



## **Water speciation in melts: searching the consistency between physico-chemical arguments and experimental data**

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The dissolution mechanism of water in melts/glasses is somehow questioned in literature. If the existence of T-OH groups is well ascertained in hydrated alkali-silicate glasses, things may be different for aluminosilicate melts/glasses. In particular, there is a great debate whether water dissolution in alkali aluminosilicate melts occurs either via protonation of bridging oxygens without disruption of the melt network, or through hydrolysis of T-O-T linkages and consequent depolymerization of the melt structure. Does this ambiguous structural picture, mainly arising from glasses, correspond necessarily to an intricate physico-chemical description of how water dissolves in melts? To answer this question, we shall consider alternative ways to gain insights about water speciation. Epel'baum (1973) argued that granite melts formed at different water pressures may have markedly differing basicities and therefore markedly differing degrees of oxidation. The interrelationship between oxidation and acid-base properties has been already treated in the framework of polymeric models based on the Toop-Samis approach and on the ionic notation of Temkin. A major insight of these studies is the recognition that the depolymerizing role of water has been much overrated with respect to its actual acid-based properties in melts. Although among the molten oxides forming silicate melts water is commonly perceived as the most basic one, its optical basicity has a value (0.40) very close to that of silica and alumina (0.48). Fraser (1975) stated that "like for other oxides, water can be expected to show amphoteric properties depending on the nature of the other components present". Amphoteric behavior of water in the Temkin hypothesis (complete dissociation of components) means considering protons and free hydroxyls. The dependence of this behavior on the nature of the other components, i.e. the bulk basicity of the medium, expressed by free oxygen concentration, is accounted through the solution of the polymerization equation

between free oxygens, BO's and NBO's. At parity of water content, high free hydroxyl concentration is expected in more basic melts, in agreement with ab-initio MO calculations of Xue and Kanzaki (2004) and with experimental results of Behrens et al. (2004) on water diffusivities. Reconciliation with data from InfraRed spectroscopy (the most commonly adopted tool for 'water speciation') is possible and, although uncertainties, allows to compute proportions of i) molecular water, ii) free hydroxyls, iii) protons (and T-OH groups).