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Ca-Mg and K-Mg mixing around non-bridging O atoms in silicate glasses: An investigation using ^{17}O MAS and 3QMAS NMR

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ABSTRACT

In an effort to improve the physical accuracy of models of the thermodynamics of silicate melts, we describe a systematic study of the extent of modifying cation mixing, using ^{17}O 3QMAS NMR, in a series of Ca-Mg and K-Mg silicate glasses. The spectra for the mixed cation $Ca_{2-2x}Mg_{2x}Si_2O_6$ glass show that only one large non-bridging O atom (NBO) peak occurs that encompasses the entire range of chemical shifts ranging from Ca-NBO to Mg-NBO. Comparison of the isotropic projections from 3QMAS NMR to spectra predicted by a random model show that mixing in these glasses is highly disordered, but may contain a small amount of ordering at the glass transition temperature. In contrast, cation mixing in K-Mg silicate glasses is very ordered, confirming previous results; however, the results of this study disagree with the interpretation of the previous study and show that the NBO in K-Mg silicate glasses contain mostly Mg-NBO, not a highly ordered K-Mg-NBO species. These order-disorder results have direct implications in constraining entropy models and therefore allowing better predictions of mineral-melt equilibria in silicate melts.