Bonding preferences of non-bridging O atoms: Evidence from $^{17}$O MAS and 3QMAS NMR on calcium aluminate and low-silica Ca-aluminosilicate glasses

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ABSTRACT

The fraction of O atoms as non-bridging O atoms (NBO) can be well approximated based on composition alone in many silicate glasses, but the NBO preference for specific network forming cations is much less well known. Using oxygen-17 ($^{17}$O) NMR on low-silica calcium aluminosilicate (CAS) glasses, this study shows that Al-NBO (155 ppm) can be readily distinguished from Si-NBO (110-120 ppm), and that there is a strong preference for the latter. This study also presents a consistent equilibrium constant formulation that indicates that for thermodynamic modeling of most CAS melts with Si > Al, Al-NBO are of minor importance, although they could be significant in some models of diffusion and viscosity. Al-27 one pulse NMR and analyses of spinning side bands show that AlO$_3$ and AlO$_4$ species are below detection limits (<0.5%) in the low-silica (SiO$_2$ ≤ 20 mol%) glasses of this study (NBO/T = 0.6 to 0.8). In addition, $^{17}$O MAS NMR does not detect any obvious (<2%) AlO triclusters; hence calculations of NBO assignments can be assigned unambiguously.

INTRODUCTION

Discussion of oxide glass structure relies heavily upon the principle that there are network formers (i.e., Si, Al, B) and network modifiers (i.e., Ca, Na, K etc.). The network formers provide the framework and rigidity of the glass while the network modifier oxides break apart this structure through the formation of non-bridging O atoms (NBO). An NBO is an O atom bonded to only one network former leaving the network modifiers to balance the remaining valence charge.

Network connectivity plays a significant role in the thermodynamic (Navrotsky 1995; Hess 1995) and transport properties (Hess et al. 1995, 1996) of magmas and glasses. For instance, the orthosilicate composition (33 mol% SiO$_2$) of the binary compositions of SiO$_2$-alkali or alkaline earth glasses is thought to contain the most NBO of any composition (Hess 1980). In binary silicate glasses, as the amount of silica is increased from the orthosilicate composition (increasing the network connectivity and reducing the number of NBO), enthalpies, free energies, component activities, and viscosity are all strongly affected (Hess 1995; Navrotsky 1995; Hess et al. 1995, 1996). This is the result of increasing the network connectivity as $Q^0$ species are being converted to $Q^1$, $Q^2$, and even more connected species, where 0, 1, and 2 represent the number of bridging O atoms (BO) bonded to the Si tetrahedron. Similar effects are expected for other network forming cations. The average degree of network connectivity is relatively well known for silicate and aluminosilicate glasses, but the distribution of NBO on different network cations is much less well understood. Certain combinations of framework cations in some composition ranges show no preference in competing for NBO, such as B and Si in the Ba-borosilicates (Zhao et al. 2000). In contrast, there is much indirect evidence that suggests that Si has a strong preference over Al for NBO in the alkali and alkaline earth aluminosilicate systems (Mysen 1988 and references therein).

Most previous studies of NBO preferences in aluminosilicates have used relatively indirect methods for NBO detection such as Raman spectroscopy (Mysen et al. 1981, 1985; Domine and Pirou 1986), X-ray and/or neutron scattering (Petkov et al. 1998, 2000; Cormier et al. 2000), and $^{27}$Al and $^{29}$Si magic-angle spinning (MAS) NMR (Engelhardt et al. 1985). For example, Engelhardt et al. (1985) used the observed $^{29}$Si chemical shifts to estimate the average $Q$ speciation for Si and Al in “low silica” (<10% SiO$_2$) glass as $Q^0$ and $Q^1$, respectively. However, the uniqueness of such conclusions is uncertain because of the lack of resolution among $^{29}$Si peaks for different network species and the dependence of $^{29}$Si MAS chemical shift on both the average $Q$ speciation and next nearest neighbor effects (Si vs. Al).

Oxygen-17 NMR can provide a much more direct evaluation of this issue. Previous $^{17}$O NMR spectra have shown the presence of NBO in several calcium aluminosilicate (CAS) glasses on the CaAl$_2$O$_4$-SiO$_2$ join (Stebbins and Xu 1997; Stebbins et al. 1999; Oglesby et al. 2002; Lee and Stebbins 2002). The observed $^{17}$O MAS chemical shifts for NBO in these glasses are similar to those found in calcium silicate glasses in which all NBO are bonded to Si (Stebbins 1995; Stebbins et al. 1997). In addition, a recent $^{17}$O MAS study of an NBO-containing impurity phase in crystalline CaAl$_2$O$_4$ showed that the Al-NBO peak is shifted to a higher frequency by 30 to 40 ppm...