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The many facets of apatite

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Abstract

In the past 150 years, with the discovery of petroleum and the invention of the gasoline-powered internal combustion engine, the rate of extraction of minerals from the Earth has made humans a geologic agent for the first time in the history of the planet. Unprecedented changes have resulted in human society as a result of this extraordinary use of minerals, and perhaps no mineral illustrates that linkage more than the mineral apatite; even the exponential growth of the human population to seven billion Earth inhabitants has been allowed by the extraction of sufficient P from apatite ore to provide fertilizer to feed the planet's population. Apatite is used extensively in various geological applications, including dating techniques and studies of rare earth element variation in rocks, and is also widely used in material science and medical applications. Apatite forms virtually all hard parts of the human body, and the bioengineering of anion exchange in the apatite material of human tooth enamel through fluoridation is considered one of the top ten public health achievements of the twentieth century by the U.S. Centers for Disease Control. In addition, the carbonate content of apatite calcifications is currently being investigated as a non-invasive tool in distinguishing between benign and malignant breast tumors. In material applications, apatite is the principle raw material in the fluorescent lighting industry, and its unique crystal chemical properties make it useful in the production of lasers

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with controllable properties. Apatite is increasingly being employed in the environmental remediation industry through the process of PIMS (*phosphate-induced metal stabilization*), and its properties make it a useful material for the storage of radioactive waste as substituents in the Ca sites.

Despite its remarkable utility and its fundamental role in feeding the world's population, the details of the apatite atomic arrangement are not fully understood. The Ca phosphate apatites are an anion solid solution (F = fluorapatite; OH = hydroxylapatite; Cl = chlorapatite), and the anion positions in binary and ternary members of the solid solution are not predictable from the anion positions in the pure end-members because of steric effects of anion-anion interactions. Recent attention has focused on a more complete understanding of the apatite atomic arrangement and its properties, both in inorganic and biominerals apatites, and knowledge of the atomic arrangement is advancing. Apatite illustrates the role of minerals in the evolution of modern society, and also the importance of research in the mineral sciences in the broadest sense.

Keywords: Apatite, phosphate, crystal structure, minerals and society

Introduction

With the first extraction of petroleum from the Earth in 1859, and the subsequent development of the gasoline-fired internal combustion engine in the late 19th century, humans became a significant geologic agent for the first time in the 4.6 billion year history of the Earth. Dramatic change in all aspects of society occurred as a result of the extraction and utilization of large quantities of minerals; modern transportation systems, communications systems, water systems, the generation, transmission and harnessing of electrical power, the modern built

environment, massive increases in agricultural production, advances in medicine, and countless other aspects of today's world result from this use of minerals that has occurred only in the past 150 years. One example, perhaps the quintessential example, of how the use of a single mineral has shaped the evolution of society in the past 150 years is the mineral apatite; indeed, the very growth in world population in the past 100 years was enabled by extraction of sufficient quantities of apatite to support increasing agriculture production necessary to feed that rapidly growing population. In this paper, I will introduce the mineral apatite, illustrate how it is utilized in geological applications and by Society, and ultimately comment specifically on the crystal chemistry of the mineral. The reader is also referred to a recent (forthcoming?) *Elements* volume (Harlov and Rakovan 2015) that is devoted to the mineral apatite.

Apatite in Geologic Studies

The Ca phosphate apatites, $\text{Ca}_{10}(\text{PO}_4)_6(\text{F},\text{OH},\text{Cl})_2$ (fluorapatite, hydroxylapatite, chlorapatite, respectively) are collectively the tenth most abundant mineral on Earth, and the most abundant phosphate mineral. Apatite forms the base of the P cycle, which begins when the $(\text{PO}_4)^{3-}$ phosphate group is released as apatite weathers at the Earth's surface. The mineral occurs in igneous, metamorphic, sedimentary, and hydrothermal rock systems, and is the principal reservoir for P in all these rock types.

Apatite is used widely in the analysis of many geologic processes. One such analytical method is the determination of the rates and dates of geologic processes using fission-track techniques. ^{238}U substituting in the Ca1 and Ca2 sites in apatite spontaneously fissions, leaving damaged "tracks", revealed by etching, where the apatite structure is destroyed. The density of tracks is proportional to the amount of substituent ^{238}U and *time* since the apatite grain passed

through the closure temperature, when annealing ceased. Fission-track dating is used extensively in elucidating rates of mountain building, the dating of archeological material, and in provenance studies of Earth materials. In addition, many of the elements that the apatite structure can accommodate have isotopes that are commonly used in radiometric dating, for example U, Th, Sr, La, Sm, and Lu. Hence, the dating of apatite by radiometric techniques has become an important tool for determining the ages of the rocks in which it is found (Chew and Spikings 2015). Recent studies of metasomatic mineral replacement reactions also show that apatite can change its chemistry by a process of dissolution and reprecipitation during fluid-involved metamorphic events (metasomatism), and thus can be used to date not only the age of a given rock formation but also the age of the post-formational metamorphic events (Harlov and Austrheim 2013).

Because of its robust atomic arrangement, Ca phosphate apatite is a host to many substituents, and the two Ca sites afford two distinct environments for the rare earth elements (REEs). Apatite has generally very high partitioning coefficients for the REEs, although they do vary for the individual elements (Fleet et al. 2000); Hughes et al. (1990) have shown that, on the basis of site bond-valence, the LREEs generally prefer the Ca₂ site, whereas the HREEs generally prefer the Ca₁ site as substituents, and REEs near Nd, with the highest partition coefficients, are accommodated in either Ca site. Apatite, although typically found in accessory amounts in igneous rocks, exerts a large and disproportionate control on the REE variation in those rocks.

