

Constraints on the incorporation mechanism of chlorine in peralkaline and peraluminous Na₂O-CaO-Al₂O₃-SiO₂ glasses

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ABSTRACT

Incorporation mechanisms of Cl in peralkaline and peraluminous Na₂O-CaO-Al₂O₃-SiO₂ glasses as a model system for phonolitic melts were investigated using ³⁵Cl, ²³Na, ²⁷Al, and ²⁹Si magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. The size and large distribution of electric field gradients for ³⁵Cl causes loss of signal in the MAS NMR experiment and this, in combination with the low concentration of Cl and the large chemical shift dispersion, means that even at the highest available fields we are at the limits of MAS NMR. Nevertheless clear differences in the Cl environment in peralkaline and peraluminous glasses can readily be seen. In both glass types Cl exists in relatively symmetric Na-Ca-Cl environments. The ³⁵Cl chemical shift indicates that the Cl environment is dominated by the presence of Na cations, consistent with the Na/Ca ratio of 5/1 in the glasses. ³⁵Cl MAS NMR spectra of the peraluminous glasses show a larger chemical shift distribution and a more positive isotropic chemical shift, ~-75 ppm, than the peralkaline glasses, ~-100 ppm. They also have a larger quadrupole coupling constant with a larger distribution, indicating greater disorder in the peraluminous glasses. It is likely that there are more Ca cations present in the Cl environments in the peraluminous glasses than in the peralkaline glasses despite their having the same Na/Ca ratio. In the peralkaline glasses the formation of Na-Ca-Cl environments leads to a decrease in the number of network-modifying cations, which causes a polymerization of the glass network. No effect on the glass polymerization was observed in the peraluminous glasses. Some ³⁵Cl signal is also lost in the static spectra indicating that ~20% of Cl for a peralkaline glass and more than ~70% for a peraluminous glass must be in environments where there is a large enough electric field gradient that the resulting very broad line is unobservable. These environments could be simply Na-Ca-Cl with higher electric field gradients than those producing the observed ³⁵Cl signal or non-bridging Cl environments like for example Al-Cl. The Cl environment in the present mixed Na₂O-CaO aluminosilicate glasses appears to be more disordered than was to be expected from previous NMR spectroscopic studies on simpler glass compositions.

Keywords: Chlorine, aluminosilicate, glasses, phonolites, ³⁵Cl, ²³Na, ²⁷Al, ²⁹Si, NMR