Interaction between composition and temperature effects on non-bridging oxygen and high-coordinated aluminum in calcium aluminosilicate glasses

LINDA M. THOMPSON* and JONATHAN F. STEBBINS

Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305, U.S.A.

ABSTRACT

The configurational changes that occur with temperature, and how these vary with composition, affect the thermodynamic and transport properties of aluminosilicate melts but are not well understood. We present here high-resolution $^27$Al and $^17$O NMR data on several calcium aluminosilicate glasses along two silica isopleths crossing the metaluminous (SiO$_2$-CaAl$_2$O$_4$) join, prepared with varying quench rates and thus with fictive temperatures spanning approximately 100 K. In all compositions, five-coordinated aluminum increases with increasing fictive temperature. For glasses along the 60 mol% SiO$_2$ isopleth, NBO also increases with increasing fictive temperature; this is less obvious for the glasses along the 30 mol% SiO$_2$ isopleth. The data suggest the mixing of bridging oxygen contributes to the magnitude of the observed temperature effect on NBO and continue to suggest the existence of multiple mechanisms that generate NBO and $^3$Al.

Keywords: NMR spectroscopy, non-bridging oxygen, five-coordinated aluminum, temperature effects

INTRODUCTION

Understanding the structure of aluminosilicate melts and glasses and its impact on their properties has been the subject of much research (see reviews of Mysen and Richet 2005; Stebbins et al. 1995) because of their importance to both geological processes (most magmas) and technology (e.g., flat-panel displays). Network connectivity (melt polymerization) in particular has been highlighted as a significant factor in thermodynamic and transport properties (Lee et al. 2004; Lee and Stebbins 2006) and is often predicted from composition using “standard” models of the melt structure.

These “standard” models of aluminosilicate structure use simple concepts from known crystal structures to approximate the melt structure, assuming that in an ambient-pressure melt with modifier oxides equal to or in excess of alumina (e.g., mol% Al$_2$O$_3$ $\leq$ CaO or K$_2$O), all Al$^3$ cations are four-coordinated ($^{33}$Al). Oxygen anions connecting two network formers (e.g., Si$^4+$ or Al$^{3+}$) are described as bridging O atoms, while O atoms coordinated to only one network former are known as non-bridging O atoms (NBO) and rely on network modifiers to compensate the remaining valence charge. Along the metaluminous (charge-compensated) join (e.g., CaAl$_2$O$_4$-SiO$_2$), it is assumed that all O atoms are bridging; additional modifier oxide results in the formation of NBO with the concentration predictable by stoichiometry.

It should now be recognized, however, that this “standard” model is only a first approximation and fails to account for several observed structural species that are of relatively low concentration but are potentially important in models of both thermodynamic and transport properties. For example, high-resolution $^{27}$Al NMR spectroscopy has demonstrated that, for most glasses in the CaO-Al$_2$O$_3$-SiO$_2$ system, there is significant (4–8%) $^3$Al, with complex relationships between concentration and composition (Neuville et al. 2004, 2006; Stebbins et al. 2000; Thompson and Stebbins 2011). Significant quantities of $^3$Al have also been found in ambient-pressure Mg- and alkali aluminosilicates (Allwardt et al. 2005b; McMillan and Kirkpatrick 1992; Toplis et al. 2000). Evidence from melts quenched at pressures up to 10 GPa has shown that cation field strength (cation size and charge) affects the average Al coordination, with higher field strengths corresponding to increases in the $^3$Al content (Allwardt et al. 2005b, 2007; Kelsey et al. 2009); ambient-pressure aluminosilicate and aluminoborate glasses have similar trends (Allwardt et al. 2005b; Florian et al. 2007; Ifekwunyishi et al. 2011; Thompson and Stebbins 2012).

Similarly to the “non-standard” presence of $^3$Al, $^17$O NMR has detected between 1–8% NBO in several compositions along the metaluminous join in the CAS system, where its concentration is predicted to be zero by the “standard” model and therefore its presence requires additional structural changes (such as $^3$Al and/or three-coordinated oxygen) to maintain local charge balance (Lee and Stebbins 2006; Oglesby et al. 2002; Stebbins et al. 2008, 1999; Stebbins and Xu 1997). Subsequent work has shown NBO persisting well into the peraluminous compositional region (Thompson and Stebbins 2011), where its presence was predicted from variations of melt viscosity with composition (Toplis and Dingwell 2004; Toplis et al. 1997b) and has also been examined by Raman spectroscopy (Mysen and Toplis 2007). Studies of the potassium aluminosilicate and barium aluminosilicate systems have also found NBO in metaluminous and peraluminous glasses (Thompson and Stebbins 2011, 2012); the limited evidence presented suggests that cation charge has a more important effect on NBO content than does cation radius for a given valence. However, NMR evidence also suggests that in highly peralkaline or peralkaline earth compositions, NBO contents are consistent with those predicted by stoichiometry (Allwardt et al. 2005a; Stebbins et al. 2008; Thompson et al. 2012).

To apply these data to systems of interest (e.g., melts in