

# 1 The Crystal Structure of Apatite, $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{OH},\text{Cl})$

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## INTRODUCTION

As illustrated by the broad range of topics presented in this volume, the mineral apatite,  $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{OH},\text{Cl})$ , is of importance in a greater variety of fields than virtually any other mineral. It is of particular significance in Earth science, life science, and material science; the foundation of this significance is the apatite atomic arrangement.

Apatite is the most abundant naturally occurring phosphate on Earth. Consequently, it is the major source of phosphorous, both as an ore and the base of the global phosphorous cycle. As the major ore mineral of phosphorous, apatite is critical for the production of huge quantities of fertilizers, detergents and phosphoric acid; the extracted phosphorous is also used in many other applications such as phosphors, rust removers, motor fuels, and insecticides to name but a few (McConnell 1973). The global biogeochemical cycling of phosphorous starts by its release from apatite at the Earth's surface and ultimately leads to the formation of other geological apatites through sedimentary processes or tectonic recycling. Along the way, however, it is an essential element to all life on Earth (Filippelli, this volume).

The structure and chemistry of apatite allow for numerous substitutions, including a multitude of metal cations (i.e., K, Na, Mn, Ni, Cu, Co, Zn, Sr, Ba, Pb, Cd, Sb, Y, REEs, U) that substitute for Ca in the structure, and anionic complexes (i.e.,  $\text{AsO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{SiO}_4^{4-}$ , etc.) that replace  $\text{PO}_4^{3-}$  (Pan and Fleet, this volume). Indeed, apatite incorporates half the periodic chart in its atomic arrangement. These substitutions are usually in trace concentrations, but large concentrations and even complete solid solutions exist for certain substituents. This complex and variable chemistry has great implications, and is utilized in all areas of apatite research.

Geologically, apatite is a ubiquitous accessory mineral in igneous rocks, and because it is the most abundant phosphate it is essential to understanding phase equilibria of systems containing P. The presence of apatite can also strongly influence the trace element evolution of magmas (Piccoli and Candela, this volume). Many studies have shown apatite to be one of the most important minerals affecting REE trends in igneous rocks (e.g., Nash 1972; Bergman 1979; Watson and Capobianco 1981; Kovalenko et al. 1982; Gromet and Silver 1983; Watson and Harrison 1984a,b). Thus, apatite chemistry plays a critical role in understanding and modeling of igneous petrogenetic processes.

Apatite is also commonly found in metamorphic rocks (Spear, this volume), low-temperature sedimentary environments (Knudsen and Gunter, this volume), as well as a precipitate from hydrothermal solutions (Rakovan and Reeder 1994). Because of its high affinity for many trace metals, the presence of apatite in all of these environments can strongly influence their trace element signature and evolution (Bergman 1979; Watson and Capobianco 1981; McLennan 1989). Many of the elements (i.e., U, Sm, etc.) that the apatite structure can accommodate have radioisotopes that are commonly utilized as geochronometers. Hence, the dating of apatite has become an important tool for studying

the rocks in which it is found (Harrison, this volume; Farley and Stockli, this volume; Gleadow et al., this volume).

In the realm of biology, hydroxylapatite is the main mineral constituent of human bones, teeth, and many pathological calcifications. Indeed, except for small portions of the inner ear, all hard tissue of the human body is formed of apatite materials. Hence it is a focus of the medical fields of orthopedics, dentistry, and pathology (Elliott 1994; Elliott, this volume). It is important to recognize that although this inorganic material is part of bone tissue, skeletal apatite is by no means inert, and plays an important role in the metabolic functions of the body. For example, heavy metal sequestering by apatite is important in our understanding of the fate and transport of toxic species in the body. The presence of certain elements in trace concentrations is also known to inhibit as well as promote apatite growth in the body (e.g., McLean and Bundy 1964; Posner 1987; Hahn 1989). Because the bones and teeth of animals can persist for relatively long periods of time in geologic environments, modern to ancient biogenic apatites have been important in paleontology, archeology, and more recently in studies of paleoclimates (Kohn and Cerling, this volume), animal diets and tracing environmental pollutants (Trumen, this volume).

Finally, because of their physical and chemical properties, apatite and the apatite group minerals are utilized in many materials applications. The presence of Mn, REE, U and other activators in apatite gives it luminescence properties that are of great utility in both the phosphor and laser industries (Waychunas, this volume). The fact that the apatite structure can accommodate many radionuclide species is not only of utility in geochronology but has led to the serious evaluation of apatite as a radionuclide solid waste form for anthropogenic radioactive wastes (Ewing, this volume). Because bone and teeth are comprised of apatite it follows that surgical replacements of natural apatite precipitates are formed of the synthetic phase. Indeed, to increase biocompatibility, apatite coatings are applied to metal and ceramic prostheses (Gross and Berndt, this volume).

The foundation for understanding the complex chemistry and the many and varied uses of apatite starts with an understanding of its atomic arrangement. For this purpose we review the structure of apatite *sensu stricto* in this chapter.

