Five-coordinated silicon in silicate melts and glasses: effects of pressure, temperature, composition and analogies to borates and germanates

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Five-coordinated silicon (SiO_5) was discovered by ^{29}Si NMR in high- and ambient-pressure alkali silicate glasses almost 30 years ago [1,2]. This species has often been considered to play a key role in both melt densification and as a 'transition structure' in models of network bond-swapping, diffusion, and viscous transport. However, only very recently has a detailed picture emerged as to temperature and compositional effects on SiO_5 concentrations in the simple model system K_2O-SiO_2 [3]. In glasses formed at 1 bar pressure, rapidly-cooled samples have higher SiO_5 contents, demonstrating a systematic effect of fictive temperature. As K_2O is added to silica, SiO_5 contents increase, reaching a maximum of about 0.3 % at 10 mol% K_2O, then decrease to near-undetectability (ca. 0.02%) above about 25% K_2O. This pattern of network cation coordination increase, then decrease, is remarkably similar to much better-known systematics in alkali borate and germanate binaries, although in the latter the fractions of high-coordinate cations (BO_4, GeO_5/GeO_6) are orders of magnitude higher. A mechanism common to all three, involving the reaction of non-bridging oxygens to increase network cation coordination, is implied. A simple thermodynamic model for non-ideal mixing of non-bridging oxygens produces curves for network cation coordination vs. composition that at least roughly resemble the data in all three types of system, suggesting an underlying fundamental similarity in structural energetics that has not previously been fully appreciated. One consequence of these findings is that, as in germanates and borates, in silicate liquids at pressures high enough to convert substantial fractions of SiO_4 to SiO_5 (and SiO_6), physical properties such as molar volume are likely to be highly non-linear with composition, and predictive models will need to be correspondingly complex.

[1] Stebbins & McMillan (1989) *Am. Min.* **74**, 965-968.
[2] Stebbins (1991) *Nature* **351**, 638-639.
[3] Stebbins (2019) *J. Non-Cryst. Solids: X*, **1**, 100012 1-12.