Structurally Robust, Chemically Diverse: Apatite and Apatite Supergroup Minerals
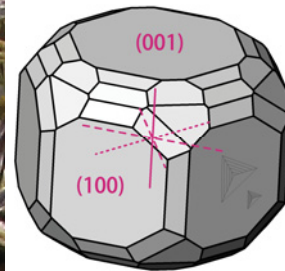
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Apatite is ubiquitous in igneous, metamorphic, and sedimentary rocks and is significant to more fields of study than perhaps any other mineral. To help understand why, one needs to know apatite's structure, composition, and crystal chemistry. Apatite has a robust hexagonal atomic framework based on two distinct metal-cation sites (*M*1, *M*2), a tetrahedral-cation site (*T*), and an anion column along four edges of the unit cell. These cation and anion sites can, among them, incorporate more than half of the long-lived elements in the periodic table, giving rise to the "apatite supergroup," which contains over 40 mineral species. The structure and composition impart properties that can be technologically, medically, and geologically very useful.

KEYWORDS: apatite structure, fluorapatite, chlorapatite, hydroxylapatite, apatite supergroup

WHAT IS APATITE?

Apatite, in the strictest sense, is not a single mineral. The "apatite" most familiar to geologists is really a subgroup within the apatite group within the apatite supergroup (TABLE 1). The apatite group of minerals share a common atomic arrangement (FIG. 1) as do all of the supergroup minerals, in which there is a dominant element—Ca, Pb, Sr, Ba, or Mn—in two of the cation sites, and P, V, or As in a third cation site. Most common among these minerals are the calcium phosphate apatites, the specific species of which vary in the occupancy of another structural site that can accommodate F (forming fluorapatite), Cl (forming chlorapatite) and OH (forming hydroxylapatite). Commonly, these three species, and solid solutions among them, are referred to simply as "apatite" (especially when the exact composition of a sample is unknown). Other species in the apatite group do not share the same root name, for example pyromorphite. The apatite structure can accommodate many other substituents, and this leads to over forty known mineral species collectively called the apatite supergroup, which is described later in this article. In this issue of *Elements*, unless otherwise stated, the name "apatite" will refer to the three calcium phosphate apatites with the general formula, $Ca_5(PO_4)_3(F,Cl,OH)$.

WHY IS APATITE IMPORTANT TO US?

The atomic arrangement of apatite and its variable chemical composition yield properties that have resulted in applications to more fields of study than probably any other mineral: agronomy, mineralogy, petrology, economic geology, biology, medicine, dentistry, geochronology, environmental remediation, and materials science (Elliott 1994; Kohn et al. 2002; and other articles in this issue). Apatite is the most abundant phosphate mineral on Earth; it forms the foundation of the global phosphorus cycle (Filippelli 2002, 2008), and it is the most abundant ore of phosphorus. Apatite is stable in, and can form under, a wide variety of conditions ranging from the Earth's surface to the lithospheric mantle (O'Reilly and Griffin 2013). Apatite is geologically ubiquitous: it forms in igneous, metamorphic, sedimentary, and hydrothermal environments. Although normally a minor phase, apatite can become an important rock-forming mineral in sedimentary phosphorites and in igneous apatite–magnetite cumulate deposits (Martin and Rakovan 2013; Harlov 2015 this issue). In addition, human teeth, bone (though not the small bones of the inner ear, which are composed of vaterite, a rare polymorph of $CaCO_3$), some urinary calculi, and arterial plaque are formed from apatite (specifically hydroxylapatite), indicating a remarkable link between the inorganic and organic genesis of the mineral. Along with calcite and aragonite, apatite is among the most common biominerals on Earth and forms the endoskeleton for a variety of species.

These remarkable characteristics and uses of apatite arise from the arrangement of atoms in the apatite structure. Understanding this structure is key to the successful use of apatite in its myriad applications, now and in the future.

