The nature of hydroxyl groups in aluminosilicate glasses

Wim J Malfait[1], Xianyu Xue[2]

[1]Institute for Geochemistry and Petrology, ETH Zurich, Switzerland, [2]Institute for Study of the Earth's Interior, Okayama University, Misasa, Japan

E-mail: wim.malfait@erdw.ethz.ch

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 ^{27}Al-^{1}H and ^{1}H-^{29}Si-^{1}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 ^{27}Al-^{1}H cross polarization and ^{1}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):

Eq. 1: Si-O-Si + Al-O-Al = 2 Si-O-Al
Eq. 2: Si-O-Si + H2O = 2 Si-OH
Eq. 3: Si-O-Al + H2O = Si-OH + Al-OH
Eq. 4: Al-O-Al + H2O = 2 Al-OH

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.