



Temperature and pressure effects on silicate glass and melt structure: recent results from NMR

J. F. Stebbins, J. A. Allwardt, E. V. Dubinski and K. E. Kelsey

Dept. of Geological and Environmental Sciences, Stanford University, Stanford, CA, USA
(stebbins@stanford.edu / Fax: 650-725-2199)

As models of melt thermodynamic and transport properties become more sophisticated and quantitative, there is an increasing need for accurate constraints on melt structure. Examples include formulations of transport properties that include configurational (structural) terms, and new structure-based “associated solution” models (Ghiorso and colleagues). Structural information at magmatic temperatures and pressures are of course most useful for understanding phase equilibria, viscosity, density, etc., but limitations in technical capabilities and in quantitation currently restrict what can be gleaned from *in situ*, high T and/or P spectroscopic and scattering measurements. Theoretical (molecular dynamics) simulations are continuously improving, but are often still limited by the challenge of calculating dynamics at time scales appropriately long to represent temperatures low enough to compare with physical experiments.

Studies of glasses, where a clear, quantitative picture of many aspects of short- to intermediate-range structure can be obtained, thus remain of key interest. Recent high-resolution NMR studies of ambient pressure glasses have quantified several key aspects of order/disorder. For example, “aluminum avoidance”, although not complete, leads to significant Si/Al ordering in aluminosilicate melts at the low temperatures sampled during quenching to glass (i.e. the glass transition T_g). As indicated long ago by Raman spectroscopy (Mysen et al.), non-bridging oxygens are highly ordered onto higher-charged network cations (Si vs. Al). Modifier cations, when not too different in size or charge (e.g. Mg^{2+} , Ca^{2+}), are nearly randomly distributed; in contrast, large size/charge differences (e.g. Mg^{2+} , K^{+}) can lead to strong ordering. Al and Si are highly ordered into tetrahedral sites, but detectable amounts of five-coordinate species occur in many compositions. Especially for Al, there are obvious effects of composi-

tion, with higher field-strength modifiers promoting the formation of AlO₅ groups.

In cases where such significant ordering is detected in glasses (and thus in melts at T_g), there are obvious possibilities for increased disorder at higher T, and thus for significant contributions to configurational properties including entropy, enthalpy, and thermal expansivity. To measure such effects directly, we have begun a systematic study of the structural differences between rapidly quenched (high “fictive T,” T_f) and annealed (low T_f) glasses that display such ordering. Very recent results, for example, clearly show the enhanced Si/Al disorder in alkali aluminosilicate melts with increased T_f.

Glasses quenched from melts at high pressure have the added complication of possible structural relaxation during decompression, as well as effects of quench rate (and thus of T_f). We have evaluated these effects by varying both thermal history and quench rates in multi-anvil apparatus, and have found in some cases that they can be quite significant. We have also measured densities of recovered glasses to compare with recent results on high P/T density from falling sphere methods. It appears that much of the inelastic (configurational) densification is retained on quench, suggesting that structural changes in at least the network components do record much of the changes that are present at high P and T_g. Also, network structural changes, especially in Al coordination (as quantified by Al-27 MAS NMR at 18.8 Tesla), are highly correlated with recovered molar volume. Our observations of strong compositional effects (e.g. of modifier cation field strength) on Al coordination are thus likely to be quite relevant to understanding high P/T magma properties. Ongoing studies of the mechanism of this structural change, by Al-27, Si-29, Na-23, and O-17 high resolution NMR, continue to support the hypothesis that non-bridging oxygens on SiO₄ groups are directly involved in the formation of high-coordinate Si and Al. We are beginning to resolve the complexities of O-17 spectra of multi-component glasses that contain AlO₅ and AlO₆ groups by systematic study of appropriate crystalline model phases, including garnets and pyroxenes.