THE STRUCTURE AND ANION CRYSTAL CHEMISTRY OF APATITE

Structure

Apatites are (predominantly) hexagonal, a = 9.4–9.6 Å, c = 6.8–6.9 Å, with a space group symmetry of $P6_3/m$. In that space group there are two {00l} mirror planes perpendicular to the 6_3 screw axis, located at z = ¼ and ¾. In the apatite structure there are three cation sites (FIG. 1). The tetrahedral site (*T* site) is a PO_4 tetrahedron with a P–O distance of ~1.53 Å; there are six tetrahedra per unit cell.

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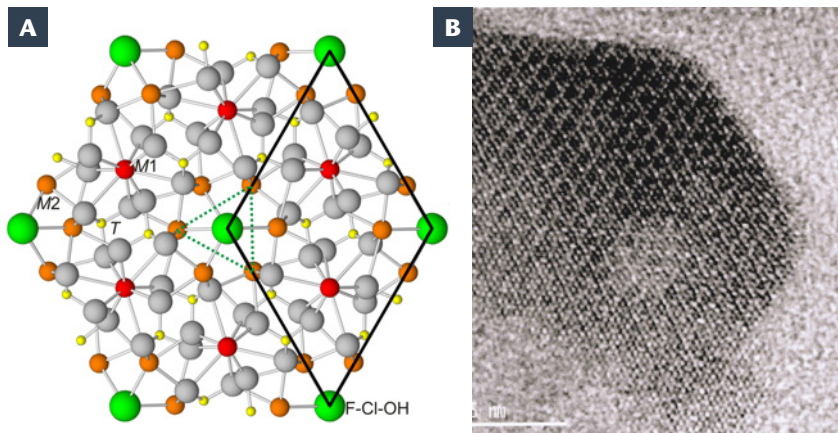   E-mail: rakovajf@miamioh.edu

FIGURE 1 (**A**) Apatite atomic arrangement projected down the *c* axis with the unit cell in black. Green ions at corners of unit-cell are those in the F–Cl–OH column. The *M*1 (Ca1) sites are in red; *M*2 (Ca2) sites are in orange; *T* (P) sites are in yellow. IMAGE AFTER HUGHES (2015). (**B**) High-resolution transmission electron photomicrograph of apatite looking down the *c* axis. The external crystal morphology and structural repeat seen in the image both reflect the hexagonal symmetry of the apatite atomic structure. MARK KREKELER IMAGE.

The *M*1 site (*M* = metal; also called Ca1 site for the calcium apatites) is a CaO_9 tricapped-trigonal prism (FIG. 2A); there are four *M*1 sites per unit cell. The *M*2 site (or Ca2 site for the calcium apatites) is an irregular CaO_6X_1 polyhedron, where X = F, Cl, and OH (FIG. 2B); there are six *M*2 sites per unit cell. Thus, in the reduced chemical formula, which has a stoichiometry of half the unit cell contents (i.e. Z = 2), two of the five *M* sites are *M*1 and three are *M*2. This helps in better understanding how the chemical formula relates to the structure of the entire range of mineral formulas for the apatite supergroup (see TABLE 1). The F, Cl, and OH anions exist in [0,0,*z*] columns along the edges of the unit cell (FIG. 1). Collectively, F, Cl, and OH are termed "column anions."

Anion Solid Solution and Symmetry

The calcium phosphate apatite minerals form one of the rarer examples of a mineral group with *anion* solid solutions. The *M*2 (Ca2) atomic site is of particular interest in the apatite atomic arrangement because it helps accommodate the three different column anions (F, Cl, OH), which differ significantly in size. Whereas there is little structural response to anion substitutions in the other cation sites (*M*1 and *T*) (Hughes et al. 1989), there are dramatic differences in the spatial environment of the *M*2 (Ca2) polyhedra in fluorapatite, chlorapatite, and hydroxylapatite. Three *M*2 (Ca2) cations exist in a triangle surrounding each anion column. An *M*2 (Ca2) triangle exists in each of the mirror planes in the unit cell. In fluorapatite an F anion easily fits at the center of the *M*2 (Ca2) triangle and is coplanar with the three *M*2 (Ca2) cations. In contrast, in chlorapatite and hydroxylapatite, the Cl and OH anions are too large to fit in the center of the triangle, forcing the Cl or OH to be displaced below *or* above the triangle (~1.3 Å for Cl; ~0.35 Å for OH). If the anion moves above the mirror plane, the site below the mirror will remain vacant and vice versa.

