American Mineralogist, Volume 95, pages 946–952, 2010

Solution calorimetric investigation of fluor-chlorapatite crystalline solutions

Guy L. Hovis[1,*] and Daniel E. Harlov[2]

[1]Department of Geology and Environmental Geosciences, Lafayette College, Easton, Pennsylvania 18042, U.S.A.
[2]Deutsches GeoForschungsZentrum Potsdam, Telegrafenberg, D-14473 Potsdam, Germany

Abstract

Solution calorimetric measurements have been made on 17 synthetic fluorapatite-chlorapatite crystalline solutions at 50 °C in 20.0 wt% HCl under isoperibolic conditions. Analysis of the calorimetric data indicates that heats of mixing across the series may reach values as high as 8.3 kJ/mol. Normally such a high degree of thermodynamic nonideality would be associated with immiscibility, yet no such miscibility gap is indicated by either synthetic or natural fluor-chlorapatite specimens. Based on full chemical analyses, all Cl-rich samples ($X_{Cl} > 0.65$) of this study have halogen deficiencies that imply the presence of 4–11 mol% vacancies in the anion sites, which are interpreted to be associated with oxyapatite substitution. Separate analysis of data for the vacancy-free samples produces a linear fit for enthalpy of solution vs. composition, which yields an alternative interpretation of thermodynamic ideality. Together these models define the limits of enthalpy behavior for the fluor-chlorapatite system.

Keywords: Enthalpies of mixing, fluorapatite, chlorapatite, thermodynamics