

A new semi-micro wet chemical method for apatite analysis and its application to the crystal chemistry of fluorapatite-chlorapatite solid solutions

GEORG SCHETTLER,¹ MATTHIAS GOTTSCHALK,^{2,*} AND DANIEL E. HARLOV²

¹Department Climate Dynamics and Landscape Evolution, Deutsches GeoForschungsZentrum, Telegrafenberg, D-14473 Potsdam, Germany

²Department Chemistry and Physics of Earth Materials, Deutsches GeoForschungsZentrum, Telegrafenberg, D-14473 Potsdam, Germany

ABSTRACT

A series of synthetic apatite crystals along the fluorapatite-chlorapatite $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl})$ join have been synthesized at 1220 to 1375 °C from $\text{Ca}_3(\text{PO}_4)_2$ dissolved in a CaF_2 - CaCl_2 melt. The solid solutions have then been characterized both chemically and structurally. Because of well-known difficulties in measuring the chemical composition of apatites containing F and Cl by electron microprobe a new semi-micro wet chemical method has been developed. Apatite is relatively well dissolved in mineral acids including HNO_3 . Nitric acid digestion of apatite for analysis of F and Cl has not been applied in the past to our knowledge. One reason is the potential risk of losing gaseous HF and HCl during acid decomposition. We present an analytical procedure that enables the analyses of F, Cl, Ca, P, and trace elements after digestion of 10 mg apatite with a small amount of 1 N HNO_3 in gas-tight PTFE tubes at 80 °C. Analytical results from three independent closed acid digestions of 20 synthetic fluor-chlorapatites are presented. The reliability of this method was tested on the basis of charge balance, the Ca/P, Ca/(F+Cl), and P/(F+Cl) ratios, and the total cation sum. Independently derived Cl/F ratios by XRD using Rietveld refinement of apatite crystals from the same synthesis experiments are additionally presented.

The apatite solid solutions were characterized by IR spectroscopy, X-ray powder diffraction using Rietveld refinements (XRD), and single-crystal diffraction (SCXRD) structure determinations. IR spectra indicate no or only a very minor hydroxylapatite component in the solid solutions. Lattice parameters of the apatite solid solutions vary systematically with composition. The *a*-lattice parameter varies linearly. In contrast to F^- , which occupies a special position at (0,0,1/4) in the unit cell, Cl^- occupies split positions ranging from 0.346(4) to 0.4428(2) in the *z*-coordinate because of the larger ionic Cl^- radius. Single-crystal structure determinations reveal that the Ca2 site is also split into Ca2A and Ca2B sites for F^- and Cl^- as nearest neighbors, respectively. In comparison to the Ca2A- F^- arrangements, the larger Cl^- ion presses the triangular arrangement of Ca-ions outward to facilitate an energetic more favorable constellation resulting in the formation of Ca2B- Cl^- arrangements. The occupancies of the Ca2A and Ca2B sites, as determined by SCXRD, correlate strictly with the F-Cl content.

Apatites rich in Cl ($x_{\text{Cl}} > 0.5$) show a deficiency in halogens, which is probably charge balanced by oxygen ($\text{Cl}^- + \text{Cl}^- \leftrightarrow \text{O}^{2-} + \square$) forming an oxyapatite component. The oxyapatite component prevents the F-absent, Cl-rich apatite from crystallizing with a monoclinic symmetry and stabilizes the observed hexagonal symmetry.

Keywords: Crystal structure, analysis, chemical (mineral), crystal synthesis, IR spectroscopy, apatite