Material Applications of Apatite

Apatite as a Source of Fertilizer

Apatite is mined extensively for many uses, but approximately 90% of mined apatite is used to produce fertilizers and animal feed; the P extracted from apatite is essential for the production of fertilizer, and, like many other resources, humankind is facing the age of Peak P. Figure 1 illustrates the dramatic rise in world production of P since 1900, mined principally from apatite, and superimposes the growth in human population in that same time period; human impact on the global P cycle has been profound in the past 150 years (Filippelli 2002). Sufficient apatite is necessary to feed the world's population; 2007 world per capita consumption was $3.7 \text{ kg P capita}^{-1} \text{ yr}^{-1}$ ($\approx 20.0 \text{ kg apatite}$), but that value varies widely by country, largely correlated with bovine meat consumption and, more recently, with production of bioenergy, as 10% of the US phosphate fertilizer is used to produce ethanol (Elser et al. 2012). As apatite is necessary to produce sufficient phosphate fertilizer to feed the world's population, significant debate surrounds the timing of "peak P" (Cordell et al. 2009), but it is clear that after four decades of a nearly constant price for "phosphate rock", a dramatic instability in price began in 2007 and continues today (InvestMine 2014). As this consumed phosphate from fertilizers enters the waste stream, it is known to foul waste treatment systems as the phosphate mineral struvite precipitates from the waste, but recent attention has been focused on actually mining the precipitated struvite from water systems and using it as a source of phosphate fertilizer (Etter et al. 2011).

Apatite in Environmental Remediation

Apatite is an important phase in environmental remediation of contaminated groundwater in a process known as PIMS (Phosphate Induced Metal Stabilization; Wright and Conca 2002), a rapidly growing area of apatite science. In the PIMS process, a permeable reactive barrier of apatite is constructed through which contaminated groundwater will flow. As the groundwater

reacts with the apatite in the reactive barrier, apatite and phosphate phases will precipitate that incorporate the groundwater contaminants in insoluble, nonbioavailable phases (Rakovan 2008). The engineered formation of apatite in contaminated soils and sediments is a new and promising method for sequestering metals (including radionuclides) and environmental remediation (Magalhães and Williams 2007). This technique is currently being used to remove radioactive ^{90}Sr from the groundwater that enters the Columbia River, a contaminant that originated at the nuclear reactors at the U.S. Department of Energy Hanford Site (State of Washington 2010).

As in the removal of ^{90}Sr from contaminated groundwater, the sequestering of environmental contaminants in apatite is particularly germane to radioactive waste products from weapons manufacture or spent nuclear fuel (Ewing and Wang 2002). Radionuclides contained in liquid waste can be incorporated into the stable apatite structure by coprecipitation, and then the non-soluble, solid-state contaminants can be more easily disposed of and isolated from the biological environment; disposal of the radionuclides in the form of apatite greatly decreases the potential of their being dispersed into the environment through ground-water contamination after they are buried. Apatite has several characteristics that make it ideal for applications of this nature including: 1) a high capacity for the incorporation of many radioactive elements of concern, as well as selected fission products resulting from their decay; 2) a reasonable chemical durability (e.g., low solubility in natural waters) depending on the geochemical environment for disposal; and 3) a propensity for rapid annealing of radiation damage—the same characteristics that make apatite an important mineral for dating rocks and geological processes (Rakovan and Pasteris 2015).

Industrial Applications of Apatite

Apatite is widely used in industrial and material science applications. Every Li-Fe-phosphate battery in an electric car contains 60 kg of P (Elser et al. 2012), extracted principally from apatite ore. Beginning largely in the 1950s, the lighting industry consumed huge quantities of apatite (fluor-chlorapatite doped with Sb and Mn) as the fluorescent tube lining in fluorescent lights, although in response to efficiency concerns the lining has been largely changed to triphosphate compounds in the 1990s, also using apatite-derived P. In addition to its optical properties that are used in the lighting industry, apatite is also used extensively as a lasing material; the extensive substitutions that can be made in the apatite, and the control of substituent sites by co-doping, allows crafting of lasers with desirable optical properties (e.g., Payne et al. 1994).

Phosphoric acid, manufactured from extracted apatite, has many uses other than its dominant use in the manufacture of fertilizers. Nearly 40 million metric tons of phosphoric acid are produced annually for use as a food and drink additive, an animal feed additive, in the treatment of metals, an agent of water treatment, and the manufacture of detergents, gasoline additives, insecticides, and rust removers.

Biological Apatite

In the past several decades, mineral scientists have turned considerable attention to biominerals, or minerals formed through biological processes. Although apatite can form by inorganic processes, it is also one of the most abundant biominerals; biological apatite has received considerable attention in the fields of medicine and dentistry, and research on the phase is truly multidisciplinary (Elliot 2002). Bone material has long been known to be an apatite-type compound, and recently Pasteris et al. (2014) undertook a detailed study that demonstrated the relationship between hydroxylapatite and “bone apatite”; that study is of particular importance to

those who study diseases of the bone (Hughes 2014). Two of the primary functions of bone are to support and protect soft tissue and organs in the body. It is important to recognize, however, that although this inorganic material is part of bone tissue, skeletal apatite is by no means inert; it plays an important role in the metabolic functions of the body. For example, it is a reservoir for Ca and P that are essential for cellular function, and exchange of these elements between bone and body fluids is essential (Elliott 1994; Rakovan and Pasteris 2015).