The local mirror symmetry is attained only in fluorapatite, yielding the expected hexagonal $P6_3/m$ symmetry. In pure hydroxylapatite and chlorapatite, with no substituents in the anion column, all the OH or Cl anions in one column will be ordered above the plane, and all the anions in an adjacent column are ordered below the plane. This destroys the mirror symmetry, yielding monoclinic $P2_1/b$ symmetry (Hounslow and Chao 1970; Elliott et al. 1973). However, over the crystal as a whole, an average $P6_3/m$ symmetry can exist in impure hydroxylapatite and chlorapatite. This is because OH and Cl occupy only half the sites available on both sides of the mirror planes. This average symmetry, however, occurs if there are sufficient "impurities" in the anion column to allow a reversal of the order of anions within a column (i.e. anions above the plane or below the plane). Less than 10% substitution of other column anions (e.g. F) or vacancies is sufficient to destroy this ordering and yield a disordered, hexagonal $P6_3/m$ symmetry.

Unlike many cation solid solutions, the atomic arrangement in the mixed-anion apatites cannot be predicted from the positions in the individual end-members. Steric interactions among the different anion species in the binary or ternary anion column force the structure to create new anion positions that are not seen in end-members; this then provides the adequate anion–anion distances in the anion column (Hughes et al. 1989). For example, the typical end-member positions of the three anions in the ternary apatites, with essentially equal amounts of F, Cl, and OH, cannot exist because of short anion–anion distances. However, anion solid solution in ternary apatite can be attained in two ways. First, by creating a new Cl site that relaxes ~0.4 Å toward its associated mirror plane, allowing for an adjacent OH and reversal of the sense of ordering of the anions above or below the mirrors in the column. Second, by crystallizing in a $P2_1/b$ monoclinic form with ordered anion columns, which might be a common phase in low-temperature, metamorphic apatites (Hughes et al. 1990). The conundrum of anion mixing also exists for the apatite binaries F–Cl, F–OH, and Cl–OH , and represents a fruitful area for further research (Hughes et al. 1989, 2015).
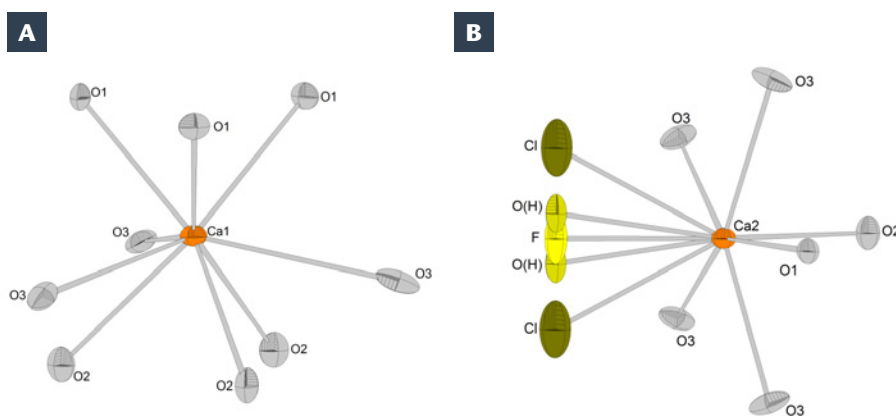
FIGURE 2 The two types of metal cation sites (*M*1 and *M*2) in the apatite structure, here both filled with Ca. (**A**) Ca1 (*M*1) polyhedra. (**B**) Ca2 (*M*2) polyhedra. Each Ca2 cation bonds to six oxygen anions and one of the column anions (F, Cl, OH). The O1, O2, Ca2 and F all reside within one of the {00l} mirror planes in the $P6_3/m$ apatite structure.

