Hydroxyl, Cl, and F partitioning between high-silica rhyolitic melts-apatite-fluid(s) at 50–200 MPa and 700–1000 °C

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ABSTRACT

Hydrothermal experiments were conducted with fluid- and apatite-saturated, high-silica rhyolitic melts at ca. 700–1000 °C and 50–200 MPa to determine the distribution of H_2O/OH, Cl, and F between melt, apatite, aqueous vapor, brine, or vapor plus brine. Seed grains of fluorapatite (1–3 μm diameter) were added to starting charges to serve as apatite nucleation sites. $CaHPO_4$ and $Ca(OH)_2$ were used to stimulate apatite crystallization, and temperature was cycled daily, ±10 to ±15 °C, to promote growth of relatively equant apatite crystals large enough for electron probe microanalysis (EPMA). The experiments were conducted with gold capsules and run in cold-seal pressure vessels on a hydrothermal line and an internally heated gas pressure vessel for durations of 165 to 1149 h.

The run-product glasses were analyzed by EPMA and Fourier transform infrared spectroscopy, apatites by EPMA, and most fluid phases by chloridometer; Cl contents of fluids were also estimated by mass-balance calculations. The fluids contained 0.3–39 wt% Cl at run conditions. Most experiments were conducted at 50 MPa, and these glasses contain 0.02–0.42 wt% Cl, 1.8–3.1 wt% H_2O, and 0.01–0.19 wt% F. The molar Al_2O_3/(CaO+Na_2O+K_2O) (=A/CNK) and molar Na_2O/(Na_2O+K_2O) (=N/NK) ratios of the 50 MPa glasses range from 0.88 to 1.04 and 0.48 to 0.68, respectively, and straddle the A/CNK and N/NK of the starting glass (0.99 and 0.59, respectively). The measured wt% Cl and F in the 50 MPa apatites range from 0.14 to 3.8 (X_{Cl}^{Ap} of 0.02 to 0.56) and 0.32 to 2.4 (X_F^{Ap} of 0.08 to 0.63), respectively. Stoichiometrically constrained X_{OH}^{Ap} ranges from 0.14 to 0.7.

Partition and exchange coefficients were determined for OH, Cl, and F distribution between apatite and melt±fluids. The distribution of these volatile components varies with pressure and melt and apatite compositions. The exchange of F and Cl between apatite and melt, for example, fluctuates with the Si, P, Mg, Na, Ce, Fe, and S±Ca contents of the apatite and with the molar A/CNK and N/NK ratios of the melts. Water and hydroxyl exchange between experimental apatite and melt was also investigated. It is determined empirically that the: $(X_{H_2O}^{melt}/X_{Cl}^{melt}) = [(-19.66) + (39.13)(X_{OH}^{Ap}/X_{Cl}^{Ap})]$ for felsic melts at 50 to 200 MPa, having molar A/CNK ratios between 0.88 and 1.1, N/NK ratios >0.55, and containing ca. 2–6 wt% H_2O. The apatites are characterized by per formula unit (6 > Si/Mg > 0.3). We test this relationship by comparing H_2O contents measured in melt inclusions from Augustine volcano, Alaska, with calculated H_2O concentrations of melts based on compositions of apatites from 9 samples from 7 of its felsic eruptive units. The results for both approaches are consistent within precision for 6 of the samples.

The empirical volatile exchange relationships determined for melt-apatite, melt-fluid, and apatite-fluid pairs are applicable to various magmatic systems. One implication of this study is that the H_2O concentrations of felsic melts may be calculated from apatite compositions for volcanic systems involving equilibrium between these phases at 50 to 200 MPa, if estimates for the Cl contents of the melts are available. This approach, however, will require additional experimentation and testing. The compositions of igneous apatites could also provide fundamental constraints on the concentrations of H_2O and other volatiles in mineralizing plutonic systems for which melt inclusions are small, rare, and/or crystallized. Magmatic apatites may also support assessment of H_2O concentrations in melts derived from melt inclusion compositions.

Keywords: Apatite, melt, fluids, hydroxyl, chlorine, fluorine