Early in the 1900s, it was noted that children who consumed groundwater in the Colorado Springs, CO area had disfiguring, mottled brown teeth, known in the dental literature as “Colorado Brown Stain”. In a fascinating story of research and discovery, two dental researchers (Drs. F. McCay and G.V. Black) documented that disfiguring condition in other, isolated areas of the nation, and eventually correlated the condition with high F contents of local groundwater. They also noted that the mottled teeth “were surprisingly and inexplicably resistant to decay” (National Institute of Dental and Craniofacial Research 2014). That discovery led to the bioengineering of the fluoridation of tooth enamel apatite through fluoridation of water supplies and toothpaste, which is considered one of the ten greatest public health achievements of the twentieth century (U.S. Centers for Disease Control and Prevention 1999). Apatite has other medical uses as well. Because of the differing levels of substituent carbonate in hydroxylapatite calcifications associated with benign and malignant breast tumors, recent research has demonstrated that apatite composition may be useful in distinguishing between benign and malignant breast lesions in a non-invasive manner (Kerssens et al. 2010). For decades, hydroxylapatite has also been used as a coating on prostheses that are inserted into human bone, improving the healing rate as the prosthesis more easily melds with the patient’s bone (Constantz and Osaka 1994).

The Crystal Chemistry of Apatite

The remarkable applicability of apatite in geologic and societal uses results from the properties that derive from its atomic arrangement. The structure of apatite is very robust, and more than half the long-lived elements in the periodic chart can be incorporated in apatite supergroup minerals (Hughes and Rakovan 2015).

The atomic arrangement of apatite is formed of three cation-centered polyhedra: the $M1O_9$ tri-capped trigonal prism, the $M2O_6X$ irregular polyhedron (where X is an anion, F, OH, or Cl), and the TO_4 tetrahedron (Fig. 2); the X anions are located in columns along the $[0,0,z]$ edges of the unit cell. In the Ca phosphate apatites, $M1 = M2 = Ca$, and $T = P$, but the three sites can be occupied by a great variety of substituents, leading to the minerals of the apatite supergroup. The apatite supergroup of minerals has the largest number of mineral constituents of any mineral group except the amphiboles, the micas, and the zeolites, illustrating the remarkable ability of the apatite atomic arrangement to incorporate substituent elements.

The extensive cation substitutions in the M1, M2, and T sites in the apatite atomic arrangement are treated thoroughly by Pan and Fleet (2002). Those authors detail the cation substitutions that lead to the incorporation of more than half of the long-lived elements in the periodic chart being incorporated in the apatite supergroup minerals (Hughes and Rakovan 2015). Because of the need for organization of the large number of apatite species, the International Mineralogical Association Commission on New Minerals and Mineral Nomenclature recently revised the nomenclature of apatite-supergroup species (Pasero et al. 2010) based on cation type and site preference. That report defined over forty apatite species in five distinct apatite groups

of the apatite supergroup of minerals, demonstrating the remarkably accommodating nature of the apatite atomic arrangement.

Although the apatite structure can accommodate a large variety of cations in its three cation sites, of particular interest and focus of this work is the accommodation of anions in the apatite $[0,0,z]$ anion columns. Apatite is one of the more rare minerals that forms an *anion* solid solution, with the Ca phosphate apatites forming solid solutions among fluorapatite ($X = F$), hydroxylapatite ($X = OH$), and chlorapatite ($X = Cl$). Because of the disparate size of the three column anions, and steric interactions between and among those anions in the anion columns, anion solid solution in the apatite atomic arrangement is particularly complex.

In the $P6_3/m$ apatite unit cell, there are $\{0,0,\ell\}$ mirror planes at $z = 1/4, 3/4$, and the $[0,0,z]$ F, OH and Cl anions are located either in the plane of those mirror planes or in half-occupied sites disposed on either side of those mirror planes. In fluorapatite, the F anion is of ideal size to occur within the mirror planes, at sites $(0,0, 1/4)$ and $(0,0, 3/4)$, located in the center of a triangle of Ca₂ atoms coplanar within the mirror plane (Fig. 3). In hexagonal hydroxylapatite, the slightly larger OH is split into two half-occupied sites approximately 0.35 Å above or below the mirror plane; at each mirror plane that contains a OH *either* one of the sites is occupied. In hexagonal chlorapatite, the much larger Cl atom is displaced approximately 1.3 Å above or below the mirror plane, leading to two half-occupied Cl sites. The five possible anion sites associated with any mirror plane (F, 2 x OH, 2 x Cl) are illustrated in Figure 3. It has been shown that, with no impurities or vacancies in the anion columns, both hydroxylapatite and chlorapatite will form monoclinic, $P2_1/b$ variants with ordered occupants in each column, either above or below the plane, with adjacent columns being ordered in the opposite sense (Hounslow and Chou 1970;

Elliot et al. 1973). However, with less than 10% impurities or vacancies, reversal of any anion column is effected, yielding $P6_3/m$ symmetry and disordered anion columns.

