



Pressure and temperature effects on oxide melt structure: progress and prognoses (Bunsen Medal Lecture)

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Thanks to decades of study by diffraction and spectroscopy, many aspects of the short-range structure of oxide glasses, and the effects of composition on them, are relatively well known. In most cases, these results represent (at best) the structure of the liquid at the glass transition, which is often far below the magmatic conditions of greatest interest for geological processes. At the same time, detailed thermodynamic and calorimetric studies at ambient pressure, and a few pioneering in-situ, high-pressure melt property measurements, have documented the fact that melt structure must change considerably as temperature and pressure are increased. Closing the gap between magma properties and our atomic-scale view thus requires much better information about temperature and pressure effects on melt structure.

Recent progress on temperature effects has been made both by in-situ studies, and by work at ambient conditions on glass samples prepared with different cooling rates and thus capturing the melt structure at different fictive temperatures. The former type has the advantage of a greater accessible range of temperatures but can be limited by the inherent difficulties of high temperature experiments; for the latter, any structural tool may be applied but changes over the accessible range (typically T_g to T_g+200 K or less) can be subtle. We now know, for example, that in some systems local structural changes can be detected for network cations such as B, Al, and even Si, but that these can lead to either coordination decreases with T (e.g. B), correlated with thermal expansion, or to increases with T (e.g. Al in Ca aluminosilicates), correlated with entropic effects. In some systems, increases in the disorder of the network with T can be measured and correlated with heats of reaction among various bridging oxygen species. In a few cases, network modifier environments (e.g. Ni, Mg, Na) can be seen to change with T as well. But in general, extrapolating results from one system to another must be done with caution, as there are clearly compositional effects on the response of the structure to temperature.

Structural methods that can yield useful information on high temperature, high pressure melts are even more limited, and future progress in this area will be critical to understanding deep-Earth magmatic processes. Most of our (very limited) understanding of pressure effects on melt structure comes from in situ studies of glasses at ambient temperatures and high P, and from spectroscopy of glasses quenched from high P,T melts. The latter have the advantage of at least having started in a fully relaxed, equilibrium state at P and T, but questions of possible structural relaxation during decompression are not fully resolved. Nonetheless, recent studies of such high pressure glasses, with enough complexity to begin to emulate natural magmas, have begun to reveal trends with composition and P, and correlations between quenched-in density increases and structure, that must have bearing on the high T, P systems. Most obviously, higher field-strength modifier cations (e.g. $Mg > Ca > Na > K$) lead to more rapid increase with P in both density and Al coordination (Al-27 NMR), which seems to delay increases in Si coordination. Corresponding changes in the types of oxygen species present (i.e. decreases in non-bridging oxygens) are also clearly measurable by O-17 NMR. However, much of the recovered density change must be related to compression of the modifier cation sites through decreases in network bond angles. Depending on the cation, this can lead to shorter M-O bonds distances (e.g. Na), or to coordination increase and longer distances (e.g. La).

Finally, we note that important insights for high-pressure silicate systems may be gleaned from other oxide melts in which the network cations undergo large changes in coordination with composition. As a modifier such

as Na₂O is added to pure B₂O₃ or GeO₂, for example, the B or Ge coordination increases significantly, then decreases. This suggests that in aluminosilicate melts in the pressure range (perhaps 10-30 GPa?) of mixed network cation coordinations, the Si and Al speciation may be strongly dependent on composition. This complexity may make modeling of high-pressure melt properties difficult, but suggests a richness in behavior that will be well worth exploring as experimental and theoretical methods improve.