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Thermal expansion behavior of fluor-chlorapatite crystalline solutions

G. Hovis (1), D. Harlov (2), M. Gottschalk (2), W. Hudacek (1), and S. Wildermuth (1)

(1) Lafayette College, Geology and Environmental Geosciences, Easton, Pennsylvania, 18042, United States (hovisguy@lafayette.edu), (2) GeoForschungsZentrum, Section 3.3 Chemistry and Physics of Earth Materials, Telegrafenberg, D-14473 Potsdam, FR Germany

Apatite $Ca_5(PO_4)_3(F,Cl,OH,CO_3)$ occurs widely as an accessory mineral in many igneous and metamorphic rocks and in nature displays a wide range of F-Cl-OH-CO_3 mixtures (e.g., O'Reilly and Griffin, 2000) that have been used 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 understand the thermodynamic behavior of these solid solutions, including their thermal expansion properties.

Fluorapatite - chlorapatite samples were synthesized at the GFZ-Potsdam (Hovis, Harlov, Hahn and Steigert, 2007) using an adaptation of the molten flux method of Cherniak (2000). Dry CaF_2 and $CaCl_2$ (0.1 mole total) were mixed with $Ca_3(PO_4)_2$ (0.03 moles), placed in a Pt crucible, equilibrated for 15 hours at 1375°C, cooled to 1220°C at 3°C/hour, removed from the oven and cooled in air. Crystals were separated from the flux by boiling the quenched product in water. F:Cl fractions for each sample were determined via Rietveld refinement of X-ray powder diffraction data. Chemical homogeneity was confirmed by Rietveld refinement and high-contrast back-scattered electron imaging.

Room-temperature unit-cell volumes were determined at the GFZ-Potsdam through Rietveld analysis of X-ray powder diffraction data and also at Lafayette College by standard unit-cell refinement techniques (Holland and Redfern, 1997) using NBS/NIST 640a Si as an internal standard. High-temperature unit-cell dimensions were calculated from X-ray powder diffraction data collected at Cambridge University from room temperature to 1000°C on a Bruker D8 X-ray diffractometer. NBS Si again was utilized as an internal standard; high-temperature Si peak positions were taken from Parrish (1953).

Results indicate that despite the considerable size difference between fluorine and chlorine ions, reflected by substantially different unit-cell sizes at room temperature, the coefficient of thermal expansion across the fluor-chlorapatite series is little affected by composition. This contrasts with relationships in alkali feldspars (Hovis and coworkers, 1997, 1999), which show that K-rich feldspars expand less than Na-rich feldspars. It contrasts also with the behavior of additional $AlSi_3$ feldspars (Hovis and others, 2008), in which room-temperature chemical expansion limits the degree to which the structure can expand thermally. It also differs from expansion in kalsilite crystalline solutions (Hovis and coworkers, 2003, 2006), which depends on K:Na ratio. Among the minerals we have studied previously, only nepheline displays expansion behavior similar to that of fluor-chlorapatite crystalline solutions in that thermal expansion shows little sensitivity to composition.

In $AlSi_3$ feldspars and kalsilite one observes a single crystallographically distinct alkali site and a dominating SiO_4 tetrahedral framework that limits the vibrational characteristics of the alkali-site occupant(s). Fluor-chlorapatite crystalline solutions have no such structural framework. Moreover, the anion site in the latter changes structural character in the transition from fluorapatite to chlorapatite. This flexibility apparently allows anion vibrational characteristics, coupled with those of Ca polyhedral components, to change continuously and in a compensating manner across the series. The thermal expansion data also imply that volumes of F-Cl mixing in fluor-chlorapatite are constant from room temperature to 1000°C.

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