In hexagonal end-member apatites, the three column anions assume different positions in the $[0,0,z]$ anion columns of their respective members. However, Hughes et al. (1989) demonstrated that the anion positions in binary and ternary (F, OH, Cl) apatites cannot be predicted from their positions in the end-members, as interactions between the anions yield steric constraints that prohibit coexistence of column anions in their end-member positions. Figure 4 illustrates that conundrum, depicting a Cl atom disordered *below* the plane at $z = 3/4$, and its five possible adjacent neighbors at the mirror plane at $z = 1/4$, based on their positions in the end-members. The distance between that Cl atom at $z = 3/4$ and the Cl disordered above the adjacent plane (0.92\AA), the OH disordered above that plane (1.81\AA), the F atom at $(0,0, 1/4)$ (2.11\AA) and the OH disordered below the $z = 1/4$ plane (2.52\AA) are all too short to exist as neighbors in the anion column. The only possible neighbor at that plane, *ad infinitum*, is another Cl disordered below its associated plane, at a distance of $c/2$, or $\sim 3.4\text{\AA}$, demonstrating that the anion positions in the end-member Ca phosphate apatites are incompatible in solid solution.

Hughes et al. (1990) examined two natural ternary apatites in order to determine the method of accommodation of all three anions in the apatite anion column in ternary solution. In a high-temperature, volcanic apatite, they found that solid solution is attained by addition of a second Cl site, termed Cl_b , that relaxes toward its associated mirror plane, increasing the distance between an adjacent OH to an acceptable 2.95\AA and allowing a reversal of the anion sequence in any individual column, thus maintaining the $P6_3/m$ symmetry over the crystal as a whole (Fig. 5). They also found, in a low-temperature apatite, that solid solution can also be achieved by symmetry reduction to monoclinic, with a $P2_1/b$ ordered structure of the anion column. Although

it is not commonly determined, it may be that many low-temperature ternary apatites are indeed monoclinic; researchers are cautioned not to assume the putative hexagonal symmetry in natural apatites, particularly those formed at low temperatures.

Similar to the complexities seen in ternary apatites, the anion arrangements in the anion columns of the three binary systems of the (F, OH, Cl) apatite system are not predictable from the anion positions in the three end-member apatites. For any combination of anion occupants, the positions of anions are affected by several factors, including the size of the resident anions, the specific anion nearest-neighbors and the electrostatic repulsions from those neighbors, the electrostatic attractions to the surrounding Ca₂ atoms, any dissymmetrization that occurs, and, in hydroxyl-bearing apatite, the hydrogen bonding that occurs between the OH hydrogen and neighboring column anions. Taken together, these factors will yield the position of any individual occupant in the anion column.

Figure 6 displays the sequence of F and Cl atoms in the Ca phosphate F-Cl binary, and shows the hypothetical placement of anions in anion positions from the fluorapatite and chlorapatite end-members that would allow the maximum distance between F and Cl, and also allow reversal of the anion column to attain the observed $P6_3/m$ symmetry. Clearly, the anions in that sequence are incompatible due to the impossibly short F-Cl distance of 2.12Å. Using carefully synthesized material, Hughes et al. (2014a) extended the earlier prescient work of Mackie and Young (1974), and demonstrated that solid solution in the hexagonal F-Cl apatite binary is achieved by addition of a new, off-mirror-plane F site at $\sim(0,0,0.17)$ that allows sufficient distance between anion column occupants, thus overcoming the steric constraints in the mixed anion column (Fig. 7). Subsequently, a natural fluor-chlorapatite that is essentially

devoid of OH was found, and the structural accommodation of F and Cl in the anion column was also confirmed in natural material (Hughes et al. 2014b).

Similar conundrums exist in the atomic arrangement of the anion occupants in the other binary systems in the (F, OH, Cl) apatite system. In the fluorapatite-hydroxylapatite binary, particularly germane to dental apatite because of the fluoridation of human teeth in approximately 2/3 of the U.S. population, Young et al. (1969) demonstrated using NMR spectroscopy that two distinct environments exist for F ions in the anion column of fluor-hydroxylapatite (Fig. 8). Fluorine occupants can gain hydrogen bonding from one or two OH neighbors in the anion column; if there is one OH neighbor, the asymmetric steric environment shifts the F atom $\sim 0.10\text{\AA}$ off the mirror plane, whereas with two nearest neighbors the symmetric hydrogen bonding keeps the F atom fixed at the “normal” (0,0,1/4) F position. In either position, the F atom gains additional bonding from the neighboring hydrogen atom(s), and the additional bond valence “secures” the F atom in the anion column. Young et al. noted that diffusion of OH ions along the [0,0,z] anion column is inhibited by the presence of the hydrogen-bonded F atoms, diffusion that is necessary for dissolution of the apatite that is attendant with enamel caries.

In the final binary system in the F-OH-Cl apatite ternary system, the OH-Cl binary, steric constraints also exist that make the atomic arrangement of the anion column unpredictable from the anion positions in the hydroxylapatite and chlorapatite end-members. Garcia-Tunon et al. (2012) undertook a study on OH-substituted chlorapatite, and their results suggested that the OH's occupied two separate sites, the site normally associated with a OH in hydroxylapatite as well as the site normally associated with F in fluorapatite, at (0,0,1/4). However, their study did not provide detailed structural information for the samples, and a sequence of anion sites that allowed the reversal of the anion column occupants in the $P6_3/m$ apatite was not elucidated or

apparent. Experiments by this author are being undertaken to elucidate the anion sequence in hydroxyl-chlorapatite, and preliminary results suggest that hydrogen bonding between hydroxyls and Cl atoms is important in effecting the anion sequence in that binary member of the F-OH-Cl apatite system.

