

The dissolution mechanisms of water in depolymerized silicate melts: ^1H and ^{29}Si NMR spectroscopy and ab initio calculations

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The dissolution of water in magmas significantly affects phase relations, and physical and thermodynamic properties. In an attempt to shed light on this issue, we have applied ^1H and ^{29}Si nuclear magnetic resonance (NMR) spectroscopic techniques to hydrous silicate glasses (quenched melts) in the CaO-MgO-SiO_2 , $\text{Na}_2\text{O-SiO}_2$, $\text{Li}_2\text{O-SiO}_2$ and $\text{Na}_2\text{O-CaO-SiO}_2$ systems. We have also carried out ab initio molecular orbital calculations on representative clusters to gain insight into the experimental results.

The most prominent result is the identification of a narrow peak at about 1.1 to 1.7 ppm in the ^1H MAS NMR spectra for all the hydrous glasses in the CaO-MgO-SiO_2 system. This peak can be attributed to free hydroxyl ($(\text{Ca,Mg})\text{OH}$) group with very weak hydrogen-bonding, on the basis of experimental NMR data on crystalline phases and ab initio calculation results. This represents the first direct evidence for the presence of a substantial amount (13 to 29%) of free hydroxyl groups in hydrous silicate glasses (quenched melts). Free hydroxyls have been found to be favored by (1) more depolymerized melts and (2) network-modifying cations of higher field strength (Z/r^2). The formation of free hydroxyls is expected to result in an increase in the polymerization and viscosity of silicate melts, contrary to the effects of SiOH formation. The ^{29}Si MAS NMR results are consistent with such an interpretation. This dissolution mechanism could be particularly important for mantle-derived magmas.

The ^1H MAS NMR spectra for all the studied glasses contain peaks in the 4 to 17 ppm region, which can be ascribed to SiOH groups and molecular H_2O . The hydrogen-bonding strengths of SiOH in all the glasses cover a similar range from weak to very strong; the relative populations of strong hydrogen-bonding grow with decreasing field strength of the network-modifying cations. Ab initio calculations suggest that this trend may reflect hydrogen-bonding between SiOH and nonbridging oxygens.