Alkali influence on the water speciation and the environment of protons in silicate glasses revealed by $^1$H MAS NMR spectroscopy

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ABSTRACT

Water can form different chemical bonds with the ionic entities composing silicate melts. Because of that, its influence on the physico-chemical properties of magmas can vary with silicate composition and water content, temperature, and pressure. To further our understanding of how silicate chemical composition governs proton distribution in magmas, the environment of protons in hydrous alkali (Li, Na, K) silicate glasses was varied as a function of the type of alkali metal and total water content. From $^1$H MAS NMR spectroscopy, H$^+$ are distributed among five different structural environments in alkali silicate glasses. One of these environments is in the form of H$_2$O molecules (H$_2$O$_{mol}$). The four others are the proton environments associated with Si-OH bonding, and perhaps also with M-OH bonding (with M = Li, Na, or K). Those environments differ in their O-O distance and extent of hydrogen bonding. H$_2$O$_{mol}$ species are located in an environment with an O-O distance of ~290 pm. OH$^-$ groups are in environments with O-O distances from 240 to 305 pm. The ionic radius of the alkalis, and hence their ionic field strength, determines the fraction of water dissolved as H$_2$O$_{mol}$ and OH$^-$ groups, as well as the distribution of protons in the various OH$^-$ environments. The mean volume of the H$^+$ oxygen coordination sphere was calculated using the $^1$H NMR signal intensity and the mean O-O distance around H$^+$. Increasing ionic radius of the alkali metal in silicate glasses results in a decrease of this mean volume. The partial molar volume of water in the corresponding melts determined through other technics seems to vary in a comparable way. Therefore, the chemical composition of silicate melts may control the partial molar volume of dissolved water because of its influence on the structural environment of protons. This probably also plays a role in determining water solubility.

Keywords: Water, silicate glasses, proton solid-state NMR, proton environment

INTRODUCTION

Water plays a fundamental role in the dynamics of the past and present Earth because of its major impact on the physicochemical properties of silicate materials. As the main volatile component in natural magmas, water profoundly decreases their viscosity (Richet et al. 1996) so that, for instance, it partly controls the behavior of volcanic eruptions. Liquidus phase relations and volume properties of magmas are also influenced by dissolved water (e.g., Kushiro 1972; Ochs and Lange 1999).

Since the work of Wasserburg (1957), it is commonly assumed that water dissolved in silicate melts breaks their Si-O-Si linkages, as described by:

$$\text{H}_2\text{O}_{mol(melt)} + \text{Si-O-Si}_{(melt)} \rightarrow 2\text{Si-OH}_{(melt)}$$

(1)

In this suggested solution mechanism, H$_2$O$_{mol}$ is molecular water dissolved in the melt. The Si-OH bonds are formed through H$_2$O$_{mol}$ dissociation into OH$^-$ groups via reaction with Si-O-Si bonds. A consequence of reaction 1 is depolymerization of the silicate melt structure, which, in turn, may lead to changes in its physical properties. For example, this simple solution mechanism explains qualitatively the decrease of the viscosity of alumino-
silicate melts observed upon water addition (Richet et al. 1996).

Infrared absorption studies of hydrous glasses and melts have demonstrated the presence of both OH$^-$ groups and H$_2$O$_{mol}$ species (Davis and Tomozawa 1996; Efimov and Pogareva 2006; Malfait 2009; Scholtze 1960; Stolper 1982). Results of recent NMR spectroscopic studies of depolymerized silicate glasses (Cody et al. 2005; Mysen and Cody 2005; Xue and Kanzaki 2004, 2006, 2007, 2008) have led to the suggestion that water also can react with alkali and alkaline earth, M, network modifying cations to form M-OH bonds in depolymerized melts. Results from thermodynamic modeling of silicate melts (Moretti 2005; Moretti et al. 2014) and Raman studies (Le Losq et al. 2013; Mysen and Virgo 1986a, 1986b) reinforce such hypothesis. Notably, whereas formation of T-OH bonds (T = tetrahedral coordination cations such as Si$^{4+}$ and Al$^{3+}$) in melts might cause network depolymerization, formation of M-OH bonds may lead to melt polymerization (e.g., Fraser 1977; Moretti 2005; Moretti et al. 2014; Xue and Kanzaki 2004, 2006, 2007, 2008).

Temperature controls the ratio of OH$^-$ to H$_2$O$_{mol}$ species in silicate melts (Behrens and Yamashita 2008; Nowak and Behrens 1995; Shen and Kepller 1995). The effect of the melt chemistry is less evident. Most studies focus on glasses, which preserve a record of the structure of melts at their glass transition temperature (T$_g$). The latter depends on water content and on silicate composition (see for a review Mysen and Richet 2005). It follows that the