Halogens partitioning between apatite, fluid and silicate melts

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The fluctuation of halogen contents (chlorine and fluorine) of volcanic gases is a good precursor signal of volcanic crises, yet the Cl and F behavior in magmas is complex due to the interplay between melt, fluid and halogens bearing crystals. In magmatic rocks, Cl and F are the main constituents of apatite, an ubiquitous accessory magmatic mineral.

As a result, apatite is increasingly being used as a geochemical tool for unravelling halogen behavior as it allows to record the fugacities of key volatile species. In this context, the behavior of Cl and F in coexisting apatite, fluids and a variety of silicate melts (rhyodacite, basalt, phonolite) has been investigated experimentally as a function of pressure, temperature, oxygen fugacity, and fluid composition. Experiments have been done using internally heated pressure vessels at 50-200 MPa, 800-1100°C, fO2 from NNO-1 to NNO+2 and with either a Cl-bearing aqueous fluid. Run products were analysed by SEM, EPMA and Raman spectroscopy. F and Cl contents of fluids were estimated by mass-balance.

The results show that halogens partitioning in the apatitemelt-fluid system is dependent on all investigated parameters. Indeed, Cl concentrations in the rhyodacite melts increase with increasing Cl content in the fluid phase. With constant Cl concentration in the fluid phase, the amount of Cl in melts (between 0.1 and 1 wt%) and apatites (2.2 to 2.7 wt%) increases as the pressure decreases. We observed the same variations in phonolitic and basaltic melts. Though in several run products, the behavior of F is difficult to evaluate owing to analytical errors for its measurement in melts at low contents (<1000 ppm). With the gathered data, a solubility model of Cl (and F) is developed for the magma compositions investigated, using the method of Piccoli & Candela [1] to obtain Cl and F fugacities.

Finally, in situ experiments using a transparent IHPV connected to a Raman spectrometer are carried out in order to determine the fluid composition in equilibrium with the melt and the conditions of salt (Na-K)Cl saturation in silicate melts.

[1] Piccoli and Candela (1994) Am J Sci 294 92-135.