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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_5 and AlO_6 species are below detection limits (<0.5%) in the low-silica ($SiO_2 \leq 20$ mol%) glasses of this study (NBO/T = 0.6 to 0.8). In addition, ^{17}O MAS NMR does not detect any obvious (<2%?) Al_3O triclusters; hence calculations of NBO assignments can be assigned unambiguously.