water speciation, the presence of Raman signal at relatively low wavenumbers does not a priori imply the presence of molecular water. In fact, there are numerous minerals that contain hydroxyl groups with O-H stretching vibrations far below 3600 cm^{-1} (Behrens and Muller 1995; Libowitzky 1999).

In summary, both the Raman (Fig. 2) and infrared absorption (Fig. 3) spectroscopic data provide strong evidence for the predominance of OH over H_2O_{mol} in the $K_2Al_2SiO_6$ glasses. Thus, the vibrational spectroscopic data confirm the prediction of the OH/H_2O_{mol} speciation based on NMR spectroscopic data on samples with lower Al contents (Fig. 1) and validate the analytical procedure and speciation model (Malfait and Xue 2010a, 2010b, 2014) with independent methods.

IMPLICATIONS

The strong dissociation of water in the $K_2Al_2SiO_6$ glasses is directly related to the instability of the Al-O-Al linkages associated with the strong aluminum avoidance in potassium aluminosilicate glasses, evidenced by high equilibrium constants for reactions 2 and 5. The strong tendency for Al-O-Al linkages to hydrolyze compared to other oxygen bridges has also been observed for zeolite materials (Stebbins et al. 1999). The potassium aluminosilicate glasses provide a model system where the strong variation of the OH/H_2O_{mol} speciation can be rationalized in terms of the nature of the cations to which the hydroxyl groups are bonded. Future work on the nature of the cations to which the hydroxyl groups are covalently (e.g. Si^{4+}, Al^{3+}) or ionically (e.g. Mg^{2+}, Ca^{2+}) bonded may help to rationalize, and ultimately predict, the compositional variations of the OH/H_2O_{mol} specia-

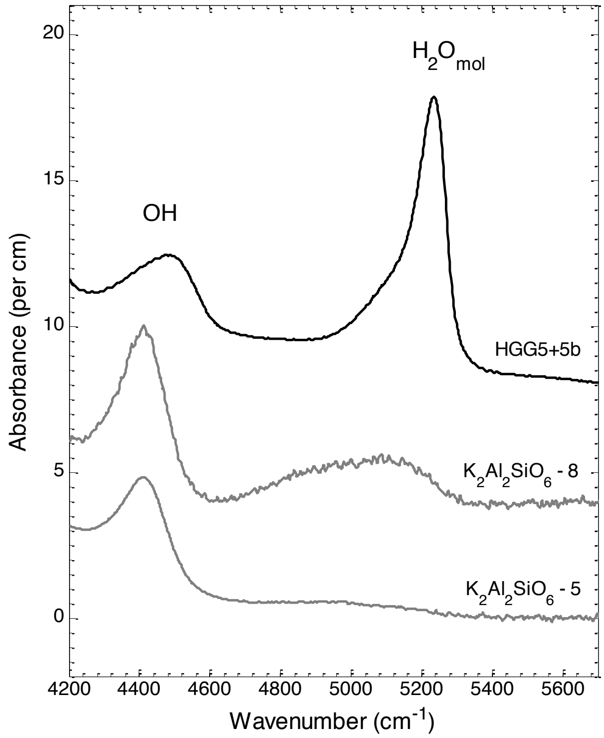

FIGURE 3. FTIR spectra of a hydrous haplogranitic (HGG5+5b, 7.7 wt% water) and two hydrous $K_2Al_2SiO_6$ glasses (nominally 5 and 8 wt% water); intensities are normalized to a section thickness of 1 cm. For the haplogranitic glass, the band near 5200 cm^{-1}, related to H_2O_{mol}, is larger than the band near 4500 cm^{-1}, related to hydroxyl groups; this is reversed for the $K_2Al_2SiO_6$ glasses.

tion in geologically relevant melts and glasses. The strong dissociation of water in $K_2Al_2SiO_6$ glasses with high water content strongly contrasts to what was observed for all other investigated compositions, for which H_2O_{mol} is the dominant species at high water contents (Behrens and Yamashita 2008; Stolper 1982a, 1982b). This strikingly different behavior exemplifies the role of aluminum avoidance on the water speciation and indicates that the classical picture of water dissolution, with predominantly molecular water at high water contents, may not apply near extremes in compositions.

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