

## Acid base properties, structures and the thermodynamic properties of silicate melts

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The interpretation of the thermodynamic properties of silicate melts and slags in terms of oxide acid-base reactions (Flood and Förland 1947, Fincham & Richardson 1954) has had widespread use in metallurgy where the thermodynamic activities of oxide species are of primary concern. Quasi-chemical models (e.g. Toop & Samis 1962, Esin 1973) and polymer models (e.g. Masson et al. 1970, Lahiri 1971) have attempted to relate these thermodynamic data on oxide activities to speciation in melts and slags.

The focus of interest in the earth sciences and in the glass industry is on the crystallization of silicate minerals from silicate melts and on the physical properties of the melts and glasses themselves. This requires adequate expression, not of oxide activities, but of silicate components. The relationship of the acid-base properties of melts to their thermodynamic properties requires description of the acid-base reactions and of the amphoteric properties of oxide components (Fraser 1975). The role of basicity in controlling the thermodynamic properties of silicate melts has recently been revisited by Beckett (2002). Moreover, new NMR data (Xue and Kanzaki 2002) show that water displays important amphoteric behaviour in molten silicates. Thus in basic melts such as  $\text{CaMgSi}_2\text{O}_6$ , the acid reaction of  $\text{H}_2\text{O}$  with OH leads to increased polymerisation of the melt with increasing water content. This has important consequences for phase equilibria and the crystallization of even nominally anhydrous phases (Fraser 1977).

In the present paper, a quasi-chemical model will be examined that relates activities of silicate components to oxide activities. This uses an extension of the quasi-chemical structural theory of Huggins (1970). It can be used to calculate the proportions of silicate structural units using acid-base models for silicate liquids. The results will be used to examine the effects of added acid, base and amphoteric oxide components on phase equilibria characterised in binary systems.

### References

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## New directions in molecular isotopic analyses

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Molecular stable isotopic analyses have expanded from initial efforts using hydrocarbons and carbon isotopes to embrace a broad range in compound classes, elements and applications. This presentation will highlight two examples of new avenues in molecular and isotopic studies: lipid hydrogen isotopic analyses and isotopic studies using RNA monomers.

The past several years have witnessed advances in isotopic analyses of non-exchangeable hydrogen in compounds from natural settings and geologic samples. This approach provides an exciting prospect for paleohydrologic reconstructions, especially in regions where carbonate mineral preservation is limited or non-existent. Such efforts represent a true scientific frontier, since much fundamental work is needed to understand isotopic relationships among and between hydrogen in water, plant tissues, and individual compounds. The tools provided by continuous-flow inlet systems for isotopic analyses of H in solids, liquids and gases will prove essential in elucidating hydrogen isotope fractionation in biosynthetic pathways, during diagenetic processes and with geologic thermal maturation of natural organic matter. Field-based studies of molecular properties, isotopic signatures and environmental properties provide an important starting point for this work, by allowing us to establish empirical relationships that serve as framework for more detailed biological or chemical studies. I will present recent work on molecular hydrogen isotopic analyses for the purposes of hydrologic reconstructions in ancient grasslands, lakes and marine samples.

Hydrocarbons and other lipid-derived structures serve as an important class of biomarker compounds. Lipid-derived compounds offer the important advantage of being more readily preserved over longer timescales than most other biochemical compound classes. Indeed, lipid structures recorded in Archean Shales provide an extreme example of long-term preservation. However, lipid-derived compounds in truth give very limited taxonomic information. For example, many compounds provide only kingdom or domain-level source designation ("eukaryotes" or "archaea," for example). In contrast, nucleic acids are typically poorly preserved in geologic materials, and RNA is especially ephemeral in natural samples. However, nucleic materials provide the ultimate "biomarker" because they can be highly taxonomically specific. I will survey recent work that combines molecular biological methods with isotopic studies. I will present results from our efforts to analyze isotopic abundances in individual RNA nucleosides as well as specific purine and pyridamine bases liberated by the cleavage of the glycosidic bond on RNA monomers.