### THE $P6_3/m$ APATITE STRUCTURE

As will be illustrated in subsequent chapters, numerous variants of the apatite atomic arrangement exist. The variant structures, all sub-symmetries of the atomic arrangement of apatite *sensu stricto*, result principally from chemical substitutions (or, in the case of pure chlorapatite and pure hydroxylapatite, *lack* of chemical substitutions) on cation and/or anion sites. To provide a framework for discussion, we here describe the holosymmetric apatite structure, in space group  $P6_3/m$  (#176).

The term apatite *sensu stricto* defines three unique minerals, *fluorapatite*  $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$ , *chlorapatite*  $[\text{Ca}_5(\text{PO}_4)_3\text{Cl}]$ , and *hydroxylapatite*  $[\text{Ca}_5(\text{PO}_4)_3(\text{OH})]$ , all with  $Z = 2$ . As shown by numerous authors, most recently Hughes et al. (1989), the atomic arrangements of the three apatite phases differ principally in the positions of the occupants of the  $0,0,z$  anion positions, i.e., fluorine, chlorine, and hydroxyl for the three end-members, respectively. Below we compare the component polyhedra of the three phases and use this comparison as a basis for subsequent discussion of other apatite group phases. Portions of the comparison are taken from Hughes et al. (1989), which also cites previous works that provide a rich history of research on mineralogical apatite. Table 1 provides the atomic parameters for well-characterized samples of fluorapatite, hydroxylapatite, and chlorapatite (Hughes et al. 1989).

**Table 1.** Positional parameters ( $x,y,z$ ) and equivalent isotropic temperature factors ( $B$ ) for fluor-, hydroxyl-, and chlorapatite. Lattice parameters are at the base of the table (from Hughes et al. 1989).

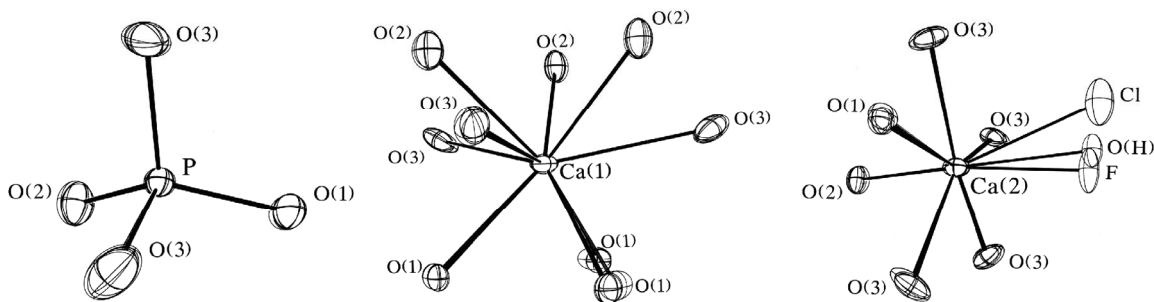
<i>Atom</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
<b>Ca1</b>				
F	2/3	1/3	0.0010(1)	0.91(1)
OH	2/3	1/3	0.00144(8)	0.929(7)
Cl	2/3	1/3	0.0027(1)	0.99(1)
<b>Ca2</b>				
F	-0.00712(7)	0.24227(7)	1/4	0.77(1)
OH	-0.00657(5)	0.24706(5)	1/4	0.859(9)
Cl	0.00112(6)	0.25763(6)	1/4	1.14(1)
<b>P</b>				
F	0.36895(8)	0.39850(8)	1/4	0.57(1)
OH	0.36860(6)	0.39866(6)	1/4	0.62(1)
Cl	0.37359(7)	0.40581(7)	1/4	0.77(1)
<b>O1</b>				
F	0.4849(2)	0.3273(3)	1/4	0.99(4)
OH	0.4850(2)	0.3289(2)	1/4	1.00(3)
Cl	0.4902(2)	0.3403(2)	1/4	1.34(4)
<b>O2</b>				
F	0.4667(2)	0.5875(3)	1/4	1.19(5)
OH	0.4649(2)	0.5871(2)	1/4	1.25(3)
Cl	0.4654(2)	0.5908(2)	1/4	1.47(4)
<b>O3</b>				
F	0.2575(2)	0.3421(2)	0.0705(2)	1.32(3)
OH	0.2580(1)	0.3435(1)	0.0703(2)	1.57(2)
Cl	0.2655(2)	0.3522(2)	0.0684(3)	1.88(3)
<b>X</b>				
F	0	0	1/4	1.93(6)
OH	0	0	0.1979(6)	1.31(8)
Cl	0	0	0.4323(4)	2.68(5)
F:	$a = 9.397(3)$ Å	$c = 6.878(2)$ Å		
OH:	$a = 9.417(2)$	$c = 6.875(2)$		
Cl:	$a = 9.598(2)$	$c = 6.776(4)$		

Several comments are warranted about the apatite structure before its description is proffered. As noted in Table 1, the atoms lie on or near four (00*l*) planes in the atomic arrangement. Ca2, P, O1, O2, and the X anion (where X = F, OH, Cl) lie on (or are disordered about) special positions on the mirror planes at  $z = 1/4$  and  $3/4$ . Intercalated approximately halfway between these planes are Ca1 (in a special position at  $z = \sim 0, \sim 1/2$ ) and O3, in the general position with  $z$  values of  $\sim 0.07$  and  $\sim 0.57$ . On the basis of the layer structure of the atomic arrangement, O’Keeffe and Hyde (1985) noted the similarity between the cation positions in the apatite structure and the Mn<sub>5</sub>Si<sub>3</sub> intermetallic phase, and offered a description of apatite as a *cation*-closest-packed atomic arrangement. Dai et al. (1991) and Dai and Harlow (1991) elucidated that intriguing cation-closest packing relationship in an examination of arsenate apatites, and their work is worthy of detailed review.

