

## Chemical dependence of the speciation and structural position of water in silicate melts Chemical dependence of the speciation and structural position of water in silicate melts

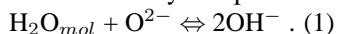
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Water is the main volatile component affecting the thermodynamic, structural and rheological properties of magmatic liquids in the Earth's interior resulting in major influence on past history and present magmatic activity of the Earth. Previous experiments and modelling have shown that water can be dissolved as H<sub>2</sub>O molecules (H<sub>2</sub>O<sub>mol</sub>) and OH<sup>-</sup> groups, with the OH<sup>-</sup> groups bonded to the silicate network to form Si-OH or Al-OH bonds and perhaps alkali-OH and alkaline earth-OH complexes. However, important questions remain as to how bulk chemistry governs the link between the different OH groups and the silicate network, and the global H<sub>2</sub>O<sub>mol</sub>/OH ratio.

It is now widely accepted that dissolved water reacts with the O<sup>2-</sup> oxygen composing the silicate network following:



As O<sup>2-</sup> from the silicate network is involved in this reaction, its equilibrium constant must depend on the activities of bridging (BO), non-bridging (NBO), and free oxygen species potentially present in silicate melts, and hence on their global chemistry. Even if Al-OH and Si-OH bonding were the only variables (and, therefore, the Al/Si ratio of a melt), reaction (1) implies that the H<sub>2</sub>O<sub>mol</sub>/OH should depend on silicate melt composition. However, as the activity of NBO species is also affected by the ionic field strength of alkali and alkaline earth cations, we expect the equilibrium of reaction (1) to be affected by those cations.

To test and to quantify the occurrence and the impact of chemical effects on the speciation of water in quenched, hydrous silicate melt (glass), we analysed M<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> glasses (M = Li, Na or K) containing different amounts of water (from 3.3 up to 17.6 mol%) with the help of <sup>1</sup>H and <sup>29</sup>Si MAS NRM, Raman and Infrared spectroscopy. Glasses were formed by temperature quenching (~100 °C/s) at 1.5 GPa. Raman and infrared spectroscopy show three different bands close to 2300, 2800 and 3600 cm<sup>-1</sup>. These are assigned to O-H stretching from OH groups bonded to silicate components and from H<sub>2</sub>O molecules. Correlation of those frequencies with the O...O distances in minerals suggest that those three bands arise from OH stretching in two main different environments: one with a mean O...O distance close to ~0.26 nm and another one with a ~0.29 nm O...O distance. In the <sup>1</sup>H MAS NMR spectra, we retrieved signals near 15 and 5 ppm arising from the ~0.26 and ~0.29 nm environments respectively. Increasing the alkali radius tends to increase the intensities of the 15 ppm <sup>1</sup>H MAS NMR peak and of the 2000-2900 cm<sup>-1</sup> Raman region, indicating an increase of the population of OH groups in the ~0.26 nm environment. In addition, the higher the alkali radius the higher the effect of water on the polymerization degree is, as testified by changes of the <sup>29</sup>Si NMR and Raman signals.

Those NMR and Raman observations suggest that the H<sub>2</sub>O<sub>mol</sub>/OH ratio in quenched hydrous silicate melts decreases in the order Li, Na, K. The greater the radius of alkali, the higher the proportion of OH<sup>-</sup> the smaller the mean O...O distance in their environment, and hence the more extensive hydrogen bonding. We propose that this structural evolution arises from a combination of steric hindrance and electron distribution around alkali elements that affects both equilibrium reaction (1), which will decrease in the order K > Na > Li, and the local environment of the formed OH<sup>-</sup> groups. This interplay between the nature of the alkali modifier, the speciation of water and the polymerization of the silicate network must result in non-negligible differences in viscosity of Li, Na and K silicate melts. Therefore, following this study, variation of the concentration of alkali and alkaline-earth elements in natural hydrous magmas, following their origin, will result in changes of their rheological properties, not only because of the different effects of alkali/alkaline earth elements on Si-O bonds, but also because of differences in the water speciation and OH<sup>-</sup> environments.

キーワード: water, silicate glass, Raman spectroscopy, NMR spectroscopy

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