

## Effect of the bonding and the speciation of water on the polymerization and the viscosity of silicate melts

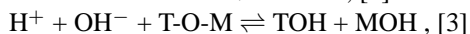
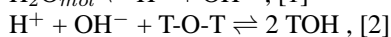
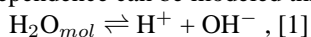
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Degassing of water during the ascent of hydrous magma in a volcanic edifice produces dramatic changes in the magma density and viscosity. This can profoundly affect the dynamics of volcanic eruptions. The water exsolution history, in turn, in part is driven by the water solubility and solution mechanisms in the silicate melt and in part by the decompression history of the magmatic liquid. Previous studies pointed to dissolved water in silicate melts as molecules ( $H_2O_{mol}$  species) and hydroxyl groups, OH. The later are commonly considered bonded to  $Si^{4+}$ , but may form different bonding, such as with alkali or alkaline-earth cations. Those various bonding mechanisms influence the structure of hydrous melts in different ways, and therefore, the melt properties. As a result, exsolution of water from magmas may have different eruptive consequences as a function of the initial solution mechanisms of water dissolved in the magmatic liquid.

However, and despite their importance, the bonding mechanisms of water in silicate melts are not clear, particularly in regards of their variation with the chemical composition of the melts. In this experimental study, pieces of such information are reported from determination of how water bonds with the ionic network of alkali (Li, Na and K) silicate quenched melts. From <sup>29</sup>Si Single-Pulse Magic-Angle Spinning Nuclear Magnetic Resonance (<sup>29</sup>Si SP MAS NMR) and Raman spectroscopy, decreasing ionic radius of alkali in silicate melts results in decreasing the fraction of water dissolved as OH groups as well as in changing the OH bonding mechanism. Indeed, in K silicate glasses, water resides mostly as OH groups bonded to Si, whereas in Li silicate glasses, the OH content is low and the OH groups are not bonded exclusively to Si. Therefore, present data support previous inferences about a control exerted by the ionic field strength of alkali and alkaline-earth cations on the  $H_2O_{mol}/OH$  ratio as well as on the bonding of OH groups with the ionic network of hydrous silicate melts.

This implies that water has different effects on the polymerization of melts as a function of their chemical composition. Such dependence can be modeled through the following reactions:



where T = Si, Al and M is an alkali or an alkaline-earth cation. Equation [1] is the self-ionization reaction of water. The product ions can react with bridging oxygen in T-O-T bonds (eq. 2) or with non-bridging oxygen in T-O-M bonds (eq. 3). The fraction and ionic field strength of the various T and M elements will influence the equilibrium constants of equations 1, 2 and 3. As a consequence, the water effect on the melt viscosity must change with its chemical composition, because equations 2 and 3 have different implications for the melt polymerization. Such effect is highlighted when comparing the viscosity reduction produced by water solution in rhyolitic and andesitic melts for instance. Indeed, solution of 1 wt% water produces a viscosity reduction  $\sim 1$  order of magnitude greater in a rhyolitic melt than in an andesitic melt.

This conclusion, in turn, may affect the eruptive processes linked to viscous phenomenon, such as, for example, the fragmentation of magmas in explosive eruptions. Indeed, the fragmentation of an ascending magma in a conduit can occur when the elongation strain rate of the magmatic flow becomes greater than the magma viscous relaxation time, because at this point the magma behaves as a fragile solid. Magmas with different compositions will present differences in the equilibrium constants of equations 1, 2 and 3 as well as in water solubility, because the formers define the latter. This will define different evolution paths as a function of depth for their viscous relaxation time and their vesicularity that will eventually affect their fragmentation threshold.

Keywords: water speciation, water bonding, silicate melt, silicate glass, viscosity of magma, fragmentation