The atomic arrangement of apatite *sensu stricto* is formed of three cation polyhedra, and the structural variations among the three anion end-members is perhaps best understood by examining variations that occur in the three polyhedra concomitant with substitution of the three column anions. The three polyhedra as they occur in fluorapatite, hydroxylapatite, and chlorapatite are compared and superimposed below.

### The PO<sub>4</sub> tetrahedron

Phosphorous occurs in apatite *sensu stricto* in tetrahedral coordination, with the central P atom in the 6*h* special position (Table 1). Typical of such rigid polyhedra, the tetrahedron is essentially invariant in fluor-, chlor-, and hydroxylapatite. Figure 1 displays the superposition of PO<sub>4</sub> tetrahedra for fluorapatite, hydroxylapatite, and chlorapatite, and illustrates the invariance of the polyhedron among the three end-members.



**Figure 1.** Drawings of PO<sub>4</sub> tetrahedron (left) and Ca1 and Ca2 polyhedra for the three apatite structures. Each overlay is a superposition of the analogous polyhedra from the fluorapatite, hydroxylapatite, and chlorapatite end-members, drawn to the same scale and with coincident central cations. From Hughes et al. (1989).

### The Ca1O<sub>9</sub> polyhedron

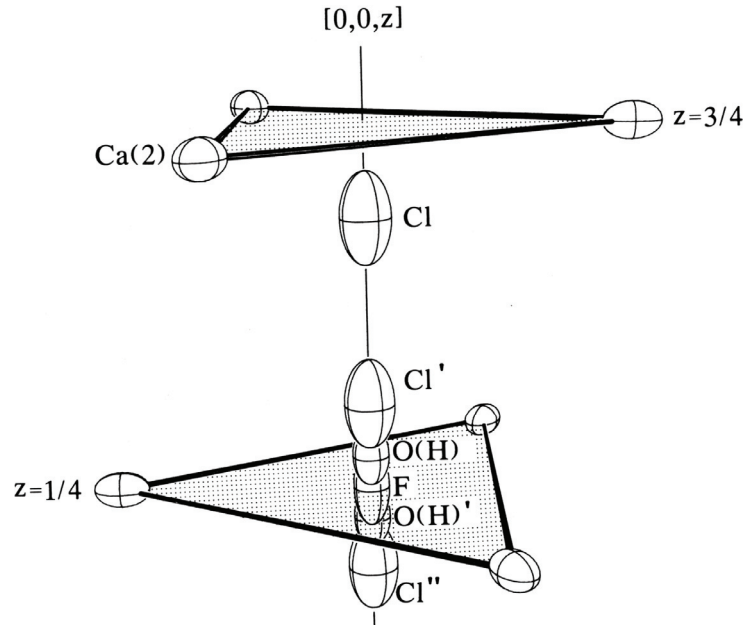
In apatite *sensu stricto*, the ten Ca ions in the unit cell exist in two polyhedra. Ca1, with the central cation in the 4*f* ( $1/3, 2/3, z$ ) position, is coordinated to nine oxygen atoms in the arrangement of a tricapped trigonal prism. Ca1, with *z* values near 0 and  $1/2$ , bonds to six of those oxygen atoms ( $3 \times O1$ ,  $3 \times O2$ ) in planes  $1/2$  unit cell above and below the central cation, forming a trigonal prism. Three more oxygen atoms ( $3 \times O3$ ), essentially coplanar with Ca1, are bonded through the prism faces to form the tricapped trigonal prism.

Figure 1 displays the superposition of Ca1 and its ligands for fluorapatite, hydroxylapatite, and chlorapatite. As revealed by the figure, the Ca1 polyhedron shows little response to incorporation of the different column anions in the three end-members of apatite *sensu stricto*.

### The Ca2O<sub>6</sub>X polyhedron

Ca2, in the 6*h* special position of space group *P6<sub>3</sub>/m*, bonds to 6 oxygen atoms (O1, O2,  $4 \times O3$ ) and one column anion (*X*). The major structural response to substitution of the three column anions occurs in this polyhedron. Figure 1 displays the superposition of the three Ca2 polyhedra for the pure anion end-members, and illustrates the large shifts that occur in the positions of the *X* anions in the [00*z*] anion column.