Summary

Apatite is one of over 4,000 naturally occurring compounds on Earth. In the past 150 years, humankind's increased ability to extract minerals such as apatite from the Earth, and the technological advancements that have allowed its use in various products, have altered Society in a way that has never been seen in the 4.6 billion year history of the Earth. Because of apatite's essential use in the production of fertilizers and humankind's newfound ability to extract the mineral in large quantities, the agricultural production on Earth has risen to allow unprecedented growth in human population, an occurrence that must be reconciled with the diminishing supply of apatite-derived P, diminishing on a human timescale.

This link between a mineral and human society that is illustrated by apatite is not unique to that phase, but the link does serve to underscore the fundamental importance of minerals in the evolution of humankind. It is imperative that we continue to support and undertake all aspects of research in the broad area of mineral sciences, as the link between minerals and the health and well-being of humankind is inextricable.

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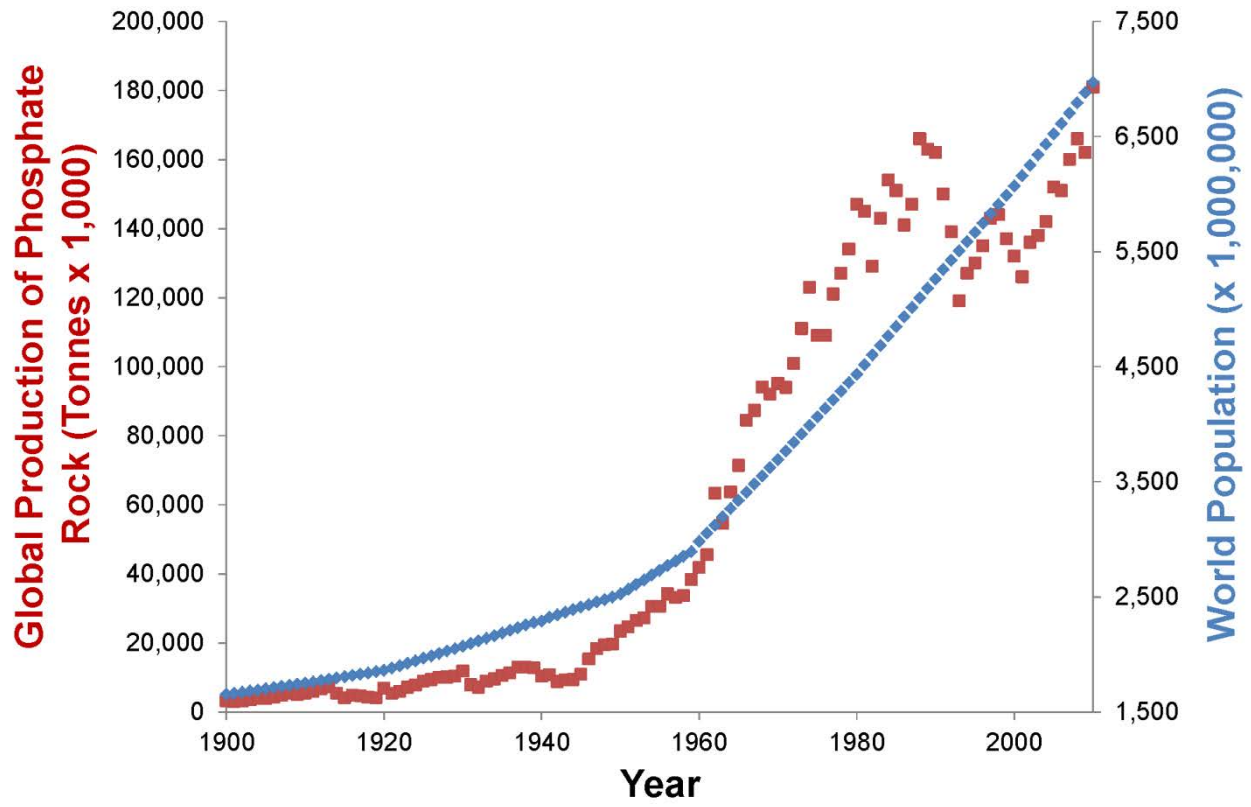


Figure 1. Global production of Phosphate Rock and estimated world population.

