

## The nature of hydroxyl groups in aluminosilicate glasses

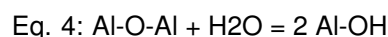
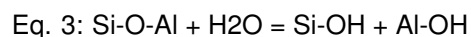
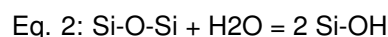
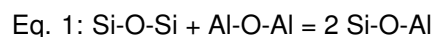
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The nature of hydroxyl speciation in aluminosilicate glasses has long been controversial. On the one hand, a model was proposed that leaves the degree of polymerization unchanged: hydroxyl groups are present as Na-OH and bridging OH. On the other hand, water was considered to depolymerize the aluminosilicate network through the formation of non-bridging hydroxyl groups. Recently, combined <sup>27</sup>Al-<sup>1</sup>H and <sup>1</sup>H-<sup>29</sup>Si-<sup>1</sup>H cross polarization NMR data unambiguously confirmed the depolymerization of the metaluminous aluminosilicate network through the formation of Si-OH and Al-OH groups. In addition, free hydroxyl groups, associated with the network modifiers, are present for highly polymerized compositions.

For the metaluminous sodium aluminosilicate system, we quantitatively determined the proportions of Si-OH and Al-OH from <sup>27</sup>Al-<sup>1</sup>H cross polarization and <sup>1</sup>H NMR spectroscopic data: the hydroxyl speciation was shown to be governed by degree of aluminum-avoidance (Eq. 1) and the different hydrolysis reactions (Eqs. 2-4):



In the present study, we extend this approach to calcium and potassium aluminosilicate glasses and compare the results with those of the sodium aluminosilicate system. For the calcium aluminosilicate glasses, the NMR data provides conclusive evidence for Al-OH, but the spectral resolution is insufficient to quantify its abundance. For the potassium aluminosilicate glasses, the resolution was high enough to determine the proportion of Al-OH and Si-OH and the equilibrium constants associated with Eqs. 1-4. Compared to the sodium aluminosilicate system, the potassium system is characterized by the increased instability of Al-O-Al linkages, leading to a higher degree of aluminum avoidance (Eq. 1) and a larger tendency for Al-O-Al bonds to hydrolyze (Eq. 2). The corresponding equilibrium constants imply that water will dissociate almost completely in metaluminous potassium aluminosilicate glasses with Al>Si and this prediction is confirmed by infrared absorption measurements on such glasses.

## Determination of water speciation in hydrous Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> melt at high temperature and high pressure

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Though in situ measurements of water speciation were widely conducted for rhyolitic melts and their analogues [e.g., 1, 2, 3], only limited data are available for depolymerized silicate melts. We performed in situ near-infrared and Raman spectroscopic measurements of Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> (structural analogue of depolymerized, basaltic melt) with a fixed water content (5.9 wt%) in an externally heated diamond anvil cell (HDAC) [4]. Experiments were carried out at temperatures to 800 degree C and at pressures to 2 GPa. Temperature was controlled to plus-minus 1 degree C with chromel-alumel thermocouples in contact with the anvils near the sample chamber of the HDAC. Pressure inside the sample chamber was monitored with the pressure- and temperature-dependent Raman shift of the <sup>13</sup>C diamond marker [5]. Only single, homogeneous liquid phase was stable at temperatures above 650 degree C and at pressures above 1.6 GPa; neither crystallization nor fluid exsolution was observed. At lower temperatures (hence at lower pressures) crystallization of solid Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> was observed and conformed by Raman spectroscopy. Near-infrared spectra of the homogeneous liquid phase contain absorption peaks corresponding to both molecular H<sub>2</sub>O (near 5200 cm<sup>-1</sup>) and structurally bound OH groups (near 4500 cm<sup>-1</sup>). Assuming a constant ratio of the molar absorptivities for these bands, OH/H<sub>2</sub>O is estimated to be 0.9 in the quenched glass at ambient conditions and 1.9 in the homogeneous liquid phase at 800 degree C (both OH and molecular H<sub>2</sub>O as H<sub>2</sub>O, in wt%). Thus, one may expect that in the homogeneous liquid phase, the OH/H<sub>2</sub>O increases as temperature increases. This trend is similar to those reported for highly polymerized silicate melts [1, 2].

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