The Ca2 cations form triangles on the planes at  $z = 1/4$  and  $z = 3/4$  (Fig. 2). Each of the three Ca atoms at the corners of the triangles is bonded to the central anion in the [00*z*] column. Fluorine, the smallest of the three anions, lies on the planes at  $z = 1/4, 3/4$  (at  $0, 0, 1/4$  and  $0, 0, 3/4$ ) with Ca2-F bonds lying in (001). The larger OH anionic complex and



**Figure 2.** Depiction of possible anion positions in the hexagonal ternary apatite structure. Stippled planes represent mirror planes at  $z = 1/4, 3/4$ , each containing a triangle of Ca2 atoms (connected by “bonds”). Atom Cl represents a Cl atom disordered below the mirror plane at  $z = 3/4$ , and other column anions represent five possible anion neighbors associated with the mirror plane at  $z = 1/4$  (Cl' = Cl disordered above plane; O(H) = OH oxygen disordered above that plane; F = fluorine atoms at  $0, 0, 1/4$ ; O(H)' and Cl'' represent OH and Cl disordered below the mirror plane at  $z = 1/4$ ). From Hughes et al. (1990).

Cl anion are too large to lie on the rigid plane defined by the Ca atoms, and the OH or Cl anion associated with the plane is displaced above *or* below the plane. Such a displacement locally destroys the  $P6_3/m$  symmetry by eliminating the mirror plane, as only one of the two mirror-symmetric sites above and below the plane is occupied. However, except in rare cases discussed below, over the crystal as a whole each mirror-related site is half-occupied, thus preserving the average  $P6_3/m$  symmetry.

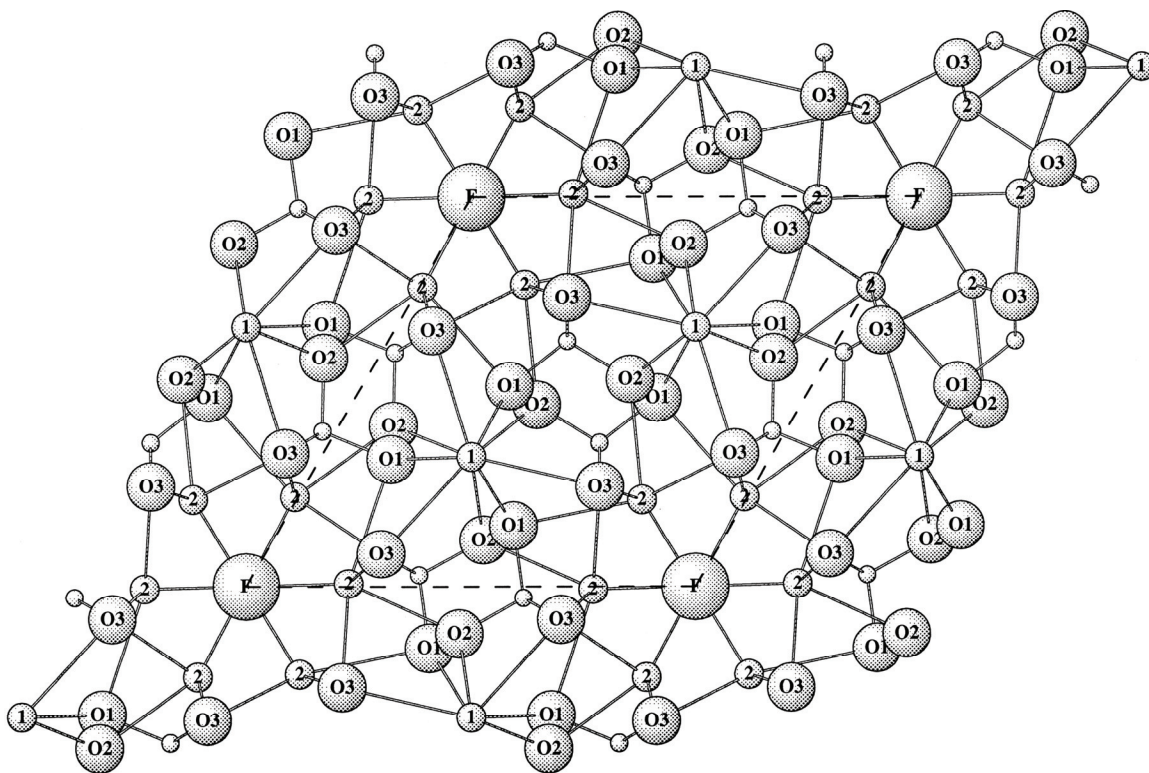
The polyhedral components of the apatite atomic arrangement combine to form the atomic arrangement pictured in Figure 3. That [001] projection shows the packing of the three polyhedra described above to yield the atomic arrangement of apatite *sensu stricto*.

### APATITE *SENSU STRICTO* STRUCTURAL VARIANTS

Numerous structural variants of the apatite atomic arrangement exist, all related to the holosymmetric structure depicted in Figure 3. Many of the substructures result from ordering of cation substituents on the Ca and P sites, and those structures will be discussed in subsequent chapters. Here we elucidate structural changes in apatite *sensu stricto* that result from anion substitutions or ordering in the anion column.