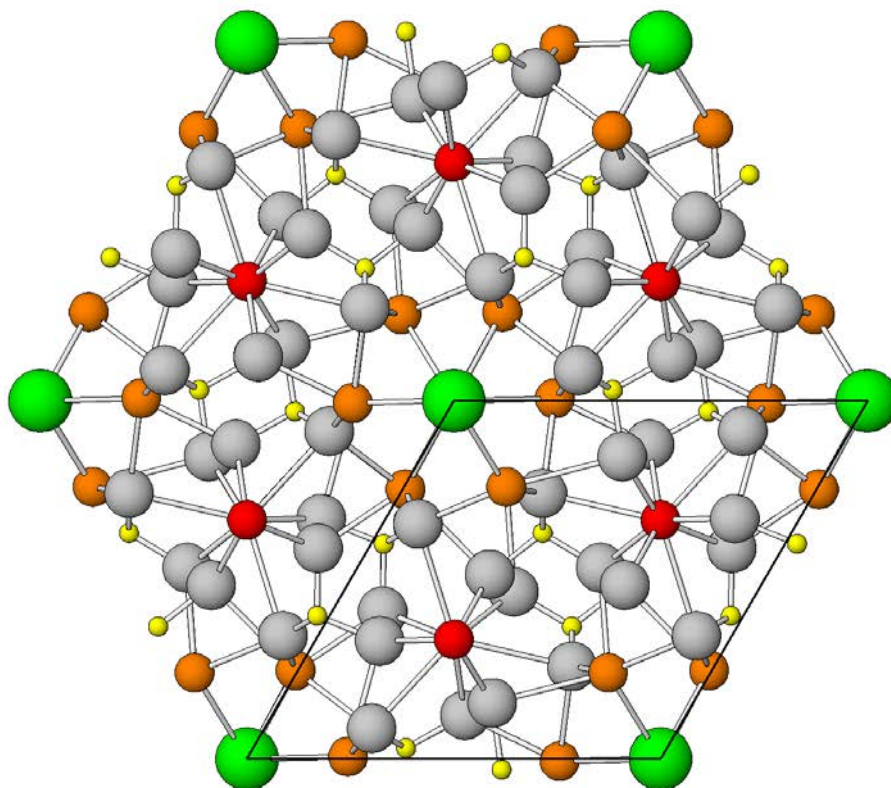


Figure 2. The atomic arrangement of Ca phosphate apatite projected on (001). Red atoms are Ca1, orange atoms are Ca2, yellow is P, gray is O, and the green atoms at the corners of the unit cell represent the $[0,0,z]$ projection of the F-OH-Cl anion columns.

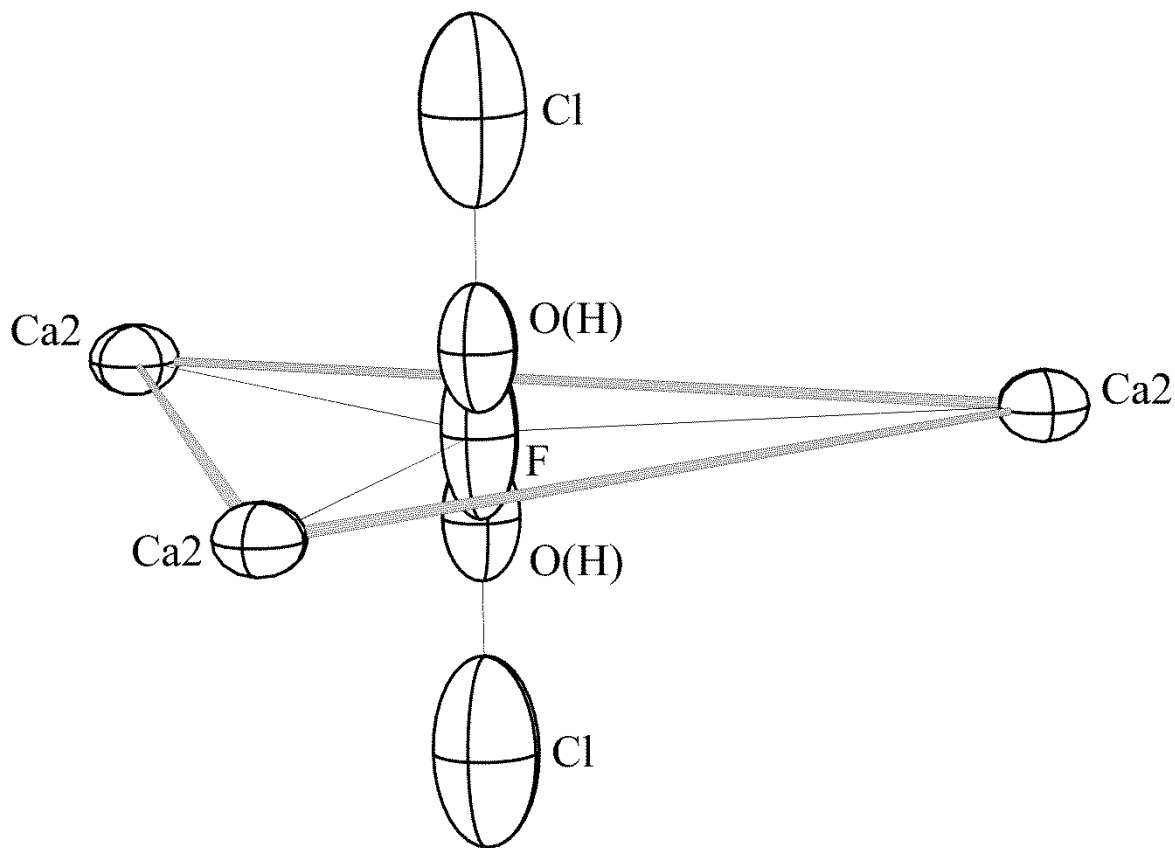


Figure 3. Depiction of Ca2 triangle in (0,0,1/4) and (0,0,3/4) mirror planes in $P6_3/m$ apatite. Cl, O(H), and F atoms represent possible anion positions at each mirror plane, only one of which will be occupied; Ca2 and F atoms are coplanar within the plane. From Hughes et al. (2014a).