Understanding the nature of these anion substitutions is more than an academic exercise. It is essential for making use of apatite to determine the volatile (F, Cl, water as OH) behavior and budgets in melts and related fluids. The use of apatite as a recorder of volatile behavior is being applied to rock-forming systems on Earth and to extraterrestrial bodies, such as the Moon and Mars (see articles in this issue by Harlov 2015, Webster and Piccoli 2015, and McCubbin and Jones 2015). Anion substitution is also why we brush our teeth with fluoridated toothpaste. Hydroxylapatite in the enamel of our teeth is more soluble (i.e. less stable) in acids created by bacteria in our mouths than is fluorapatite. Over time fluorine from the toothpaste slowly replaces OH in the enamel, thus making our teeth more resistant to decay.

A Cornucopia of Substitutions

The complexity of the anion column in apatite is mirrored in the cation composition and crystal chemistry (Pan and Fleet 2002). More than half the elements that occur as long-lived isotopes on Earth can be incorporated in the apatite structure (Fig. 3). This is in large part due to the variety of cation sites, i.e. a regular tetrahedron and two disparate M polyhedra. The remarkably robust nature of the atomic arrangement allows many compounds to adopt the apatite structure. The two distinct M polyhedra ($M1$ and $M2$) provide substitution sites for many divalent cations—Sr, Ba, Pb, Cd, Mg, Fe, Mn, Co, Ni, Cu, Zn, and Sn (see Table 1 for minerals formed from these elements). In most cases, there is significant site preference by the substituents, indicating the different steric environments afforded by the two sites: Sr strongly prefers the $M2$ site (Rakovan and Hughes 2000), whereas Mn strongly prefers the $M1$ site (Hughes et al. 1991a).

Trivalent ions can also substitute in the $M1$ and $M2$ sites. However, substituting a trivalent cation for divalent calcium must be coupled with another substitution to maintain charge balance. Hughes et al. (1991b) documented the extensive substitution of rare earth elements (REEs) in apatite, reporting the structures of four REE-enriched apatites with up to 25 wt% REE_2O_3. They demonstrated that charge balance is maintained by two coupled substitutions: $Na^+ + REE^{3+} \leftrightarrow 2Ca^{2+}$ and $Si^{4+} + REE^{3+} \leftrightarrow P^{5+} + Ca^{2+}$. Among the REEs, the light REEs prefer the $M2$ site, whereas the heavy REEs prefer the $M1$ site. The REEs near Nd in their ionic radii exhibit no site preference. Tetravalent substituents do show site preferences, for example Luo et al. (2009) reported partial segregation of U^{+4} and Th^{+4} among the M sites in calcium phosphate apatite.

Because of this cornucopia of cation substitutions, the presence (or absence) of apatite can strongly influence the minor and trace element composition of rocks in which it is contained. Apatite is one of the most important minerals affecting REE behavior in geological systems. The concentration of REEs in apatite can be so significant that apatite can become an ore of these elements. Trace elements, such as the REEs, often hold the key to the origin of a magma or fluid and the geochemical processes that they have undergone. Thus, apatite composition plays a critical role in the understanding and modeling of petrogenetic processes (Piccoli and Candela 2002; Spear and Pyle 2002; Harlov 2015; Webster and Piccoli 2015). By applying knowledge of the mechanisms and magnitude of cation substitutions found in natural apatites, scientists can manipulate structure–composition relationships in synthetic analogs and tailor their physical properties to suit different technological applications, such as lasers or bone prosthetics.

