

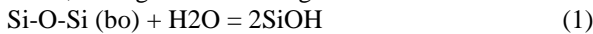
Compositional dependence of the dissolution mechanisms of water in silicate melts: a view from ^{29}Si and ^1H MAS NMR

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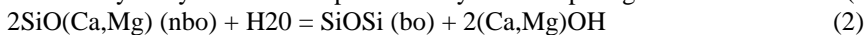
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The dissolution of water in silicate melts significantly affects their phase relations, and physical/thermodynamic properties. A knowledge of the mechanisms of water dissolution is necessary in order to gain a deep understanding of the properties and behavior of hydrous silicate melts. The nuclear magnetic resonance spectroscopic technique (NMR) is a particularly useful tool for this purpose, because it not only reveals the speciations of the dissolved water (^1H NMR), but also yields information concerning changes in the silicate network upon water dissolution (^{29}Si NMR). However, most of the NMR studies on hydrous silicate melts (quenched glasses) so far have been on a limited range of silicate compositions, and the effect of silicate compositions on the water dissolution mechanism has been largely overlooked. It is the purpose of this study to unravel the systematics of this compositional dependence by reviewing existing NMR data and collecting new NMR data for hydrous silicate glasses of a wide range of compositions.

Perhaps the most well investigated systems for hydrous silicate melts (quenched glasses) are the fully polymerized silicate (e.g. SiO_2) and $\text{Na}_2\text{Si}_4\text{O}_9$ compositions. The NMR data are consistent with a scenario that for Al-free systems, water is dissolved in the melt in both molecular H_2O and SiOH . The formation of SiOH is accompanied by the rupture of silicate network, through the following reaction:



At the 2001 Japan Earth and Planetary Science Joint Meeting, we have presented ^{29}Si and ^1H MAS NMR results for a CaMg-silicate hydrous melt (quenched glass), close to $\text{CaMgSi}_2\text{O}_6$ composition. These results indicated that a substantial part of the dissolved water are in the form of free OH ($(\text{Mg,Ca})\text{OH}$), in addition to SiOH /molecular H_2O . Here the dissolution of water as hydroxyls could be represented by two competing reactions: reaction (1) described above, and the following:



Reaction (2) drives the silicate network to a more polymerized structure.

The change of dissolution mechanisms could have arisen from one of the two silicate compositional changes: 1) the degree of depolymerization; 2) the type of network-modifying cations. Either the more depolymerized nature, or the higher field strength (Z/R^2) of the network-modifying cations (Ca/Mg vs. Na), or a combination of both, for the CaMg-silicate glass could have been responsible for the new dissolution mechanism (2).

In an effort to investigate further into the issue of compositional effect, we have surveyed literature NMR data for a wider range of hydrous silicate materials, including hydrated sodium silicate glasses and gel-formed amorphous lithium silicates. These data support the idea that it is the type of network-modifying cations, rather than the degree of polymerization of the system, that plays a crucial role in determining the dominant water dissolution mechanism. To put this issue to a more concrete test, we are in the process of synthesizing (and characterizing using ^{29}Si and ^1H NMR) hydrous silicate glasses (quenched melts) of varying degree of polymerizations, and types of network-modifying cation (Na, Ca, Mg, K, Li). The latest results will be presented at the meeting.