#### Monoclinic hydroxylapatite and chlorapatite

Although the ideal apatite atomic arrangement is described in space group  $P6_3/m$ , the pure hydroxylapatite and chlorapatite end-members actually crystallize in the subsymmetric monoclinic space group  $P2_1/b$ . As noted above, OH and Cl are too large to fit in the triangles of Ca atoms (Fig. 2). Early structure elucidation of the two end-members demonstrated (OH: Kay et al. 1964, Elliot et al. 1973; Cl: Hounslow and Chao 1968) that the OH and Cl are disordered above *or* below the Ca triangles at  $z = 1/4, 3/4$  at any

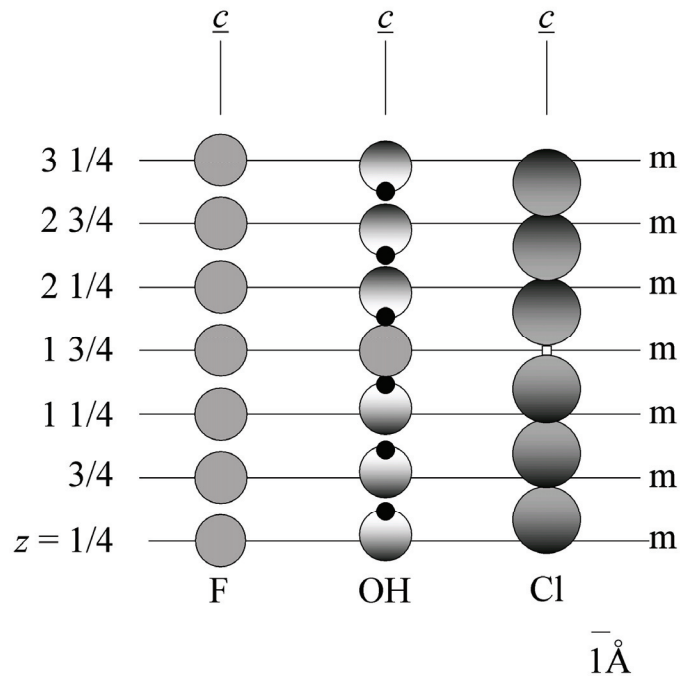


**Figure 3.** The atomic arrangement of fluorapatite projected on (001). Phosphorous (smallest atoms) are unlabeled, and Ca1 and Ca2 are labeled “1” and “2” respectively. The P bond to O3 represents two such bonds to overlying O3 atoms. Coordination polyhedra are explained in text.

individual anion site. In  $[00z]$  columns in hydroxylapatite or chlorapatite in which few vacancies or impurities occur, the OH or Cl column anions are ordered either above *or* below the mirror planes in a given anion column (Fig. 4); importantly, in any individual column in the pure phases, all anions are ordered in the same sense. The sense of ordering (e.g., anions above *or* below the plane) in any individual column is transmitted to the adjacent column along  $b$ . Tilting of polyhedra caused by the ordering in one column causes the adjacent column along  $b$  to be ordered in the opposite sense (e.g., below *or* above the plane), thereby doubling the  $b$  axis length. The symmetry thus degenerates to  $P2_1/b$ , a consequence of column anion ordering. Most natural chlorapatite and all natural hydroxylapatite, however, contain enough impurities or vacancies in the anion columns (as in Fig. 4) to destroy the ordering in the column, thus they exist in the putative  $P6_3/m$  space group. Hounslow and Chow (1968) have reported natural monoclinic chlorapatite, and, in a particularly insightful study, Elliot et al. (1973) illustrated the structural details of monoclinic hydroxylapatite. Despite the monoclinic nature of hydroxylapatite and chlorapatite at room temperature, however, the phases invert to the hexagonal structure at elevated temperatures (OH: Bauer 1991; Cl: Prener 1967, Bauer and Klee 1993).

### Anion compatibility

Fluor-, chlor-, and hydroxylapatite end-members exist with a single anion occupant of the anion columns. However, as solid solution among the column anion components occurs the  $[00z]$  columns must accommodate the variety of anions, and the means of accommodation is not straightforward. The extent of solid solution between and among the column anion constituents, and the structural response to such solution, is not well characterized (McConnell 1973). The locations of the anions in the end-members demonstrate that the structural configurations are not miscible without a structural



**Figure 4.** Anion columns in hexagonal fluorapatite, hydroxylapatite and chlorapatite depicted to scale. Column “F” depicts anions in fluorapatite located on mirror planes at  $z = 1/4, 3/4$  in successive unit cells. Column “OH” depicts three successive hydroxyls in hydroxylapatite disordered  $0.35 \text{ \AA}$  above the mirror planes and three successive hydroxyls disordered below the mirror planes, with the sense of ordering reversed by an F anion (stippled) “impurity”. Column “Cl” depicts three successive Cl anions in chlorapatite disordered above the mirror planes and three successive Cl anions disordered below the mirror planes; the vacancy ( $\square$ ) at  $z = 1^{3/4}$  must exist in order to reverse the sense of ordering, as F and OH species are prohibited. Radii: F = OH =  $1.4 \text{ \AA}$ ; Cl =  $1.8 \text{ \AA}$ . Scale of H atom (solid circles) is arbitrary. After Hughes et al. (1989).

response to solution of the binary and ternary anion columns. The structural responses to binary and ternary solid solution have not been well studied, and are a fruitful area of future research.

