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 hydrated K2AlSiO5 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 (H2O$_{mtr}$) (Eq. 1) (Scholze 1966; Stolper 1982a, 1982b).

$$\text{O}^{2-} + \text{H}_2\text{O}_{\text{mtr}} = 2 \text{OH}^{-} \text{ with } K_1 = (\text{[OH}^{-}]^2) / (\text{[O}^{2-}] \cdot \text{[H}_2\text{O}_{\text{mtr}}]) \tag{1}$$

Since these pioneering studies, a large experimental effort has been devoted to quantify the OH/H2O$_{mtr}$ 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 Keppeler 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/H2O$_{mtr}$ 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 1H, 27Al-1H, and 1H-29Si-1H NMR spectroscopy (Malfait and Xue 2010a, 2010b, 2014). The derived concentrations enabled us to constrain the equilibrium constants (Ks,Ka) for the aluminum avoidance reaction (Eq. 2) (Loewenstein 1954; Tossel 1993) and the different hydrolysis reactions (Eqs. 3–5).

$$\text{Si-O-Si + Al-O-Al} = 2 \text{ Si-O-Al} \tag{2}$$
$$\text{Si-O-Si + H}_2\text{O} = 2 \text{ Si-OH} \tag{3}$$
$$\text{Si-O-Al + H}_2\text{O} = \text{Si-OH} + \text{Al-OH} \tag{4}$$
$$\text{Al-O-Al + H}_2\text{O} = 2 \text{ Al-OH} \tag{5}$$

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