

Basis for a speciation model to quantify physical and thermodynamic properties of silicate melts

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The evolution of magmas in the Earth's crust largely depends on the properties of the silicate melt. Spectroscopic studies of simple binary silicate melts provide evidence that their physical and thermodynamic properties largely depend on their short to medium-range structure. Viscosity data suggests that this is also the case in multicomponent melts, but the complexity of the spectroscopic signals prevents a direct determination of their structure. The objective of this study is to construct a theoretical tool to calculate the speciation of chemically complex silicate melts and use this speciation to accurately quantify structure-dependent physical and thermodynamic properties, even if no spectroscopic information is available.

To construct the model, we collected detailed information on the melt structure using Raman spectroscopy, Nuclear Magnetic Resonance (NMR) and X-ray Photoelectron Spectroscopy (XPS). NMR data provide a direct measure of the speciation in silicate glasses and permit the investigation of some intermediate range order. Raman spectroscopy at high temperature was used to quantify the temperature dependence of the speciation. As this technique is not quantitative, we developed a new quantification procedure based on principal component analysis and optimization techniques. XPS yielded information on the type of bonding and the binding energies.

Based on these data, we developed a theoretical approach with which we can calculate the relative abundance of species from phase equilibria. The approach required the quantification of a large number of parameters by fitting experimental data with a highly non-linear set of equations. This precludes the use of traditional mathematical search methods and solutions were obtained by using evolutionary algorithms.

The model calculates melt properties through the properties of species. It considers the non-random distribution of speciation to result from the repulsion of adjacent charged non-bridging oxygen ions in individual silica tetrahedra. Activities of the silicate species were derived from equilibria with pure SiO₂ minerals and the activity coefficient was found to be dependent on the ionic potential of the cation.

This model was used successfully to determine melt speciation in binary silicate melts. Application to multicomponent systems yields the first speciation data in chemically complex silicate melts. Since the molecular structures dictate the physical and thermodynamic properties of melts, our model forms the basis for an accurate quantification of these properties in molten silicates. These properties are of obvious significance for the investigation of magmatic systems. As molten silicates are the prime component of glasses and glass ceramics, it will also find applications in material sciences, industry or in the study of slags.