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The speciation of hydrous aluminosilicate glasses and melts: a view from NMR, infrared and Raman spectroscopy.

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The combined results of ^{27}Al-^{1}H and ^{1}H-^{29}Si-^{1}H cross polarization NMR experiments for hydrous glasses along the SiO_2-$NaAlSiO_4$ join confirm that the dissolution mechanism of water in aluminosilicate glasses is fundamentally the same as for Al-free systems, i.e. dissolved water breaks oxygen bridges and creates Si-OH and Al-OH groups. The partial ^{1}H NMR spectra for Al-OH were derived from the ^{27}Al-^{1}H cross polarization spectra without any a priori assumptions about their lineshape. The abundance of Al-OH was then determined by fitting these partial spectra to quantitative ^{1}H spectra. The fraction of Al-OH was found to increase non-linearly with increasing Al content, with up to half of the OH groups as Al-OH for compositions close to $NaAlSiO_4$. The relative abundances of the different species are controlled by the degree of Al-avoidance and the relative tendency of hydrolysis of the different types of oxygen bridges, through the following equilibrium reactions:

Si-O-Si + Al-O-Al = 2 Si-O-Al (1)

Si-O-Si + Al-OH = Si-O-Al + Si-OH (2)

The values of the corresponding equilibrium constants can be obtained by fitting reactions (1) and (2) to the experimentally derived Al-OH/OH_{tot} ratios and the abundance of the different oxygen species, i.e. Si-O-Si, Si-O-Al, Al-O-Al, Si-OH, Al-OH and H_2O_{mol}, can be predicted for a wide range of water and Al contents.

Infrared and Raman spectroscopic studies on the same glasses indicate that the infrared absorption band near 4500 cm^{-1} is an overtone of the fundamental (Si,Al)-OH and O-H stretching vibrations near 900 and 3600 cm^{-1} respectively. This implies that free OH, e.g. Mg-OH or Ca-OH, will not contribute to the 4500 cm^{-1} band and this should be taken into account when measuring the OH/H_2O_{mol} ratio by infrared spectroscopy in highly depolymerized glasses.

In a complementary study, we have investigated the Al environment in realistic analogs to natural granitic melts, i.e. glasses in the H_2O-Na_2O-K_2O-Al_2O_3-SiO_2 system by ^{27}Al NMR spectroscopy. More specifically, we investigate the effect of pressure (up to 3.5 GPa) and water content (up to 5.24 wt% H_2O) on the Al coordination. For all measured glasses, the abundance of ^{V}Al was smaller than 2%, whilst no ^{VI}Al was detected. As expected, the amount of ^{V}Al systematically increases with increasing pressure. However, the proportion of ^{V}Al decreases with increasing water content, contrary to what has been observed previously for basaltic glasses.