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Quench rate and temperature effects on framework ordering in aluminosilicate melts

EMILY V. DUBINSKY* AND JONATHAN F. STEBBINS

Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305-2115, U.S.A.

ABSTRACT

The effect of temperature on the structure of $LiAlSiO_4$ and $NaAlSiO_4$ liquids has been studied by ^{17}O 3QMAS NMR spectroscopy using glass samples prepared with different fictive temperatures. The abundance of Al-O-Al and Si-O-Si bridging O linkages increases with increasing fictive temperature, indicating that the reaction 2 Al-O-Si ↔ Al-O-Al + Si-O-Si shifts to the right with increasing temperature in the liquid. The observed temperature dependence of Al-O-Al species abundance allows us to estimate the ΔH of this reaction to be 28.8 ± 11.3 kJ/mol for $NaAlSiO_4$ glasses and 31.7 ± 13.3 kJ/mol for $LiAlSiO_4$ glasses. Extrapolating our results to higher temperature, we estimate that 13–18% of the bridging O atoms occur as Al-O-Al in $NaAlSiO_4$ and 15–25% in $LiAlSiO_4$ at ~2000 K, as compared to 25% Al-O-Al predicted by a statistically random bridging O distribution in compositions with an Al/Si ratio of 1. Using the experimental data to estimate the contribution to configurational heat capacity from Al/Si disordering in $NaAlSiO_4$ liquid, we find that redistribution of bridging O species with increasing temperature produces a negative dC_P/dT above the glass transition and therefore cannot account for the observed positive dC_P/dT. We discuss a generalized mechanism for structural rearrangement characterized by a small initial species concentration at T_g and a large ΔH, which produces a positive dC_P/dT.

Keywords: NMR spectroscopy, ^{17}O 3QMAS NMR, alkali aluminosilicate glasses, melts, melt structure, enthalpy, configurational heat capacity, framework cation, order-disorder, Al/Si, bridging oxygen, non-bridging oxygen, network former, termperature effect, fictive temperature, quench rate