Silicate melt structure: thermodynamic inference vs spectroscopic observation

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Cautious thermodynamicists have often pointed out that their elegant equations are independent of microscopic information on real structure. However, imaginative (and even bold!) geochemists and others have long sought atomistic explanations of macroscopic observables in order to more accurately formulate models that have some capability of extrapolation in temperature, pressure, or in composition. Here we will review a few examples of recent progress in connecting real structure of silicate melts to thermodynamics, largely from high-resolution Nuclear Magnetic Resonance (NMR) spectroscopy.

Density changes with pressure

Density changes with pressure in silicate melts have been directly measured and inferred from fusion curves. In some cases, high apparent compressibilities have been assumed to be related to the formation of SiO_6 and AlO_6 groups, largely by analogy to crystalline silicates. Recent NMR work has confirmed such changes in some materials, and has provided the first clear evidence of abundant SiO_5 and AlO_5 groups as well. Documented temperature effects on structure, as well as uncertainty in the effects of depressurization, have made quantitative modelling of volumes difficult, however (Stebbins, 1995; Yargar *et al.*, 1995).

Density changes with composition

Non-constant partial molar volumes for oxide components in melts, particularly for Al_2O_3 and TiO_2, have been attributed to changes in cation coordination numbers. So far for Al, NMR has not provided evidence in support of this idea, and has apparently ruled out the present of significant amounts of AlO_5 or AlO_6 in glasses of at least metaluminous compositions, although such species are clearly found in some more aluminous liquids. Nonetheless, the doorway to such interpretations remains slightly ajar, as there is good evidence for a possible slight increase in the average coordination of Al with increasing T, even in peralkaline melts (Stebbins, 1995). Data on glasses alone may not be sufficient to resolve such questions.

Component activities

Changes with P, T, and X of activities of components in silicate melts have often been interpreted with models in which the concentrations of crystal-like "structural units" vary. In some cases, this general idea is clearly confirmed by spectroscopy, e.g. in the greater concentration of Q^4 units (SiO_4 tetrahedra connected to 4 others) in alkali silicate glasses quenched from liquids with higher silica activities (Stebbins, 1995), and correspondingly greater effects in Ca-silicate glasses (Zhang *et al.*, 1997). On the other hand, the conversion of feldspar-like "units" to structures with AlO_6 groups, either with compositional changes or at modest pressures, is not supported by NMR spectra. However, the recent observation of non-bridging oxygens in anorthite ($CaAl_2Si_2O_8$) glass clearly allows the possibility of other types of "non-feldspar" types of structures (Stebbins and Xu, 1997).

Disorder and ideal mixing

Most models of silicate melts thermodynamics assume random mixing of some components, at least with respect to entropy. The direct measurement of the extent of such disorder is very limited, however. There is good NMR evidence for at least partial aluminum avoidance, at least at the low T's at which liquids transform to glass (Stebbins and Xu, 1997). The change in this ordering with T remains to be explored. Relatively new data on the extent of disorder among non-bridging oxygens strongly supports disorder among modifier cations when they are fairly similar in size or charge, such as Na^+ and K^+ or Ba^{2+} and Ca^{2+} (Stebbins *et al.*, 1997), but indicates that ordering may occur with larger differences in field strength (e.g. K^+ and Mg^{2+}).

Configurational entropy

NMR data have provided the best (albeit incomplete) measurements of the extent of ordering among anionic network species. In glasses (representing liquids at relatively low T's of the glass transition), disorder among bridging and non-bridging oxygens is far from complete, although glasses are of course considerably more disordered than corresponding crystals (Stebbins, 1995). Systematic changes in disorder with composition correlate with known differences in melt heat capacities and entropies of fusion. Increases in disorder with T are in some cases measurable, but, in silicates, seem (so far) to account for only a minor part of the total calorimetric increase in entropy in the melt (Stebbins, 1995). In contrast, recent measurements on borate glasses indicates that spectroscopically observed changes in borate speciation with T may indeed explain most of the configurational entropy of the melt (Sen *et al.*, 1997).

References

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