The apatite end-members contain column anions associated with the mirror planes at  $z = 1/4$  and  $3/4$  in each unit cell. In fluorapatite the F atoms are located on the mirror planes, whereas in hydroxylapatite and chlorapatite the anions are disordered about each mirror plane, with OH displaced  $\sim 0.35 \text{ \AA}$  above or below the plane and Cl displaced  $\sim 1.2 \text{ \AA}$  above or below the plane. Because the anion sites in any column are separated by only  $c/2$ , or approximately  $3.4 \text{ \AA}$ , there is extensive interaction between the occupants of the adjacent sites, and the occupants of a given site can affect the occupant of the adjacent site in the same anion column along  $c$ , creating a Markovian sequence of anion occupants.

Figure 4 depicts anion columns in fluorapatite, and near-end-member hydroxylapatite and chlorapatite, and illustrates the nature of interactions in the anion columns in binary and ternary apatites. The spherical atoms are drawn to scale and illustrate that in fluorapatite, with F atoms lying on the mirror planes, the hard-sphere model allows a fluorine atom at each successive anion site.

In hydroxylapatite the hydroxyls are located  $\sim 0.35 \text{ \AA}$  above or below each mirror plane. To achieve the average disordered  $P6_3/m$  structure, half the hydroxyls in any

column must be located above the particular mirror plane, and half below; this arrangement requires “reversal sites” in which the sense of the ordering (above vs. below) is reversed. Figure 4 illustrates such a reversal site, with a fluorine “impurity” allowing reversal of the sense of the ordering; a vacancy would also allow reversal. Without such impurities, however, the hydroxyls at a reversal site would be separated by  $\sim 2.7 \text{ \AA}$ , and the hydrogen atoms associated with the hydroxyls would be  $\sim 0.8 \text{ \AA}$  distant, clearly impossible. Thus, with the addition of sufficient F or  $\square$  reversal sites, reversal of the ordering of the hydroxyls is facilitated and hydroxylapatite inverts from  $P2_1/b$  to  $P6_3/m$  symmetry. Sudarsanan and Young (1969) have shown that the well-characterized Holly Springs hydroxylapatite is hexagonal with 8% substitution of F for OH in the anion columns; their paper should be regarded as the seminal paper on the structure of natural hydroxylapatite.

Incorporation of the large Cl anion ( $1.81 \text{ \AA}$  radius) in the anion columns adds additional constraints to the structure, and hence chemistry, of the anion columns. Because the larger Cl anion is displaced  $\sim 1.2 \text{ \AA}$  above or below the plane, the interaction with the occupant of the adjacent site along the anion column is profound. As depicted in Figure 4, the reversal from a Cl ordered above the mirror plane to a Cl below the plane can only take place with a vacancy, *assuming no adjustment in anion sites*. Thus, for pure chlorapatite, the hexagonal phase must have stoichiometric vacancies to effect anion reversals in the anion columns.

The interaction of the column anions suggests that binary and ternary calcium apatite phosphates are not mere additions of the end-member structures, but that structural adjustments must occur to accommodate mixed-anion columns. Table 2 depicts the distance between anion occupants of adjacent planes, and illustrates which adjacent neighbors are allowed with mixtures of the end-member structures.

**Table 2.**

		Anion Associated with Mirror Plane at $z = 3/4$			
		OH <sub>a</sub>	OH <sub>b</sub>	Cl <sub>a</sub>	Cl <sub>b</sub>
Anion Associated with Mirror Plane at $z = 1/4$	OH <sub>a</sub>	3.41	<del>2.70</del>	4.30	<del>1.81</del>
	OH <sub>b</sub>	4.12	3.41	5.01	<del>2.52</del>
	Cl <sub>a</sub>	<del>2.52</del>	<del>1.81</del>	3.41	<del>0.92</del>
	Cl <sub>b</sub>	5.01	4.30	5.90	3.41

### Solution in the anion columns

The discussion above illustrates that various anion column occupants are incompatible as nearest neighbors, at least given the end-member structures. Yet, such solutions do indeed occur; solid solution among all three anions is not uncommon. Clearly, structural adjustments must occur to accommodate anion mixtures in the columns; for example, without such accommodations, Cl could not coexist in the columns with other anions. The situation is illustrated in Figure 2, which depicts a Cl ordered below a plane at  $z = 3/4$ , and the five possible anion occupants at the adjacent mirror plane at  $z = 1/4$ . As depicted in Figure 2, possible column-anion neighbors



associated with the adjacent mirror plane at  $z = 1/4$  are (1) a Cl located above the  $z = 1/4$  plane (Cl-Cl' distance 0.92 Å), (2) an OH disordered above the mirror plane (Cl-O(H) distance = 1.81 Å), (3) an F ion in the plane of the mirror (Cl-F distance = 2.16 Å), (4) an OH disordered below the mirror plane (Cl-O(H)' distance = 2.51 Å), and (5) a Cl ion disordered below the  $z = 1/4$  mirror plane (Cl-Cl'' distance =  $c/2 = 3.4$  Å). On the basis of anion positions in the hexagonal end-member structures, all of these anion neighbors except the Cl ion below the adjacent plane (= Cl'') are prohibited on the basis of anion-anion distances. It is thus not immediately apparent what structural accommodations must occur to achieve solid solution among the anions.

