

NMR evidence for a new water dissolution mechanism in depolymerized silicate melts: results for hydrous diopside composition

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We have studied a hydrous diopside ($\text{CaMgSi}_2\text{O}_6$) glass (3.85 wt% H_2O) (quenched from melt at 1 GPa) using ^{29}Si and ^1H NMR. The ^{29}Si MAS NMR spectrum contains an asymmetric peak near -82 ppm, resembling that of the anhydrous glass. The ^1H - ^{29}Si CP time constant is 0.39 ms, similar to those of SiOH in other hydrous silicates, suggesting that at least some of the water are SiOH. The ^1H MAS NMR spectra contain two peaks at 1.3 and 4.5 ppm. The broader 4.5 ppm peak can be ascribed to SiOH and/or molecular H_2O with a range of H-bonding strengths. The narrower and taller 1.3 ppm peak is most likely due to MgOH/CaOH. Thus, a substantial part of the dissolved water are free OH. This is a new water dissolution mechanism that has not been identified in more polymerized systems so far.

The dissolution of water in silicate melts significantly affects their phase relations, and physical/thermodynamic properties. The mechanism of water dissolution is thus a subject of intensive interest in earth sciences and has been studied by various spectroscopic techniques. However, almost all the studies thus far have been on relatively polymerized systems, from fully polymerized silicates (e.g. SiO_2) to disilicate compositions (e.g. $\text{Na}_2\text{Si}_2\text{O}_5$). These studies have shown that water is dissolved in either molecular H_2O or SiOH for Al-free systems. More depolymerized silicate melts, such as metasilicate compositions, are also geologically important, because mantle-derived magmas are known to become less silica-rich with depth of generation. Such magma could have played a particularly large role during the early evolution of the earth's mantle.

We have studied a hydrous diopside ($\text{CaMgSi}_2\text{O}_6$) glass (quenched melt) using ^{29}Si and ^1H MAS NMR in an attempt to understand the water dissolution mechanism in depolymerized silicate melts. The sample contains about 3.85 wt% H_2O and has been synthesized at 1 GPa and 1500C in a piston cylinder apparatus. Both single-pulse ^{29}Si and ^1H - ^{29}Si cross-polarization (CP) MAS NMR yield a single, asymmetric peak near -82 ppm, resembling that of anhydrous diopside glass. The ^1H - ^{29}Si CP time constant has been found to be 0.39 ms, similar to those of SiOH in other hydrous silicate glasses and crystals. Thus at least some of the dissolved water are in the form of SiOH. The ^1H MAS NMR spectra (both single-pulse and spin-echo) contain two partially resolved peaks at 1.3 and 4.5 ppm. The 4.5 ppm peak is broader and asymmetric with a broad shoulder near 14 ppm. This peak and its shoulder are similar to those observed in more polymerized hydrous silicate glasses, such as BaSi_2O_5 , and can be ascribed to SiOH and/or molecular H_2O with a range of H-bonding strengths. The 1.3 ppm peak is narrower and somewhat taller than the 4.5 ppm peak. The chemical shift of this peak indicates that it is due to OH groups that are not H-bonded. Peaks at this position have not been observed in any Al-free hydrous silicate glasses thus far and are not likely to be due to SiOH or molecular H_2O . On the other hand, MgOH in low-pressure hydrous magnesium silicates, such as talc, and CaOH in calcium silicate hydrates (CSH) are known to yield similar ^1H NMR chemical shifts. We may thus assign this peak to MgOH/CaOH, suggesting that a substantial part of the dissolved water are in the form of free OH. Therefore the water dissolution mechanisms in silicate melts/glasses change from molecular H_2O /SiOH in more polymerized systems to free OH groups plus SiOH/molecular H_2O in metasilicate compositions. Any models for water dissolution in depolymerized silicate melts/glasses must take this fact into consideration.