The effect of chlorine on the viscosity of Na$_2$O-Fe$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ melts

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ABSTRACT

The shear viscosities of Cl-bearing melts in the system Na$_2$O-Fe$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ were determined at temperatures of 550–950 °C in the range of 10$^{10}$ to 10$^{13}$ Pa·s using the micropenetration technique. The compositions are based on addition of Fe$_2$O$_3$ or FeCl$_3$ to aluminosilicate glasses with a fixed amount of SiO$_2$ (67 mol%). Although there was loss of Cl$^-$ during the glass syntheses, no loss occurred during the viscometry experiments. It is to be expected that Cl$^-$ takes the structural position of O$_2$–, and thus reduces the polymerization of the melt structure, and therefore the viscosity of the melt; as F$^-$ does. Our measurements show that the presence of Cl$^-$ increases or decreases the viscosity of the melts as a function of melt composition. In the present melts, at least 10% of the Fe exists as network-modifying or charge-balancing Fe$^{2+}$; whereas the rest exists as network-forming Fe$^{3+}$. It is proposed here that the different effects of Cl on viscosity are due to the preferred Cl$^-$-Fe$^{3+}$$_{\text{NBO}}$ bonding together with the different structure of peralkaline and peraluminous melts. In peralkaline aluminosilicate melts, the addition of Cl$_2$O$^{-1}$ will destroy 2 NBOs and create one BO if Cl$^-$ bonds primarily to the Fe$^{3+}$ creating non-bridging O atoms. This would result in an increase in viscosity. In peraluminous melts, the addition of Cl$_2$O$_3$ may result in Cl$^-$ bonds to the charge-balancing Fe$^{2+}$, creating 2 new tri-clusters [assuming (Al$^{3+}$,Fe$^{3+})$Si$_2$O$_5$ tri-clusters exist]. The preference of Cl$^-$ to form bonds to the NBO-forming Fe$^{2+}$ is indicated by the small amount of Cl$^-$ soluble in the peraluminous melt structure in comparison to that soluble in the peralkaline structure.

Keywords: Viscosity, melt structure, micro-penetration, chlorine, iron, aluminium, peraluminous, peralkaline

INTRODUCTION

There have been many investigations of the viscosity of volatile free silicate melts (e.g. Poole and Gensamer 1949; Riebling 1966; Hummel and Arndt 1985; Dingwell and Virgo 1988; Toplis 2001; Webb et al. 2004) as these data are necessary for the study of melt migration and volcanic processes; and also because the melts are relatively easy to synthesize in the laboratory. Given the ubiquitous presence of volatiles in magmas in the Earth, there are an increasing number of studies addressing the solubility and effect on viscosity of H$_2$O, CO$_2$, and F in both natural and synthetic magmatic systems (see Carroll and Webster 1994; Dingwell et al. 2004; Dingwell and Hess 1998; Bourgue and Richet 2001; Mysen et al. 2004; Giordano et al. 2004). The present study addresses the effect of the halogen Cl on the viscosity of silicate melts. Very little is known about the solubility mechanism and diffusivity of Cl in silicate melts [see Carroll and Webster (1994) for a review], and even less is known about the effect of Cl on viscosity.

In general, it has been assumed that the presence of volatiles in a melt will decrease the viscosity. Thus, as magma chambers degas, the viscosity of the melt will increase (in the absence of crystallization). If the increase in melt viscosity is large, the volatile-filled bubbles will not be able to escape and an explosive eruption may result (e.g., Jaupart and Vergniolle 1989). The recent viscosity measurements of Dingwell and Hess (1998) show that, while Cl decreases the viscosity of a Na$_2$O-Fe$_2$O$_3$-SiO$_2$ melt at high viscosity conditions (10$^{10}$ Pa·s), it appears to increase viscosity at low viscosity conditions (10$^8$ Pa·s). The addition of F to the same melt, however, reduced viscosity across the entire 10$^7$ to 10$^{10}$ Pa·s range investigated. In both cases the effect of the halogen on viscosity was larger at high viscosity conditions.

In the present study, we have investigated the effect of Cl on the viscosity of Na$_2$O-Fe$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ melts at high viscosity conditions. This system contains both network-forming and network-modifying elements and covers the compositional range from peraluminous to peralkaline—and can therefore be viewed as an analog of natural magmatic silicates.

EXPERIMENTAL METHODS

The base glasses were initially synthesized by fusion of SiO$_2$, Al$_2$O$_3$, and Na$_2$CO$_3$ powders in Pt-Rh10 thin wall crucibles. Melting-times and melting-temperatures depend on the Al$_2$O$_3$ content and varied from 10 to 24 h in the temperature range 1350–1650 °C. Base glass melts were quenched from temperatures of 1000 °C and ground in an agate mortar to powder with particle sizes not bigger than 1 mm. The components Fe$_2$O$_3$ and FeCl$_3$ were added to this glassy powder. The mixture was homogenized in a plastic bottle for ca. 15 min, followed by a short re-melting in the furnace with stirring, when needed, to remove the bubbles. The melts were cooled quickly to ca. 200 °C above the glass-transition temperature $T_g$. Around $T_g$ a slow-cooling regime was used to avoid the build up of internal stresses and resultant cracking of the glass during drilling of cores and/or their grinding and polishing. The viscosity samples are 8 mm diameter, 3 mm thick disks with plane parallel faces. The surfaces of each disk were ground, polished, and cleaned before the viscosity measurement.

All glasses were checked for chemical homogeneity (Table 1) by electron-microprobe analyses both before and after the viscosity determinations. In view of the possible beam-induced migration of alkalis, the Na$^+$ content was also measured by Atomic-Absorption-Spectroscopy. In the process of determining the Fe$^{2+}$/Fe$^{3+}$ composition of the melts, the total amount of Fe was also measured by spectral

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