

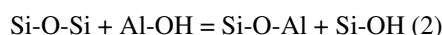


## The speciation of hydrous aluminosilicate glasses and melts: a view from NMR, infrared and Raman spectroscopy.

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The combined results of  $^{27}\text{Al}$ - $^1\text{H}$  and  $^1\text{H}$ - $^{29}\text{Si}$ - $^1\text{H}$  cross polarization NMR experiments for hydrous glasses along the  $\text{SiO}_2$ - $\text{NaAlSiO}_4$  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  $^1\text{H}$  NMR spectra for Al-OH were derived from the  $^{27}\text{Al}$ - $^1\text{H}$  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  $^1\text{H}$  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  $\text{NaAlSiO}_4$ . 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:



The values of the corresponding equilibrium constants can be obtained by fitting reactions (1) and (2) to the experimentally derived Al-OH/OH<sub>tot</sub> 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<sub>2</sub>O<sub>mol</sub>, 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  $\text{cm}^{-1}$  is an overtone of the fundamental (Si,Al)-OH and O-H stretching vibrations near 900 and 3600  $\text{cm}^{-1}$  respectively. This implies that free OH, e.g. Mg-OH or Ca-OH, will not contribute to the 4500  $\text{cm}^{-1}$  band and this should be taken into account when measuring the OH/H<sub>2</sub>O<sub>mol</sub> 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  $\text{H}_2\text{O}$ - $\text{Na}_2\text{O}$ - $\text{K}_2\text{O}$ - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  system by  $^{27}\text{Al}$  NMR spectroscopy. More specifically, we investigate the effect of pressure (up to 3.5 GPa) and water content (up to 5.24 wt% H<sub>2</sub>O) on the Al coordination. For all measured glasses, the abundance of  $^V\text{Al}$  was smaller than 2%, whilst no  $^{VI}\text{Al}$  was detected. As expected, the amount of  $^V\text{Al}$  systematically increases with increasing pressure. However, the proportion of  $^V\text{Al}$  decreases with increasing water content, contrary to what has been observed previously for basaltic glasses.