The distribution of substituents, particularly trace and minor elements, can be heterogeneous (zoned) within an apatite crystal (Fig. 4). Compositional zoning can take many forms, including concentric, oscillatory, sectoral, and intrasectoral (Rakovan 2002). Compositional zonation can provide a wealth of information about the environment that the crystal was in during its growth, including how that environment changed with time. Zonation also provides information about crystal growth, such as what controls the crystal's morphology, the differential rates of face advancement, the different growth mechanisms operating on different crystal faces, the evolution of surface microtopography (e.g. presence and location of growth hillocks, steps, etc.), and the differences in the atomic structure at the crystal's surface. All of the zoning types hold clues to the mechanisms and history of mineral and rock formation, as well as post growth alteration. Thus, elucidation and understanding of compositional zoning in apatite are essential for the correct interpretation of petrogenesis (Webster and Piccoli 2015).

Figure 3 Elements (in red) that occur in apatite supergroup minerals in amounts ranging from ppm to tens of weight percent. Derived from Pan and Fleet (2002)
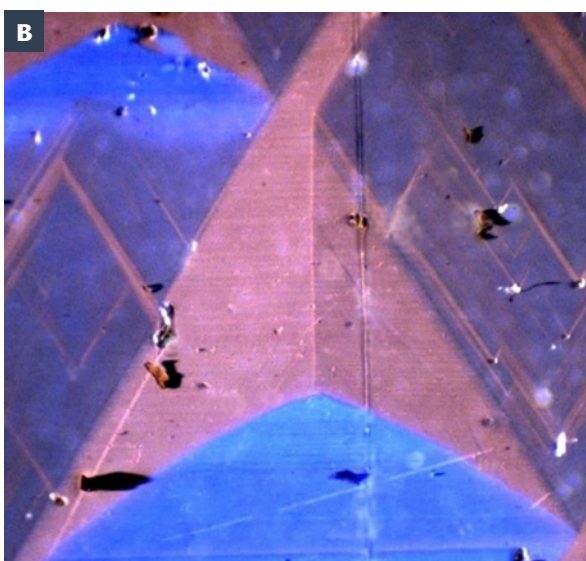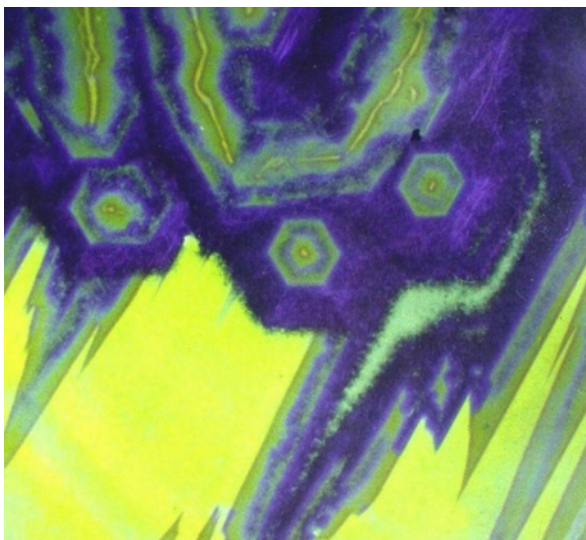
APATITE SUPERGROUP MINERALS: THE ROBUST NATURE OF THE APATITE ATOMIC ARRANGEMENT

Although many elements can occur as substituents in apatite, many other naturally occurring compounds assume the apatite atomic arrangement, but with different compositions. Indeed, because it can incorporate more than half of the long-lived elements in the periodic chart, the apatite atomic arrangement must be considered as one of the most robust mineral structures in nature. After the amphiboles, micas, and zeolites, the apatite supergroup contains more distinct species than any other mineral supergroup. TABLE 1 lists the minerals and formulae of the apatite supergroup and is divided into five crystal-chemical groups (Back 2014).

In apatite supergroup minerals, the $M1$ and $M2$ sites can be occupied by stoichiometric amounts of Ca, Sr, Pb, Ba, Mn, Na, Bi, and REE; the tetrahedral site (T site) can be occupied by P, As, V, S, Si, and B; and the anion column can be filled by F, Cl, OH, and O. Minor and trace amounts of many other elements can also be incorporated. An even larger group of synthetic apatite compounds, with an even wider variety of chemical constituents, have been created (Pan and Fleet 2002), further attesting to the robust structure of "apatite."