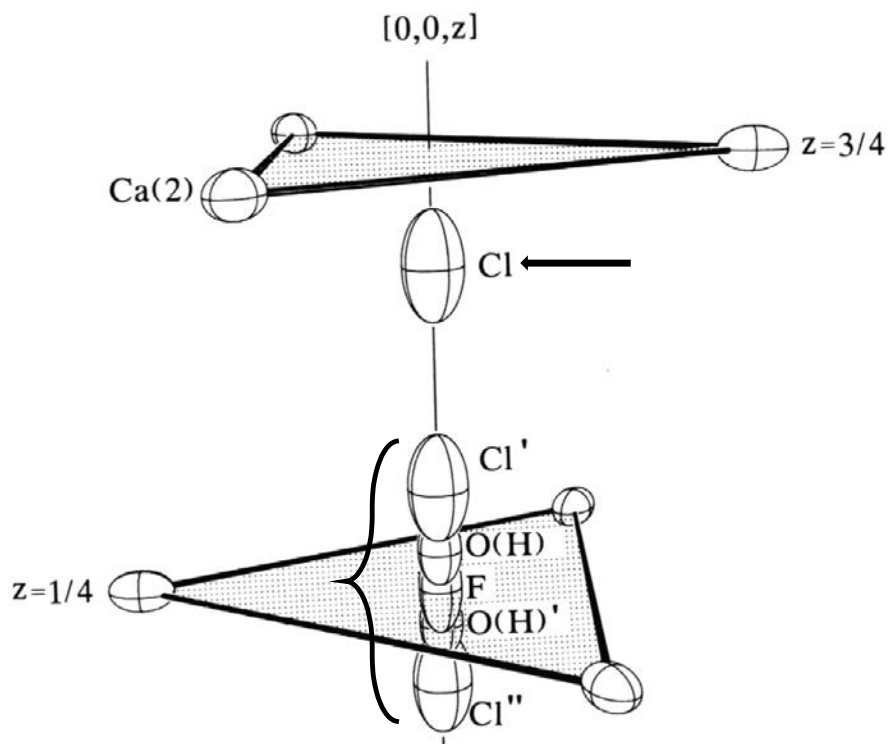


Figure 4. Depiction of possible anion positions in $P6_3/m$ apatite anion column. Atom at mirror plane at $z = 3/4$ is Cl atom (arrow) disordered below the mirror plane (stippled), and the five possible anion positions at mirror plane at $z = 1/4$ are depicted. Distances between the Cl anion disordered below $z = 3/4$ plane and the five possible neighbors associated with the $z = 1/4$ plane are given in text.

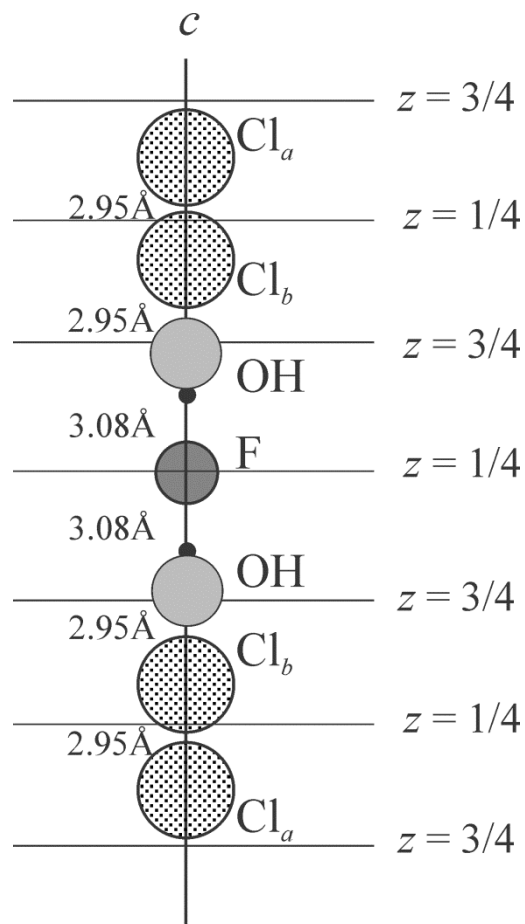


Figure 5. Sequence of anions in ternary F-OH-Cl apatite. Atom Cl_b relaxes toward its mirror plane to accommodate an adjacent OH, allowing reversal of the anion column. From Hughes et al. (2014a).

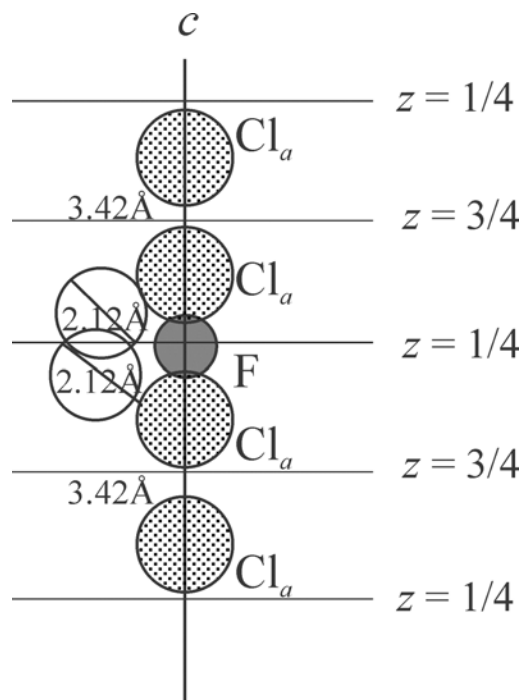


Figure 6. Depiction of anion column in fluor-chlorapatite with anion positions derived from positions in end-member fluorapatite and chlorapatite. Anions are placed to maximize the distance between Cl and F atoms and allow reversal of the anion column to retain $P6_3/m$ symmetry; the Cl-F distance is an impossibly short 2.12 \AA . Modified from Hughes et al. (2014b).

