Constraints on the incorporation mechanism of chlorine in peralkaline and peraluminous Na$_2$O-CaO-Al$_2$O$_3$-SiO$_2$ glasses

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ABSTRACT

Incorporation mechanisms of Cl in peralkaline and peraluminous Na$_2$O-CaO-Al$_2$O$_3$-SiO$_2$ glasses as a model system for phonolitic melts were investigated using $^{35}$Cl, $^{23}$Na, $^{27}$Al, and $^{29}$Si magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. The size and large distribution of electric field gradients for $^{35}$Cl 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 environments in peralkaline and peraluminous glasses can readily be seen. In both glass types Cl exists in relatively symmetric Na-Ca-Cl environments. The $^{35}$Cl 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. $^{35}$Cl 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 $^{35}$Cl 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 $^{35}$Cl signal or non-bridging Cl environments like for example Al-Cl. The Cl environment in the present mixed Na$_2$O-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, $^{35}$Cl, $^{23}$Na, $^{27}$Al, $^{29}$Si, NMR

INTRODUCTION

In natural magmas chlorine (Cl) concentration usually does not exceed 1 wt%, although alkali-rich magmas like phonolites can contain up to 1.2 wt% Cl (Carroll 2005; Aiuppa et al. 2009). Even though the abundance of Cl in natural magmatic systems is low compared to H$_2$O, the incorporation mechanism of Cl in silicate melts with compositions relevant to magmatic systems is important as the presence of Cl can lead to the formation of brines (e.g., Souriraj and Kennedy 1962; Anderko and Pitzer 1993; Signorelli and Carroll 2000) as well as ore deposits (e.g., Helgeson 1969; Webster 1997a; Candela 1997). Chlorine also influences melt rheology (Dingwell and Hess 1998; Zimova and Webb 2006; Baasner et al. 2013a). Baasner et al. (2013a) showed that incorporation of Cl into the system Na$_2$O-CaO-Al$_2$O$_3$-SiO$_2$ results in contrasting behavior with 1.1 mol% (0.6 wt%) increasing the viscosity in peralkaline melts by a factor of 10, whereas 0.6 mol% (0.3 wt%) Cl in peraluminous melts decreases viscosity by a factor of 3.

Even though the incorporation mechanism of Cl in silicate melts is the key to understand the behavior of Cl in magmatic systems, there are only a few studies about this topic. Stebbins and Du (2002) found from $^{35}$Cl magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy that in silicate and aluminosilicate glasses Cl is coordinated by mono- and divalent cations like Na or Ba rather than by Al and Si. These authors observed that in general the Cl environment is very similar in salts and glasses. For example in sodium silicate and aluminosilicate glasses Cl is coordinated by less than six (as for halides) but more than 4 Na cations (as in sodalite).

Sandland et al. (2004) concluded from $^{35}$Cl MAS NMR spectroscopy that Cl in mixed Na$_2$O-CaO silicate glasses shows no strong preference for either Na or Ca. These authors also found that the presence of Al or H$_2$O does not significantly affect the Cl environment. Evans et al. (2008) investigated $^{35}$Cl environment...