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The amphoteric behavior of water in silicate melts from the point of view of their ionic-polymeric constitution

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ABSTRACT

Dissociation of water into protons and hydroxyl ions is a fundamental feature of aqueous solutions. Although it exerts a profound influence on properties of magmas, this autoprotolysis reaction has been hitherto neglected for water dissolved in silicate melts. As made here with an acid–base model, in fact one has to deal with molecular water (H_2O_{mol}) and two kinds of hydroxyl groups, bonded or not to network-forming cations (OH and OH^-, respectively) in hydrous silicate melts. By mixing cations and anions on distinct sublattices and quantifying the disproportionation of water dissolved in silicate melts into its ionic products, H^+ and OH^-, we reconcile spectroscopic determinations of water speciation, and highlight the main compositional features involving chemical exchanges between H_2O_{mol}, T – OH and M – OH groups (T and M being a former and a modifier, respectively). In particular, water addition to depolymerized systems, such as basalts, determine a relative predominance of OH^- with respect to silicic systems, such that the increase of water concentration tends to immediately limit depolymerization rather than enhance it. This opens new perspectives to the understanding of the chemical control of hydrous magmas and their physical properties, as well as the attainment of saturation in hydrous minerals such as amphiboles or micas, particularly in depolymerized melts.

1. Introduction

One of the most fruitful concepts of general chemistry is autoionization (or autoprotolysis) of liquid water, that is, the reaction through which water molecules dissociates into solvated protons, H^+, and hydroxide ions, OH^-:

$$H_2O \leftrightarrow H^+ + OH^-. \quad (1)$$

This reaction describes solvent–solute interactions in terms of the amphoteric nature of water, which can react as either an acid or a base, but it does not make any assumption as to the structural state of the water components in the solution.

A similar description should apply to water dissolved in silicate melts that, even at low concentration, profoundly affects their chemical and physical properties. Several lines of evidences display a dual behavior of water that depends on the bulk melt composition. In silicic melts water is among the strongest network modifiers breaking the silicate network (Burnham, 1975; Stolper, 1982a; Farnan et al., 1987; Zotov and Keppler, 1998; Zeng et al., 2000; Mysen and Richet, 2005, and references therein), whereas in depolymerized melt systems water tends to stabilize the silicate network because it makes complexes with metals, thus subtracting them from their role of network modifiers. This points to the amphoteric behavior of water in melts (Fraser, 1977; Xue and Kanzaki, 2004; Moretti, 2005; Le Losq et al., 2013) and thus water autonionization.

Despite the important geochemical and geophysical implications of water dissolution, from deep mantle melting to magma fragmentation in volcanic conduits, a detailed examination of the relationship between water autoionization and the spectroscopically observed speciation in silicate melts is still lacking. This is a consequence of the fact that the distinction between solute and solvent becomes blurred in such systems, because speciation is not only complex but changes with the marked depolymerization of the silicate framework that obtains from pure SiO_2 to metal-oxide rich compositions (Toop and Samis, 1962; Hess, 1971, 1980; Ottonello, 2001; Mysen and Richet, 2005). The anionic framework of silicate melts makes in fact solute and solvents so intimately related that one cannot identify a solvation shell and then treat as a polarizable continuum the solvent outside such a shell. This poses problems to identify directly, from structural studies, the complexes needed to define acid–base reactions. For example, the connectivity of the silicate structure is such that cations and anions

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have actual charges lower than formal ones, and the residual charge distribution from bonding of bridging oxygen to silicon allows oxygen bonding with other cations (Tangney and Scandolo, 2002; Mysen and Richet, 2005; Vuilleumier et al., 2011). This makes the relative contribution of nonbridging and bridging oxygens to the oxygen coordination of the other cations poorly known (Mysen and Richet, 2005). Therefore, the oxocomplexes formed by dissolved cations are not fully discrete species because non-bridging oxygens can intervene in their coordination sphere, with rapid exchanges of oxygen atoms between the oxocomplexes and the solvent (Tilquin et al., 1997). These features do not allow proper understanding of the actual physico-chemical role of many species detected by spectroscopic techniques, Fourier Transform Infrared (FTIR) particularly, a fact which can lead to confusing notation. Melt depolymerization is, in fact, usually described by the reaction (e.g., Stolper, 1982a; Silver et al., 1990; Ihinger et al., 1994; McMillan, 1994; Dixon and Stolper, 1995; Zhang et al., 1995; Zhang, 1999; Behrens and Nowak, 2003 and references therein):

$$H_2O_{mol} + O_{(melt)} \leftrightarrow 2OH \tag{2}$$

in which water species in silicate melts are commonly assumed to be molecular water and undistinguished hydroxyl groups bonded to undistinguished tetrahedrally coordinated cations (Stolper, 1982a, 1982b; Zhang, 1999; Schmidt et al., 2001; Mysen and Richet, 2005).

Some efforts have been pursued to define possible mechanisms for specific compositional joins, essentially by mixing different types of OH (MOH, AlOH, SiOH) and bridging oxygens, for example following the Al avoidance principle (Xue and Kanzaki, 2008; Malfait and Xue, 2010). However, these studies do not provide a unique and coherent description of the chemical reactivity of water in hydrous silicate melts of any composition.

