Structure and the extent of disorder in quaternary (Ca-Mg and Ca-Na) aluminosilicate glasses and melts

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ABSTRACT

The structure of multi-component silicate melts and glasses (e.g., Ca-Mg and Ca-Na aluminosilicates) can provide insight into the properties of natural silicate melts and has implications for relevant magmatic processes. In spite of its importance, the atomic and molecular structure of most multi-components (e.g., quaternary) melts and glasses has not been fully described, primarily because of insufficient resolution obtained with conventional spectroscopic and scattering methods; the information obtained by these methods is compromised by severe inhomogeneous peak broadening due to structural complexity. Here we report the first 17O and 27Al 3QMAS NMR spectra for quaternary, Ca-Mg and Ca-Na peralkaline aluminosilicate glasses (i.e., $M/Al > 1$, $M$ is one monovalent or one-half a divalent cation). These data reveal new details into the molecular structure of multi-component aluminosilicate melts, which include the presence of a substantial fraction of $^1$Al in the Ca-Mg aluminosilicate glasses and $^{1}$Al-$^{27}$Al in both glasses at 1 atm. Traditional models of glass structure do not support the presence of such species given these high-silica, peralkaline compositions. These results suggest that Al avoidance is violated in the multi-component peralkaline aluminosilicate glasses, and that the presence of Mg$^{2+}$ in the melts increases the extent of disorder in the melts (compared with Ca$^{2+}$ and Na$^{+}$). These factors lead to an increase in configurational entropy and the activity coefficients of the oxides, and may provide an explanation for the decrease in viscosity of these complex melts.

INTRODUCTION

Studies of silicate melts and glasses are essential for enhancing our understanding of the diversity of magmatic processes. The atomic and molecular structure of silicate melts yields important constraints on their physico-chemical properties (e.g., viscosity, density, and thermodynamic properties, etc.) and geochemical processes (generation, migration, and emplacement). Therefore, it would be of immense importance to explore the atomic arrangements in silicate melts and glasses to gain a fundamental understanding of their structure-property relationships and implications for the global geochemical processes.

Among the many interesting systems relevant to generation of primary melts from the mantle, the glass composition in the CaO-MgO-Al2O3-SiO2 (CMAS) quaternary system is particularly important as it represents a major fraction of the chemical composition of the mantle and serves as an important model system to describe phase relationships between lherzolite minerals and primary mantle melts. (e.g., Gudfinnsson and Presnall 1996; Presnall et al. 2002). Highly sodic (Na-rich) aluminosilicate melts have been reported in various tectonic setting such as slab-derived melts or xenolithic glasses (e.g., Rapp and Watson 1995; Robinson et al. 1998; Coltorti et al. 2002). Therefore, establishing the structure of glasses in the CaO-Na2O-Al2O3-SiO2 (CNAS) system can provide atomistic and molecular predictors of the activity coefficients of the oxides. This information would allow for estimation of the composition of melts generated (e.g., through phase-equilibrium considerations), as well as help to explain transport properties (including viscosity) as well as the crystal-melt partitioning of trace elements (Bennett et al. 2004).

It should be noted that the structure of silicate glasses represents that of supercooled liquids at their respective glass transition temperatures; below the glass transition temperatures, these structures are frozen and, therefore, can provide insight into the structure of silicate melts. There have been numerous studies of the structure of glasses and melts using diverse spectroscopic and scattering methods as well as theoretical simulations. Although it is not possible to refer to all of these studies here, interested readers are directed to several relevant review articles and books that summarize the progress and advances in this field (e.g., Mysen et al. 1982; Murdoch et al. 1985a; Engelhardt and Michel 1987; Kirkpatrick 1988; Mysen 1988; Eckert 1992; Brown et al. 1995; McMillan and Wolf 1995; Poole et al. 1995; Stebbins 1995; Cormack and Cao 1997; Kohn 2004). These reviews highlight the evolution in our understanding of the structure of silicate melts and glasses. Most of the progress in this field has been made by focusing on relatively simple model silicate glasses and melts. Quantitative analysis of more complex, hence more realistic, multi-component silicate glasses (e.g., CMAS and CNAS) is particularly challenging and is usually limited by an inability to unambiguously resolve characteristic features. This is because inhomogeneous broadening of the spectrum or diffraction pattern

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