Redox (and acid-base) properties of aluminosilicate melts: the ionic-polymeric description

Roberto Moretti*[1]

[1]Institut de Physique du Globe de Paris - Observatoire Volcanologique et Sismologique de la Guadeloupe (IPGP-OVSG) – Guadeloupe

Abstract

The properties of melts and glasses of interest in Earth Sciences and glass-making industry are heavily affected by redox equilibria. These are not only sensitive to changes in intensive parameters, such as temperature and oxygen fugacity (fO2), because extensive parameters (composition) have major effects. This compositional control, which includes the amphoteric behaviour of some components, demands the understanding of the link between redox, acid-base properties and structure. Nevertheless, a precise and coherent chemical "syntax" is required to write chemical exchanges in aluminosilicate melts. These are in fact a special category of fused salts (oxides, in our case), in which the silicate structure is such that cations and anions have actual charges lower than formal ones, and the residual charge distribution from bonding of bridging oxygen to silicon allows oxygen bonding with other cations. This characteristics makes the relative contribution of non-bridging and bridging oxygens to the oxygen coordination of the other cations poorly known, avoiding to readily distinguish solute and solvent like in aqueous solutions and consequently the complexes needed to define acid-base reactions. Therefore, the distinction between solute and solvent becomes blurred in such systems, because speciation is not only complex, but it changes with the marked depolymerization of the silicate framework that obtains from pure SiO2 to metal-oxide rich compositions. 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. The unique validity of ionic-polymeric approaches is shown for iron redox equilibria, for which no shift of activity coefficient can explain observations. We also show the case of redox interactions involving sulfur species, and the effects that arise on biphasic gas-melt equilibria in presence of halogens, water and carbon dioxide.

Keywords: Redox, acid, base properties, amphoteric behaviour, iron, sulfur, polymerization, Lux, Flood formalism

*Speaker