FLUIDS IN THE CRUST

In-situ measurements of fluorine and chlorine speciation and partitioning between melts and aqueous fluids in the Na$_2$O-Al$_2$O$_3$-SiO$_2$-H$_2$O system†

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ABSTRACT

The effect of pressure and temperature on the structure of silicate melts coexisting with silica-saturated aqueous electrolyte fluids enriched in fluorine or chlorine in the Na$_2$O-Al$_2$O$_3$-SiO$_2$-H$_2$O system has been described. 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 temperatures and pressures up to 800 °C and 1264 MPa, respectively.

In silicate melts, the intensity of the infrared bands assigned to the stretch vibration of OH-groups is smaller than those of coexisting molecular H$_2$O when F and Cl are present in the melt structure. This difference reflects the interaction of F or Cl with H$_2$O in the melts. With decreasing pressure and temperature ($P$-$T$) conditions, SiF complexes are favored in the melt over that in coexisting fluid, perhaps because of decreasing silicate concentration in fluids with decreasing temperature and pressure. In these melts, the solubility of Cl, likely in the form of NaCl, increases with decreasing $P$-$T$ conditions, whereas the abundance of such complexes in coexisting fluids decreases in favor of HCl.

Our experimental data were employed to model the ascent of a fluid-saturated magma from the upper mantle to the shallow crust. This modeling offers 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 in silicate melts during magma ascent may explain the late volcanic degassing of F and Cl compared with the degassing behavior of other volatile species.

Keywords: Fluorine, chlorine, speciation, aqueous fluids, hydrous melts, structure, spectroscopy, hydrothermal diamond-anvil cell

INTRODUCTION

Characterization of the behavior of volatile elements during magma ascent is central to constraining the cycling of volatiles from the Earth’s interior to the surface. Volatile species are released into the atmosphere mainly through magma degassing and their abundance in the emitted gases and fluids is controlled by their speciation and solubility in melts and magmatic fluids.

Previous studies have focused on the characterization of volatile species (H$_2$O, CO$_2$, S, Cl, and F) and their solubility in magmas of various compositions (e.g., Mysen et al. 1975; Mysen 1977; Eggler et al. 1979; Dixon et al. 1995; Webster et al. 1999; Brooker et al. 2001; Tamic et al. 2001; King and Holloway 2002; Signorelli and Carroll 2002; Botcharnikov et al. 2004). The solubility of volatile halogens and the depth of their exsolution depend not only on magma composition but also on the concentration of other volatiles, especially H$_2$O and CO$_2$, which affects the solubility and fractionation of halogen-bearing species in and between minerals, melts and fluids (e.g., Holloway 1976; Carroll and Webster 1994; Dixon et al. 1995; Burgisser et al. 2008; Dalou and Mysen 2013). The partitioning of F and Cl between fluid and melt has been of special interest because these volatiles tend to degas during the latest stages of magmatic evolution (Carroll and Webster 1994; Spillaert et al. 2006). While both F and Cl solubility in magmas can be quite high, their behavior in magmatic systems differs. For example, it is often concluded that Cl is dissolved preferentially in aqueous fluids, whereas F favors melts (Carroll and Webster 1994). However, comparative studies of F and Cl partitioning between fluid and melt with similar melt compositions, temperatures and pressures are rare as are data on degassing in volcanic systems (e.g., Pennisi and Le Cloarec 1998; Spillaert et al. 2006).

Earlier experiments measured species concentrations in quenched glasses and calculated the composition of coexisting fluid after equilibration at high temperature and pressure (Webster 1992, 1997; Métrich and Rutherford 1992; Lowenstern 1994; Shinohara 1994; Signorelli and Carroll 2000; Chevychelov et al. 2008; Alletti et al. 2009). However, the structure of a silicate glass is different from that of its high-temperature melt (e.g., Moynihan et al. 1976; Dingwell and Webb 1990), because silicate speciation in the melt/glass structure is temperature (and pressure)