The majority of apatite supergroup minerals are hexagonal. However, trigonal and monoclinic pseudohexagonal subsymmetries also exist. Monoclinic apatite occurs from the ordering of the column anions in the hydroxylapatite and chlorapatite monoclinic endmembers (hydroxylapatite-M and chlorapatite-M, respectively). Such symmetry lowering has also been observed in ternary (F, Cl, OH) calcium phosphate apatites (Hughes et al. 1990). In other apatite supergroup minerals, symmetry lowering results from cation ordering, such as in the britholite group of minerals, where ordering of the REE cations in the $M2$ site yields pseudohexagonal monoclinic symmetry (Noe et al. 1993). In hydroxylellestadite, the ordering of the two tetrahedral-site species (Si, S) also reduces the hexagonal symmetry to a pseudohexagonal, monoclinic symmetry (Hughes and Drexler 1991).

In a unique type of symmetry reduction, Dai et al. (1991) demonstrated that the symmetry in mimetite-M is monoclinic because the Pb^{2+} lone-pair electrons become stereoactive at ~110°C, and the lone-pair–bond-pair interactions cause the symmetry reduction. One of the most sensitive indicators of symmetry reduction is the optical behavior of a mineral. Even in cases where X-ray diffraction methods are unable to "see" symmetry lowering (dissymetrization), the optical properties may clearly reflect it. Two examples are hydrothermal fluorapatites from the Llallagua tin deposit in Bolivia and the Ashio copper deposit in Japan. Both are optically anomalous and exhibit domains of lower-than-hexagonal symmetry with different optical orientation and behavior (e.g. varying nonzero values of $2V$). These domains correlate directly with sectors and subsectors of the crystals, indicating dissymetrization during growth as a result of differential surface reactivity (Rakovan 2002). The origin of these anomalies is unknown, but selective ordering among structurally different sites on the crystal surface may have occurred during growth, indicating surface-structure control on the reactivity of apatite.

Nomenclature

The large number of apatite supergroup mineral species and the confusion regarding their nomenclature led to a detailed revision of that nomenclature (Pasero et al. 2010).

Carbonate (CO_3^{2-}): An Unexpected but Important Substituent

Because of its significant effects on the physical and chemical properties of apatite, such as solubility, one substitution that is of particular interest in biological apatites is that of carbonate (CO_3^{2-}) (Fleet 2014). Apatite solubility is directly related to the body's ability to build and retain healthy bones and teeth. The carbonate ion can substitute in two places in the apatite structure, with radically different substitution geometries. In the *A-type* substitution, the carbonate ion is located in the anion column (Fleet et al. 2004). In the *B-type* substitution, the carbonate ion can substitute for the phosphate ion at the T site. In this case, the trigonal-planar carbonate ion roughly occupies the same position as one of the triangular faces of the tetrahedral site. However, some of the structural details and mechanisms of charge balance are still poorly constrained and debated. Further work is needed.

Currently, the apatite supergroup of minerals is divided into five groups on the basis of chemical composition (TABLE 1). These groups illustrate the remarkably diverse chemical composition of apatite supergroup minerals. Here, we briefly summarize each of the five groups.

