



Enthalpies and volumes of F-Cl mixing in fluorapatite - chlorapatite crystalline solutions

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Apatite $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH}, \text{CO}_3)$ occurs widely as an accessory mineral in many igneous and metamorphic rocks. In recent years, especially, apatite has been used increasingly to interpret the role of fluids, e.g. Cl, F, and OH activities, during metamorphic and igneous processes (e.g. Harlov and Förster, 2002). It is important, therefore, to establish a thermodynamic data base for this mineral group. In nature apatite solid solutions display a wide range of F-Cl-OH- CO_3 mixtures (e.g. O'Reilly and Griffin, 2000). As a starting point in establishing a thermodynamic data base for apatite, we have investigated a series of synthetic fluorapatite - chlorapatite [$\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl})$] crystalline solutions.

Apatite compositions along the fluorapatite - chlorapatite join were synthesized using an adaptation of the molten flux method as described by Cherniak (2000). Thoroughly mixed dry CaF_2 and CaCl_2 (0.1 mole total) and $\text{Ca}_3(\text{PO}_4)_2$ (0.03 moles) were placed in a Pt crucible with cover and taken to 1375 °C. The melt was allowed to equilibrate at this temperature for 15 hours and then cooled to 1220 °C at 3 °C/hour. The crucible was then removed from the oven and cooled in air. Apatite crystals were separated from the flux by boiling the quenched product in water. Fluorine and Cl fractions for each apatite composition were determined via Rietveld refinement of X-ray powder diffraction data. Chemical homogeneity of the samples was confirmed both by the Rietveld refinements and high-contrast back-scattered electron imaging (1 μm scale) of each apatite composition.

For the study of enthalpy we have employed hydrochloric acid calorimetric dissolu-

tions conducted at 50 °C under isoperibolic conditions (temperature of the surroundings stays constant) in 20.0 wt % HCl; sample sizes between 49 and 51 mg were used in each calorimetric experiment. Heats of solution at fourteen different compositions, to date, show a clear non-linear relationship with composition. A second-order polynomial fit to the data produces positive heats of mixing (H_{ex}) that are symmetrically distributed with regard to composition, reaching a maximum value of about 19 kJ/mol.

By comparison with other minerals, these solid solutions are considerably less ideal than other thermodynamically non-ideal series such as K-Na feldspars, for which H_{ex} reaches only 5 to 8 kJ/mol (depending on state of Al-Si order; Hovis, 1988), as well as nepheline - kalsilite (Hovis and Roux, 1993 and 1999). Thermodynamic non-ideality in both of the latter mineral groups is reflected in natural samples by exsolution phenomena. As noted above, however, our F-Cl apatite samples have been confirmed to be chemically homogeneous.

The unit-cell volumes for members of this series were determined from X-ray powder diffraction data both by Rietveld analysis at the GFZ-Potsdam and standard unit-cell refinement techniques (Holland and Redfern, 1997) at Lafayette College. The resulting unit-cell data behave non-linearly with composition. The compositionally asymmetric positive volumes of mixing (V_{ex}) reach maximum values of about 3 Å³/unit-cell at F-rich compositions.

The significant thermodynamic non-ideality of apatite crystalline solutions makes the need for thermodynamic characterization all the more evident. It is our intention next to measure the heat capacities of these minerals, which will enable characterization of entropy, and in turn Gibbs free energies of mixing for this F-Cl series.

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