



Ionic-polymeric models and the amphoteric behavior of water in silicate melts

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In silicate melts it is almost impossible to readily distinguish solute and solvent like in aqueous solutions. The anionic framework of silicate melts, in fact, makes solute and solvents so intimately related that one cannot identify a solvation shell and identify directly, from structural studies, the complexes needed to define acid-base reactions. Therefore, the distinction between solute and solvent becomes blurred in systems such as silicate melts, because speciation is not only complex but changes with the marked depolymerization of the silicate framework that obtains from pure SiO_2 to metal-oxide rich compositions. These features do not allow proper understanding of the actual physico-chemical role of many species detected by conventional techniques, a fact which can lead to confusing notation.

However, these may not be serious limits to account correctly for the acid-base reactions that take place in every kind of magmatic setting, provided a 'syntax' describing the effective interactions among significative cationic and anionic entities. In particular, the syntax for acid-base exchanges is needed such that constituting oxides (i.e. chemical components) can be treated independently of (but not necessarily extraneous to) structural features in defining such entities. So-called ionic-polymeric models highlight the mutual correspondence between polymerization and acid-base properties of dissolved oxides through the Lux-Flood formalism for molten oxides. They thus provide the syntax to write chemical exchanges, but have no pretension to structural description. In fact the concept of melt polymerization is used to identify basic anions and cations that can be used, along with their formal charge, to describe effectively acid-base interactions taking place in melts.

In this respect, an example is given by the description of the amphoteric behavior of water dissolved on melts, hence water autoprotolysis. Although it exerts a profound influence on properties of magmas, this autoprotolysis reaction has been hitherto neglected for water dissolved in silicate melts. By mixing cations and anions on distinct sublattices and quantifying the disproportionation of water dissolved in silicate melts into its ionic products, H^+ and OH^- , we reconcile conflicting spectroscopic determinations of water speciation, and explain the contrasting rheology of hydrous basaltic and rhyolitic melts. In fact basalts show much less depression of viscosity by water addition because of a relative predominance of OH^- , such that water increase tends immediately to limit depolymerization rather than enhance it. This opens new perspectives to the understanding of the chemical control leading to either effusive or explosive eruptions.