The *Apatite Group* (TABLE 1) is defined as having the same dominant element in the $M1$ and $M2$ sites, and having P, V, or As in the T site. Most common among these minerals are fluorapatite, chlorapatite, and hydroxylapatite ($M1 = M2 = $ Ca; $T = $ P). Particularly colorful representatives of this group include the lead-bearing apatites, mimetite [$Pb_5(AsO_4)_3Cl$], pyromorphite [$Pb_5(PO_4)_3Cl$], and vanadinite [$Pb_5(VO_4)_3Cl$], which are the staples of mineral displays in countless museums (FIG. 5).
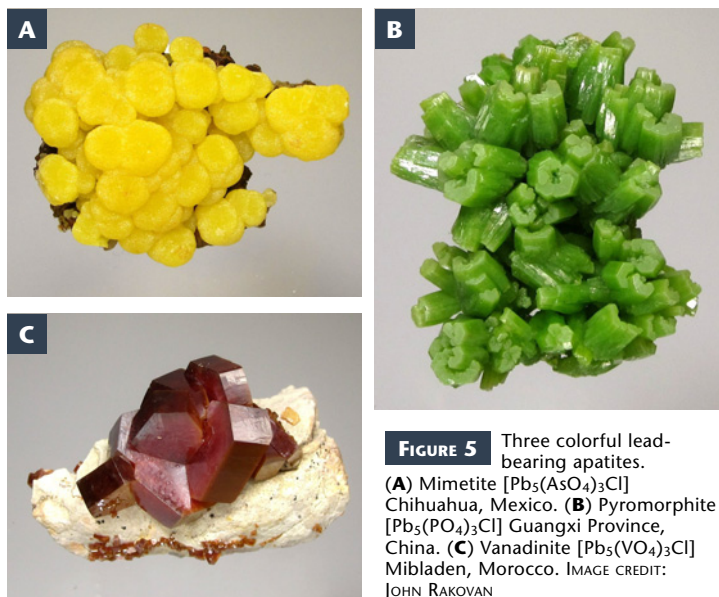
In the *Belovite Group* (TABLE 1), ordering of the cations causes the splitting of the four $M1$ cation sites in the unit cell into two sets of two symmetry-equivalent sites, the $M1$ and $M1'$ sites. Each of those sites contains different cations, as in belovite-(La) [$NaLaSr_3(PO_4)_3F$], in which the four $M1$ sites are split into the $M1$ site (Na) and $M1'$ site (La), and the $M2$ site is occupied solely by Sr.

Minerals of the *Britholite Group* (TABLE 1) are a group of silicates ($T = $ Si) that typically show only partial ordering of the $M1$ and $M2$ cations. Without exception, the Britholite Group of minerals contain stoichiometric REEs, but complete ordering of any element on the $M1$ or $M2$ site is not achieved.

In the *Ellestadite Group* (TABLE 1), the T site is occupied by three tetravalent cations (Si^{4+}) and three hexavalent cations (S^{6+}), yielding the requisite charge balance. In some cases, the ordering of these T-site cations can lead to the lowering of symmetry, as in monoclinic hydroxylellestadite (Hughes and Drexler 1991).

Finally, the *Hedyphane Group* (TABLE 1) is composed of phosphate, arsenate, and sulfate minerals in which the $M1$ and $M2$ sites are occupied by *different* atomic species. The group is typified by the eponymous arsenate mineral hedyphane, [$Ca_2Pb_3(AsO_4)_3Cl$] in which Ca occupies the $M1$ site and Pb is ordered into the $M2$ site. The site preferences for Ca and Pb in hedyphane, and for other cations in different hedyphane group minerals, arise from the differing steric environments that the $M1$ and $M2$ site afford for the resident cations.

| **TABLE 1** | IMA-ACCEPTED MINERALS OF THE APATITE SUPERGROUP WITH THEIR IDEAL END-MEMBER FORMULAE, SUBDIVIDED INTO FIVE GROUPS. AFTER BACK (2014) |

