Solid solution in the apatite OH-Cl binary system: Compositional dependence of solid-solution mechanisms in calcium phosphate apatites along the Cl-OH binary

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ABSTRACT

The method of accommodation of solid solution along the OH-Cl binary in calcium phosphate apatites is not fully understood; because of steric constraints in mixtures of OH and Cl anions in the apatite [0,0,z] anion column, the positions of OH and Cl anions in the pure hydroxyapatite and chlorapatite end-members cannot coexist in the binary anion column. We have undertaken high-precision single-crystal X-ray structure studies of eight synthetic samples along the OH-Cl apatite binary (R = 0.0159). We found that for all samples solid solution is attainable in space group $P6_3/m$, but the particular method of solid solution depends on composition. For samples with Cl > OH, three column anion sites (two for Cl, one for OH) provide allowable bond distances with the Ca2 atoms and allow a sequence of column anions that provides sufficient anion-anion distances and also effects reversal of the sense of ordering of the column anions relative to the mirror planes at $z = 1/4$ and $3/4$. In a sample with OH > Cl, three sites exist in the anion column that also provide allowable bond distances to the triangle of Ca2 atoms or its disordered Ca2' equivalent, and afford a sequence of atoms that permits reversal of the anion column and maintenance of $P6_3/m$ symmetry. One of those sites is occupied by OH and provides acceptable Ca2-OH distances, and another accommodates Cl with ideal Ca2-Cl distances. A third column anion site is unique among the calcium phosphate apatites. That site, termed the ClOH site, accommodates both OH and Cl. The site has an ideal bond distance for OH to the Ca2 atoms in the Ca2 triangle and also has an ideal bond distance for a Cl occupant to disordered Ca2' atoms; thus, because of the disordering of the Ca2-Ca2' atoms, a single site can accommodate either anion with ideal, but disparate, bond distances to Ca. Finally, in OH-Cl apatites with OH ≈ Cl, also crystallizing in space group $P6_3/m$, four anion positions are occupied in the anion column, including the ClOH site that allows occupancy by both OH and Cl. In addition to that site and distinct OH and Cl sites, OH is found to occupy the site within the mirror plane at (0,0,1/2), the site occupied by F in F-bearing apatite. Occupancy of that site is essential to reversing the sense of ordering of the anion column relative to the mirror planes and preserving $P6_3/m$ symmetry. Thus, the methods of effecting solid solution along the OH-Cl are composition dependent and complex.

Keywords: Apatite, hydroxylapatite, chlorapatite, solid solution, binary, crystal structure

INTRODUCTION

Apatite is the most abundant phosphate mineral on Earth and a phase with fundamental importance in geology, agriculture, materials science, medicine, and dentistry. In addition to the apatite that forms in igneous, metamorphic, sedimentary, and hydrothermal environments, all hard tissue of the human body except small parts of the inner ear is formed of apatite materials, indicating a remarkable link between the inorganic and organic genesis for the mineral; apatite is among the few most common biominerals on Earth. In addition, apatite forms the foundation of the global phosphorus cycle. The importance of apatite in many disciplines, indeed in even sustaining human life as the chief source of phosphate for fertilizer, cannot be overstated. The reader is referred to a recent Elements issue (vol. 11, June 2015) that is devoted entirely to apatite for a more detailed account of the chemistry, structure, and applications of the mineral.

Apatite sensu lato has a composition of $Ca_{10}(PO_4)_{6}(OH,F,Cl)_2$ and is one of the more rare anion solid solutions among minerals. Despite the importance and ubiquitous nature of the mineral, details of the apatite atomic arrangement have not been forthcoming. Hughes et al. (1989) demonstrated that the positions of the [0,0,z] column anions in the apatite end-members (fluorapatite, chlorapatite, and hydroxyapatite) are not compatible in solid solution because of steric constraints. This has led to speculation on how solid solution is effected in apatite sensu lato, but definitive structures on all the binaries are not extant. Hughes (2015) summarized the apatite atomic arrangement and the state of our knowledge of the apatite structure, and illustrated the conundrum...