

## Speciation and solubility of F and Cl in coexisting fluids and silicate melts: implications for F and Cl signature in arc

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The effect of pressure and temperature on the structure of silicate melts coexisting with silica-saturated aqueous electrolyte solutions enriched in fluorine or chlorine in the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  system has been determined. In-situ measurements were conducted with the samples at desired temperatures and pressures in a hydrothermal diamond anvil cell (HDAC) by using microRaman and FTIR spectroscopy techniques. The data were acquired at high temperature and pressure (up to 800°C and 1264 MPa, respectively), and during cooling/decompression to ambient conditions.

The intensity of the Raman bands assigned to stretch vibration of the OH-groups relative to those of coexisting molecular  $\text{H}_2\text{O}$  in silicate melts is lower in the presence of F and Cl. This difference reflects the interaction of F or Cl with  $\text{H}_2\text{O}$  in the melts. With decreasing pressure and temperature (P-T) conditions, SiF complexes are favored in the melt rather than in the fluid, perhaps because of decreasing silicate concentration in fluids with decreasing temperature and pressure. In melts, the solubility of Cl, likely in the form of  $\text{NaCl}_{(aq)}$ , increases with decreasing P-T conditions, whereas the abundance of such complexes in coexisting fluids decreases.

Our experiments data were employed to help model the ascent of a magma-fluid system from the upper mantle to the shallow crust. The information offers particular insights into F and Cl partitioning between and the speciation of F and Cl in melts and magmatic fluids. We suggest that the formation of stable SiF and NaCl complexes and their increasing solubilities during magma ascent explain the late volcanic degassing of F and Cl, compared to other volatile species.

It explains why F and Cl are often undersaturated in arc basaltic magmas (Carroll and Webster, 1994), indicating that they often do not a significant experience a degassing event. In contrast to  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and S, F and Cl signature in primary arc magmas (arc melt inclusions) can be considered as primary and likely retain information on arc magma sources.

Those results also imply that, while Cl is enriched in aqueous fluids from slab dehydration, F preferentially dissolves in slab melts or supercritical fluids, during flows from the subducted slab into the zone of melting in the mantle wedge. It is therefore expected that at given pressure and temperature, the Cl/F ratio is significantly lower in slab melt and supercritical fluids, than in aqueous fluids. This difference in Cl/F signatures decrease when slab components are dragged down to the deep mantle.

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