Approved Name	End-member Formula (reduced)
Apatite Group	
Alforsite	$Ba_5(PO_4)_3Cl$
Chlorapatite	$Ca_5(PO_4)_3Cl$
Fluorapatite	$Ca_5(PO_4)_3F$
Hydroxylapatite	$Ca_5(PO_4)_3OH$
Hydroxylapatite-*M*	$Ca_5(PO_4)_3OH$
Johnbaumite	$Ca_5(AsO_4)_3OH$
Johnbaumite-*M*	$Ca_5(AsO_4)_3OH$
Mimetite	$Pb_5(AsO_4)_3Cl$
Mimetite-*M*	$Pb_5(AsO_4)_3Cl$
Pieczkaite	$Mn_5(PO_4)_3Cl$
Pyromorphite	$Pb_5(PO_4)_3Cl$
Stronadelphite	$Sr_5(PO_4)_3F$
Svabite	$Ca_5(AsO_4)_3F$
Turneaureite	$Ca_5(AsO_4)_3Cl$
Vanadinite	$Pb_5(VO_4)_3Cl$
Belovite Group	
Belovite-(Ce)	$NaCeSr_3(PO_4)_3F$
Belovite-(La)	$NaLaSr_3(PO_4)_3F$
Carlgieseckeite-(Nd)	$NaNdCa_3(PO4)_3F$
Deloneite	$(Na_{0.5}REE_{0.25}Ca_{0.25})(Ca_{0.75}REE_{0.25})Sr_{1.5}(CaNa_{0.25}REE_{0.25})(PO_4)_3F_{0.5}(OH)_{0.5}$
Fluorcaphite	$SrCaCa_3(PO_4)_3F$
Fluorstrophite	$SrCaSr_3(PO_4)_3F$
Kuannersuite-(Ce)	$NaCeBa_3(PO_4)_3F_{0.5}Cl_{0.5}$
Britholite Group	
Britholite-(Ce)	$(Ce,Ca)_5(SiO_4)_3OH$
Britholite-(Y)	$(Y,Ca)_5(SiO_4)_3OH$
Fluorbritholite-(Ce)	$(Ce,Ca)_5(SiO_4)_3F$
Fluorbritholite-(Y)	$(Y,Ca)_5(SiO_4)_3F$
Fluorcalciobritholite	$(Ca,REE)_5(SiO_4,PO_4)_3F$
Melanocerite-(Ce)	$(Ce,Ca)_5(Si,B)_3O_{12}(OH,F)\cdot nH_2O?$
Tritomite-(Ce)	$Ce_5(SiO_4,BO_4)_3(OH,O)$
Tritomite-(Y)	$Y_5(SiO_4,BO_4)_3(O,OH,F)$
Ellestadite Group	
Chlorellestadite (doubtful)	$Ca_5(SiO_4)_{1.5}(SO_4)_{1.5}Cl$
Fluorellestadite	$Ca_5(SiO_4)_{1.5}(SO_4)_{1.5}F$
Hydroxylellestadite	$Ca_5(SiO_4)_{1.5}(SO_4)_{1.5}OH$
Mattheddleite	$Pb_5(SiO_4)_{1.5}(SO_4)_{1.5}Cl$
Hedyphane Group	
Aiolosite	$Na_2(Na_2Bi)(SO_4)_3Cl$
Caracolite	$Na_2(Pb_2Na)(SO_4)_3Cl$
Cesanite	$Ca_2Na_3(SO_4)_3OH$
Fluorphosphohedyphane	$Ca_2Pb_3(PO_4)_3F$
Hedyphane	$Ca_2Pb_3(AsO_4)_3Cl$
Miyahisaite	$(Sr,Ca)_2Ba_3(PO_4)_3F$
Morelandite	$Ca_2Ba_3(AsO_4)_3Cl$
Phosphohedyphane	$Ca_2Pb_3(PO_4)_3Cl$

FUTURE WORK

The apatite supergroup minerals, from the ubiquitous calcium phosphate apatites that are the framework of life itself, to the other members of the apatite supergroup that demonstrate remarkable compositional complexity and diversity, are among the most important minerals on Earth. Despite this importance, there is still much we do not understand about apatite in all its forms. We need to determine the fundamental thermodynamic properties of end-member apatite group minerals and the solid solutions among them, to understand the reactivity of apatite and other geochronometers in aqueous fluids that is essential for accurate evaluation of geochronologic data, and to elucidate the still poorly explored crystal chemistry of apatite with transuranic substituents other than U and Th. The transuranic elements, along with U, Th, and other radionuclides, may someday be disposed of in apatite coprecipitates or composites. Researchers are urged to investigate these and other areas of this structurally robust, chemically diverse, and most ubiquitous of minerals.

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