A Mass Action Model for the Determining the Composition of Magmatic-Hydrothermal Fluids

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Fluids that exsolve from magmas are a vital part of ore formation and volcanic eruptions. The compositions of fluids vary as function of the bulk composition of the system, but are largely H₂O-CO₂-rich and contain metals, chlorine, fluorine, and sulfur. In order to better understand the impact of fluids in magmatic systems, it is necessary to constrain their compositional evolution. To this end, experiments were performed in internally-heated pressure vessels at 800°C and 200 MPa, wherein a rhyolitic melt was equilibrated with a saline fluid of up to ~11 wt% NaCl equiv. Run product glasses and fluids were recovered and analyzed for major and trace elements. By using these data in combination with metal speciation reactions in the H₂O-Cl-F fluid system, apparent equilibrium constants (K') for 134 aqueous species, which describe the exchange of metals between fluid and melt, were calculated. All K's vary as function of the HCl and HF concentrations in the fluid and were used to calibrated a mass action model capable of calculating the composition of exsolved magmatic fluids. The model is written in MATLAB and calculations are performed in parallel with alphaMELTS. Preliminary calculations have been performed for the isothermal decompression of the Bishop Tuff Rhyolite at 800°C and 500 to 200 MPa, and considers the exchange of Na, K, Ca, Fe, Al, Li, Rb, Cu, Zn, La, Tb, and Lu. For a bulk chlorine and fluorine content of 0.5 and 0.1 wt%, respectively, the chlorine content of the fluid ranges from 12 to 5 wt% NaCl equiv. and the fluorine content is ~0.1 wt % at all pressures. The HCl and HF concentrations of the fluid range from $10^{-5.3}$ to $10^{-6.2}$ and $10^{-2}$ to $10^{-3}$ molal, respectively. The majority of the metals are chloride species, with the dominant salts being NaCl>KCl>FeCl₂>CuCl₂. The dominant hydroxide species are Al(OH)₃, KOH, and NaOH and the dominant fluoride species is NaF. For the trace metals Cu and Zn are fluid mobile; Rb is fluid immobile; and Li and the REE’s may be either fluid mobile or immobile depending on the chlorine and fluorine concentrations in the fluid.