Relaxation and rheology of hydrous granitic melts

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The strong and nonlinear fluxing of the transport properties of silicic melts by water is one of the best-known features of the physical chemistry of silicate melts applied to geochemistry. The decrease in melt viscosity and relaxation time and increase in electrical conductivity and diffusivities have enormous consequences for all stages of the magmatic cycle including segregation and transport of melts, the kinetics of element partitioning between dissolving or growing minerals and their host melts and the efficiency of melt degassing in shallow subvolcanic systems.

In order to predict the influence of water on melt properties with adequate precision, a generalisable model for the relationship between the structural role of water and the properties of water-bearing melts is required. In order to constrain such a structure-property relationship essentially two types of investigations have been concentrated on in recent years: (1) structural investigations and (2) property determinations of hydrous melts.

A wide range of spectroscopic investigations of water in silicate melts have led to the following conclusion that water dissolves in silicate melts in at least two spectroscopically distinct forms that express themselves, for example, in FTIR spectra of melts and quenched glasses as molecular water and hydroxyl groups. The proportions of these two spectroscopic components are significantly dependent on temperature but not on pressure. The local environment of the hydroxyl component in the melt is not well-constrained (Kohn et al., 1998).

The interconversion of hydrous species has been analysed using in situ high temperature-high pressure spectroscopy (e.g. Withers et al., 1998) as well as quench-based annealing studies (Zhang et al., 1997). The former have the advantage of direct observation of species in realtime whereas the latter have the advantage of very well calibrated concentration/intensity relationships. Both types of investigation have confirmed the prediction of Dingwell and Webb (1990) that the interconversion of hydrous species in silicate melts is closely linked to the self-diffusivities of the network-forming cations in silicic melts and thus coincide in temperature-time space with the glass transition. Comparisons of estimates for volume, shear stress and structural relaxation times in hydrous granitic melts confirm this coincidence. Water speciation is "frozen in" at the glass transition (Dingwell, 1998).

A wealth of new high-precision viscosity data obtained for hydrous melts in recent years enables us to make several observations and detailed comparisons of the salient features of hydrous melt viscosities. The magnitude of the strong, nonlinear decrease in melt viscosity due to water is also highly dependent upon temperature but not on pressure. This similarity to the speciation behaviour noted above appears to strengthen the case for a link between speciation and viscosity in hydrous melts. The near-Arrhenian temperature-dependence of granitic melt viscosity becomes highly non-Arrhenian with the addition of water. In detail the oft-cited comparison between the influences of excess alkalis (peralkaline effect) and that of water, on melt viscosity, breaks down significantly in water-rich melts. At low viscosities, alkalis are more efficient in reducing melt viscosity, whereas at high viscosities, water is more efficient. This observation stands in apparent contradiction to the observation that the molecular water component in the hydrous melts is highest at low temperatures, i.e. precisely where the fluxing effect of water is greatest. Clearly this juxtaposition of observations means that the common approximation of molecular water as an inert component with respect to melt viscosity is incorrect.

Available data for the concentration-dependence of the partial molar volume of water in silicate melts at low pressure also implies that the interconversion of hydrous species does not involve a large volume term.

Quantification of the reaction enthalpy responsible for significant temperature dependence of the proportions of hydrous species in granitic melts by groups using fully independent methods yield comparable estimates of approx. 25 kJ/mol. Interestingly, this value is similar to the that derivable from the temperature dependence of the dissociation constant of pure water in its condensed (liquid) state at much lower temperatures. This might
imply that the temperature dependence of water speciation has its origin in the thermal stability of the water molecule, regardless of the matrix in which it is dissolved.

If an equilibrium involving protons and hydroxyls is responsible for the temperature- and pressure-dependence of the speciation of water in silicate melts then it is tempting to try to analyse the influence of dissolved water on melt viscosity in terms of acid-base equilibria in the melt phase (c.f., Persikov and Bukhtiyar, 1998). To do this sufficiently well will however require an adequate database on the effect of water on melt viscosity for a series of silicate melt compositions representing a significant range of acidity-basicity. The obtainment of such data over a sufficiently wide range of melt basicity and temperature represents a significant experimental challenge.

References