In a particularly insightful study, however, Sudarsanan and Young (1978) demonstrated that in Cl-bearing apatite solid solutions, a new Cl site can be created in the column with attendant shifts in the positions of the Ca atoms in the surrounding triangle. The new site allows solid solution to occur among the three-anion occupants by creation of favorable sequences in the anion column. Hughes et al. (1990) examined two natural F-, OH-, and Cl-bearing apatites ("ternary apatites"), and found that the structural adjustments proffered by Sudarsanan and Young (1978) operated in hexagonal apatites to effect solid solution among the anions. In addition to the hexagonal phase, however, Hughes et al. (1990) described a monoclinic ternary apatite in which ordering of the ternary column anions yielded a  $P2_1/b$  structure. The two phases will be used to elucidate the solution of the three anions in calcium phosphate apatite.

### Hexagonal ternary apatite

Hughes et al. (1990) refined the atomic arrangement of a hexagonal ternary apatite with the column anion composition of  $(F_{0.39}Cl_{0.33}OH_{0.28})$ , and much of the following is taken contextually or verbatim from their description of the phase.

As noted previously, the anion positions in the three end-member apatite *sensu stricto* phases are not compatible in solid solution, as demonstrated in Figure 2. As shown there, a Cl atom disordered below the  $z = 3/4$  plane could only be followed along  $-c$  by another Cl atom disordered below the mirror plane at  $z = 1/4$ , ad infinitum; on the basis of the anion positions in the hexagonal end-member atomic arrangements, all of these anion neighbors for the Cl anion except Cl'' (Fig. 2) are prohibited on the basis of anion-anion distance.

Hughes et al. (1990) noted that in "end-member" hexagonal chlorapatite, the Cl atom is unfettered by adjacent non-Cl atoms in the  $[0,0,z]$  anion columns, and the Cl half-occupies a position at  $(0,0,0.5677)$  about the  $z = 3/4$  mirror plane. In hexagonal *ternary* apatite, however, the Cl atom position shifts in response to the presence of other anion neighbors, as first demonstrated in a perceptive study by Sudarsanan and Young (1978). In mixed-anion columns, a portion of the Cl atoms shift 0.4 Å closer to the  $z = 3/4$  mirror plane, to a half-occupied  $(0,0,0.632)$  position (continuing the example of a Cl atom disordered below the  $z = 3/4$  plane). The shift in Cl position allows accommodation of an OH neighbor at the OH position disordered below the adjacent plane at  $z = 1/4$  [O(H)' in Fig. 2]. The Cl-O distance is now an allowable 2.95 Å, in contrast to 2.52 Å calculated with anion positions in the hexagonal end-member chlor- and hydroxylapatite atomic arrangements.

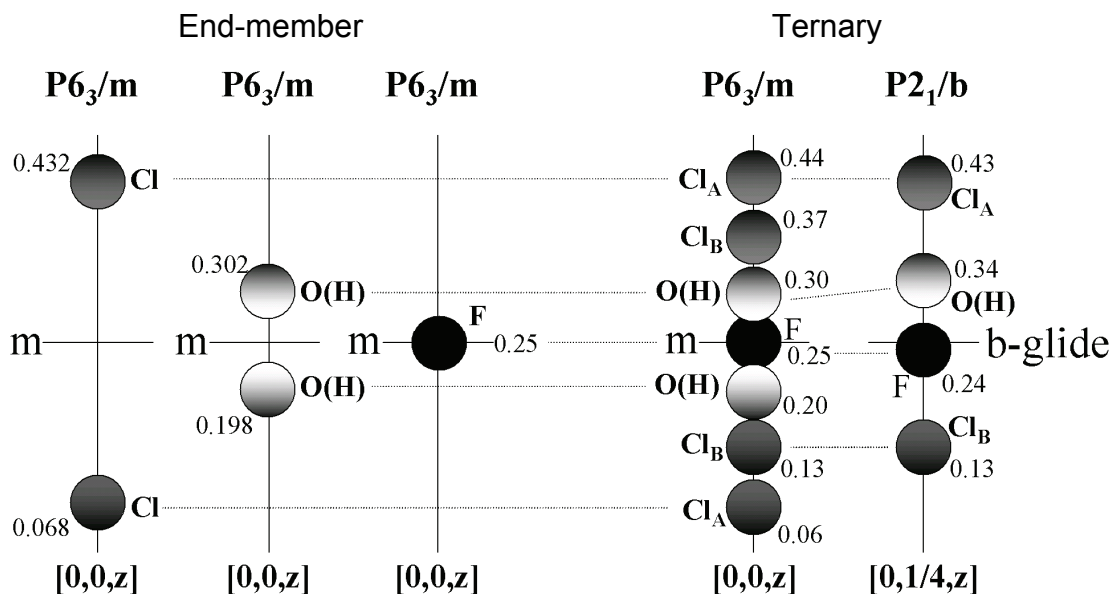
The shift of anion positions in apatite solid solutions is not without concomitant shifts of the coordinating cation positions. The shift of the Cl position causes a splitting of the single Ca2 site into two sites. In a detailed structure refinement of a ternary apatite, Sudarsanan and Young (1969) demonstrated that the shift of the Cl atoms closer to the Ca2 triangles causes a portion of the Ca2 atoms (proportional to the number of Cl atoms in the new position) to shift to a new position that enables the  $\sim 2.70$  Å Ca-Cl bond