NMR and Raman spectroscopic evidences have been provided about the existence of 'free' hydroxyls, OH^- (Zavel'sky et al., 1998; Xue and Kanzaki, 2004, 2008; Xue, 2009; Le Losq et al., 2013), i.e., groups not covalently linked to network-forming cations T (Si or Al) but associated with network-modifier cations. Their existence has long been argued to explain *i*) water solubility (Fraser, 1977; Mysen and Richet, 2005 and references therein), *ii*) Raman spectra of alkali–silicate systems (Mysen, 1998; Mysen and Cody, 2005), *iii*) high water diffusivity in andesite melts (Behrens et al., 2004) and *iv*) iron redox state in hydrous melts (Moretti, 2005). Likewise, NMR experiments have systematically detected 'free' hydroxyl groups in $CaO–MgO–SiO_2$ depolymerized glasses and have suggested the presence of NaOH groups in alkali silicate glasses (Xue and Kanzaki, 2004), therefore confirming independent 1H NMR observations on water-rich (up to 8.83 wt.%) albitic glasses (Zavel'sky et al., 1998) quenched from 1100–1200 °C. More recently, the detailed Raman study of Le Losq et al. (2013), benefitting of high-temperature measurements, has proved the joint occurrence of molecular water, H_2O_{mol}, T – OH groups (with T = Si, Al, i.e. a network former), and M – OH groups (with M = Ca,Mg, Na, K etc., i.e., a network modifier). All these data point to the relevance of the amphoteric character of water to the study of silicate glasses and melts, and confirm that the single reaction (2) cannot account for water speciation in melts essentially because it is unable to distinguish the different kinds of oxygens interacting with water. Following Le Losq et al. (2013), reaction (2) embodies the water self-dissociation products, H^+ and OH^-, hence reaction (1), because

1) if a bridging oxygen is involved, a -T-O-T-linkage is broken and two -T-OH groups are formed, one of them because of direct association of a -T-O-terminal group with a proton, H^+, freed by the water molecule;
2) if a non-bridging oxygen is involved, a -T-O-terminal group will be saturated by a proton taken from water; thus one -T-OH group and a 'free' hydroxyl anion, OH^-, or a M – OH complex, will be produced;
3) finally, if a so-called 'free' oxygen (O^{2-}) is involved, two 'free' hydroxyl anions or M – OH complexes will be formed without affecting the anionic framework.

Therefore, we must accept that current knowledge of the speciation of water in melts needs to be moved a step forward, through description of the amphoteric behavior of water in silicate melts. This can be achieved only by setting a formally consistent set of reactions, in which ionic species intervene. Only on this basis it is possible to account correctly for the acid–base behavior of water in every kind of magmatic setting. To do so, we have incorporated spectroscopic data (see references quoted in Appendix A) on water speciation into a Temkin ionic-polymeric model of molten silicate (Temkin, 1945; Ottonello et al., 2001; Moretti, 2005). Such an ionic-polymeric model has then been used to parameterize water autoionization and gives new insights into physical properties of hydrous magmas.

2. Model development

By analogy with aqueous solutions, the obvious starting point to assess water autoionization is the equilibrium constant of reaction (1), $K_1^{autoionization} = \frac{X_{H^+} \cdot X_{OH^-}}{X_{H_2O_{mol}}}$, i.e., through an ideal solution model in terms of molar fractions, X, of dissociated (ionic) and undissociated (molecular water, H_2O_{mol}) species. To treat chemical reactivity and compute quantities entering Eq. (1), we will consider, first, completely dissociated oxide components (also water) into ions and anions constituting the cationic and anionic melt matrices (Temkin-model approach), in order to assess melt polymerization. In this step, reactions will be shown in which 'free' oxygen, O^{2-}, 'free' hydroxyl group, OH^-, and 'free' proton, H^+, appear as truly free or separate species, although it is well known that their actual proportions are very low or even undetectable in conventional spectroscopic investigations because of their existence in association with other entities. Free oxygens and free hydroxyls, in particular, represent in an undistinguished way all oxide and hydroxide ions not bound to network formers, thus, including loose oxygen and hydroxyl ions and all the forms complexed with metals (e.g. $Na^+ \cdot O^{2-}$, $Ca^{2+} \cdot O^{2-}$, $K^+ \cdot OH^-$), but not covalently linked to the silicate network (Nesbitt et al., 2010).

In a second step it will be possible to re-evaluate available spectroscopic data in order to retrieve mole fractions of H^+, OH^- and H_2O_{mol} from the measured amounts of OH and H_2O_{mol} and solve the equilibrium constant of reaction (1).

2.1. Model grounds: ionic-polymeric nature of silicate melts

To obviate confusion over what is meant by 'complex formation' by metal ions, we need to extend the similarity with aqueous solutions, by adopting an analogous symbolic notation for melt species and define ionic thermodynamic identities. To do so, we define silicate melts as a fused salt mixture in which polymerization takes place through high reactivity of negatively charged anionic species (Fincham and Richardson, 1954; Bloom and Bockris, 1964; Hess, 1971; Fraser, 1977; Ottonello et al., 2001). Then, the reactive properties of silicate melts can be based on the Lux–Flood definition of acid–base equilibria in terms of exchange of O^{2-} anions, i.e. the aforementioned 'free' oxygens (Flood and Forland, 1947):

$$\text{Base} \leftrightarrow \text{Acid} + O^{2-}. \tag{3}$$

A basic oxide is the one capable of furnishing oxygen ions whereas an acidic oxide is one that associates with oxide ions, i.e., 'free' oxygens.

For an oxide MO (e.g., Fraser, 1975, 1977), the reactions:

$$MO + O^{2-} \Leftrightarrow MO_2^{2-} \tag{4a}$$

$$MO \Leftrightarrow M^{2+} + O^{2-} \tag{4b}$$