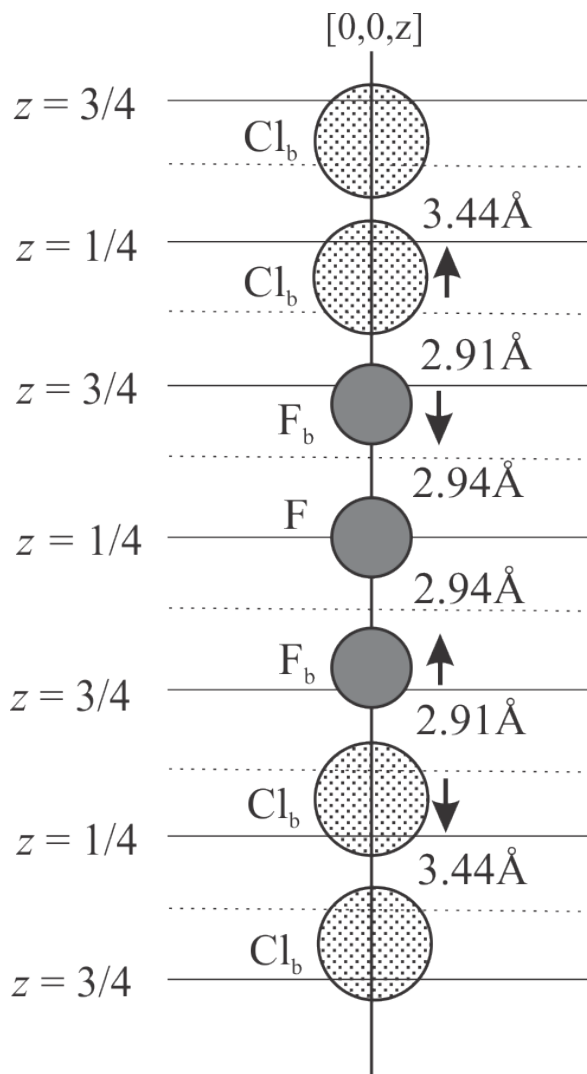


Figure 7. Depiction of anion column in fluor-chlorapatite. The F_b atoms move away from their associated mirror plane, as indicated by the arrows, and the Cl_b atom moves toward its associated plane (relative to its position in chlorapatite) to allow an acceptable F-Cl distance between F_b and Cl_b . The sequence depicted here can be capped on either end with one or more Cl atoms at $(0,0,0)$ or $(0,0,1/2)$, and the sequence can be repeated. Modified from Hughes et al. (2014b).

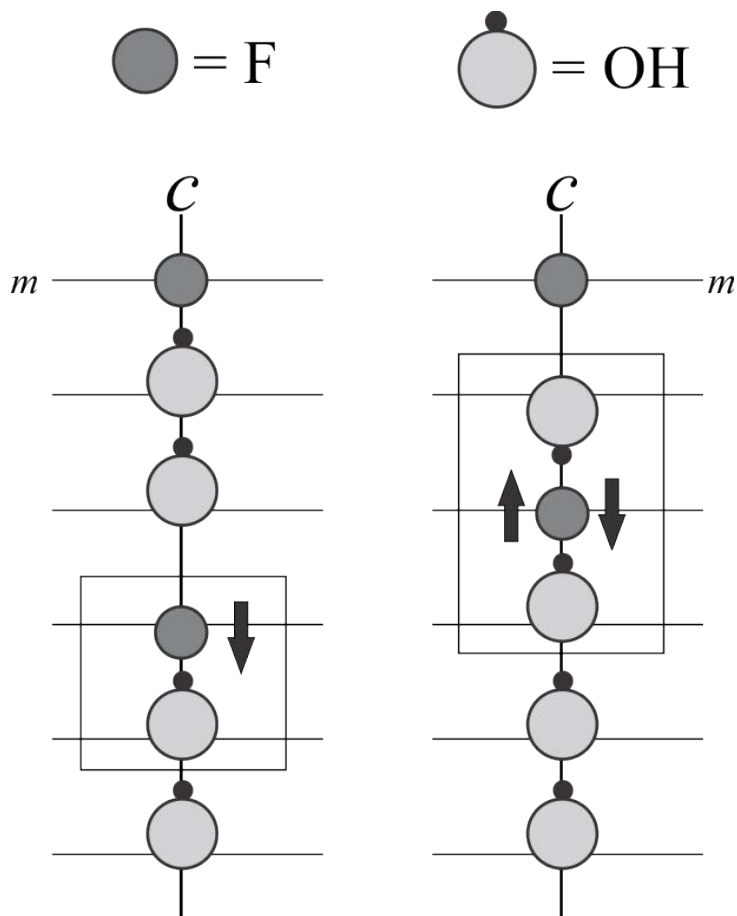


Figure 8. Two environments for F atom in fluor-hydroxylapatite. Box on left depicts asymmetric hydrogen bonding, which leads to 0.1Å displacement from mirror plane. Box on right depicts symmetric hydrogen bonding wherein F has two nearest neighbor hydrogen atoms. Mirror planes are at $z = \frac{1}{4}$ and $\frac{3}{4}$ in each unit cell.