distance to be maintained. Thus, in ternary apatites, two Ca2 positions exist: Ca2<sub>A</sub>, in which Ca2 atoms bond to F, OH, or unshifted Cl atoms, and Ca2<sub>B</sub>, which bond to the shifted Cl atoms.

Miscibility of F, Cl and OH in hexagonal ternary apatites thus results from a Markovian sequence of anions in the [00z] anion columns, i.e., a sequence in which the occupant of a given position is dependent on the occupant of the adjacent position(s). For example, to change the anion sequence in a given column from a Cl<sub>A</sub> atom disordered below a plane to a Cl<sub>A</sub> atom disordered above a plane (Fig. 2), the following sequence can be postulated. Moving down the anion column to successive mirror planes at  $z = 3/4, 1/4$ , etc., along  $-c$ , a change from a Cl<sub>A</sub> atom disordered *below* the plane to a Cl<sub>A</sub> atom disordered *above* the plane can be effected, without vacancies, by the following Markovian sequence of anions at each successive site: Cl<sub>A,below plane</sub> (~2.95 Å)– Cl<sub>B,below plane</sub> (~2.95 Å)– OH<sub>below plane</sub> (~3.08 Å)– F<sub>on plane</sub> (~3.08 Å)– OH<sub>above plane</sub> (~2.95 Å)– Cl<sub>B,above plane</sub> (~2.95 Å)– Cl<sub>A,above plane</sub>. Thus, the creation of new anion sites in response to solid solution enables accommodation of the three anions in a single column without vacancies.

### Monoclinic ternary apatite

In a study of ternary apatites *sensu stricto*, Hughes et al. (1990) revealed a monoclinic variant of ternary apatite that illustrates the unaddressed complexities of apatite crystal chemistry. In the  $P2_1/b$  variety, the positions of the non-column atoms are similar to those in  $P6_3/m$  ternary apatite, but the reduction in symmetry results from ordering in the anion columns, similar to the cause of monoclinicity in the chlorapatite and hydroxylapatite end-members. The positions of the column anions in hexagonal and monoclinic ternary apatite are depicted in Figure 5. The petrologic implications of monoclinic ternary apatite remain unexplored, and it is unknown how common the phase is.



**Figure 5.** Correlation of anion sites in end-member and  $P6_3/m$  and  $P2_1/b$  ternary apatites. Atoms represent possible anion sites associated with the mirror plane ( $P6_3/m$ ) or the  $b$ -glide ( $P2_1/b$ ) at  $z = 1/4$ . Atom size is arbitrary, and the  $z$  positional parameter is given. Dashed lines connect correlative positions in different structures. The shift of the O(H) position between the ternary structures is largely a result of the difference in Cl content. Modified from a drawing by Maryellen Cameron.

It is perhaps illustrative of the unexplored complexities of apatite crystal chemistry that a study of apatite that begins with simple film studies of a few crystals quickly uncovers a new structural variant of ternary apatite (Hughes et al. 1990). Researchers are urged to explore in detail the crystal chemistry of the apatite *sensu stricto* group of minerals, the minerals that collectively comprise the tenth most abundant mineral on Earth and perhaps the premier example of biomineralization, the biomineral that is essential to human life.

### SUMMARY

The apatite *sensu stricto* group of minerals is formed of three phases that are among the most abundant minerals on Earth, and are essential to human life. As the attention of mineralogists turns to biomineralization, it is fitting that research on apatite re-enters the forefront of mineralogical research to address the many unanswered questions on apatite crystal chemistry.

Such fundamental parameters as the extent of solid solution between the anion end-members and among the ternary anion components remain unanswered by modern studies. Indeed, the outline of column anion interactions given above does not provide a viable mechanism for binary solution of fluorapatite and chlorapatite, and the study of mineral solution along the join is of fundamental interest in petrology, as constraints on incorporation of volatile components in apatite are important. Mackie and Young (1974) addressed the incompatibility of F and Cl in the apatite anion columns, and suggested that solid solution may be possible with creation of new F sites in the anion column. However, the bond-valence sums on their proposed new F site occupant are unreasonably low, and questions remain as to the extent and mechanism of solid solution. Hughes et al. (1990) suggested that in natural apatites, OH may be an *essential* component in stabilizing fluorapatite-chlorapatite solid solution, but this observation has not been explored. In addition to X-ray diffraction studies that average larger volumes of unit cells, microbeam and atomic-scale imaging methods are of interest in elucidating local atomic constraints in the apatite *sensu stricto* phases. Such studies are of fundamental importance to the fields of petrology, medicine and material science, and are a fruitful area for mineralogical researchers.

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