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Introduction to Apatites

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Abstract

Apatite is the generic name, which was first introduced by German geologist A.G. Werner. These minerals and their synthetic analogs represent a major class of ionic compounds and the most common crystalline form of calcium phosphates, which are of interest of many industrial branches and scientific disciplines. Since, apatite (fluorapatite) is the most abundant phosphate mineral, apatite bearing phosphate rocks represents an important source of inorganic phosphorus. First chapter of this book introduces the basic concepts of nomenclature, composition, classification, crystal structure, mineralogy and properties of minerals from the supergroup of apatite. Furthermore, the minerals from the group of apatite and polysomatic apatites are described. Since, the most of the topics mentioned in this chapter will be developed in the following chapters, the key concepts provided in this chapter are important to understood before proceeding further.

Keywords: Apatite, Group of Apatite, Polysomatic Apatites, Fluorapatite, Hydroxylapatite, Chlorapatite, Vanadinite

The minerals¹ [1],[2],[3],[4],[5] from the apatite group² [6] are classified as hexagonal or pseudo-hexagonal monoclinic anhydrous phosphates containing hydroxyl or halogen of the generic formula³:

¹**Minerals** are individual components comprising rocks formed by geological processes classified according to their crystal structure and chemical composition. The total number of minerals accepted by mineralogical community is about 4000. **Mineraloids** are mineral-like phases including synthetic materials, human-treated substances, and some biological materials, which do not fulfill the criteria for the definition of mineral species [2]. **Anthropogenic substances** are not considered as minerals. If such substances are identical to minerals, they can be referred as the “synthetic equivalents” of given mineral. If the synthetic substance has a simple formula, then the preference should be given to the use of a chemical formula instead of a mineral name. **Biogenic substances** can be accepted as minerals if geological processes were involved in the genesis of these compounds [1],[3],[4].

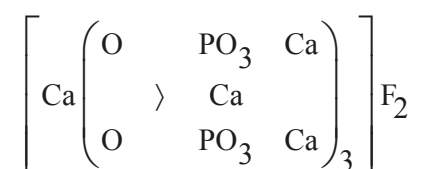
² The mineral classification system developed by German mineralogist K.H. STRUNZ.

³ The variable formula should be written as: $(\text{Ca}, \text{Sr}, \text{Pb}, \text{Y}, \text{Mn}, \text{Na})_5(\text{PO}_4, \text{AsO}_4, \text{SO}_4, \text{CO}_3)_3(\text{F}, \text{Cl}, \text{OH})$.



(DANA CLASSIFICATION [7],[8]) or as phosphates, arsenates and vanadates with additional anions without water (STRUNZ CLASSIFICATION⁴ [8],[9]), where M = Ba, Ca, Ce, K, Na, Pb, Sr and Y; X = As, P,⁵ and Si; and Z = F, Cl, O, OH and H₂O. Apatite minerals form a numerous and diverse group of minerals, while in addition a large number of synthetic compounds with the apatite type structure are known [10].

Apatite minerals can be formally derived from phosphoric acid⁶ [11] (or H₃AsO₄ and H₃VO₄ for arsenates and vanadates, respectively). According to the Werner's coordination theory [12], [13], e.g. fluorapatite was considered as a compound formed by the substitution of calcium phosphate (Ca₃(PO₄)₂) into halide mineral fluorite (calcium fluoride, CaF₂ [14]). The coordination formula of fluorapatite can then be written as follows:



The ratios of the mean sizes of ions " M " to " X " vary in the range from 1.89 to 4.43 for apatite compositions, but there are discontinuities between the ratios 2.50–2.60 and 3.25–3.35. These two gaps provide the structural base, which was used for the suggestion of classifying⁷ apatites into three groups named after well-known mineral species occurring in each group [15],[16]:

1. Vanadinite–svabite group with the $M:X$ ratio less than 2.5;
2. Apatite–mimetite group with the $M:X$ ratio in the range from 2.60 to 3.25;
3. Pyromorphite group with the $M:X$ ratio higher than 3.25.

The summary of some apatite species is listed in **Table 1**. The current nomenclature of minerals from apatite supergroup is described in Section 1.1.

⁴ A mineral group consists of two or more minerals with the same or essentially the same structure (i.e. isotypic structure belonging to one structural type) and composed of chemically similar elements (i.e. elements with similar crystal-chemical behavior). Crystal structures considered as being "essentially the same" can be denoted by the term *homeotypic*. The hierarchical scheme for the group nomenclature includes (1) mineral class, (2) mineral subclass, (3) mineral family, (4) mineral supergroup, (5) mineral group(s), and (6) mineral subgroup or mineral series [8].

⁵ The phosphorus element was discovered by a Hamburg alchemist H. Brand. As was described in the book of G.E. LEIBNITZ (1646–1716) **Historia Inventionis Phosphori**; phosphorus was extracted from "the spirit of urine" during the search for the philosopher's stone. The name of phosphorus (in Latin means "morning star") was derived from Greek word "*phosphoris*," which meaning "*bringing light*" [35].

⁶ In 3 moles of H₃PO₄, 8 H⁺ ions were replaced by 4 Ca²⁺, and the last H⁺ was replaced by Ca-Z (Z = OH, F, Cl...).

⁷ Despite the fact that this classification is out of fashion, there are some interesting structural consequences with general validity. Therefore, this classification was included to the introduction of this book.

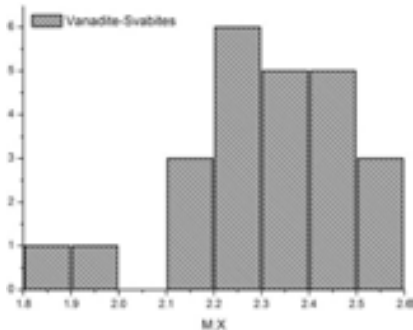
The specific gravity of *sensu lato*⁸ apatite ranges from 3.1 to 3.3 g·cm⁻³. Apatites show basal and imperfect cleavage, conchoidal and uneven fracture and the hardness on the Mohs scale is 5. The color of streak is white and luster vitreous to subresinous. Apatite occurs usually in the shades of green to gray-green, also white, brown, yellow, bluish, or reddish, transparent to translucent and some specimens can be multicolored. The habit of apatite crystals (Ca₅(PO₄)₃(F,Cl,OH)) is usually prismatic, dipyrarnidal or tabular, and also massive compact or granular. Some varieties are phosphorescent when heated, and others become electric by friction. On the other hand, the morphology of apatite crystals is very complex, and there is large amount (~53) of described forms [17],[18].

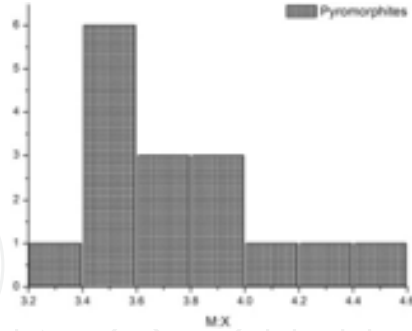
Apatite occurs in a wide range of igneous and sedimentary rocks (**Chapter 7**) and deposits as isolated crystals in grains, usually as small as 1–2 mm. The largest known apatite deposit is in Kirovsk, Russia. The largest individual crystals were found in Renfrew, Ontario, Canada [19], [20].

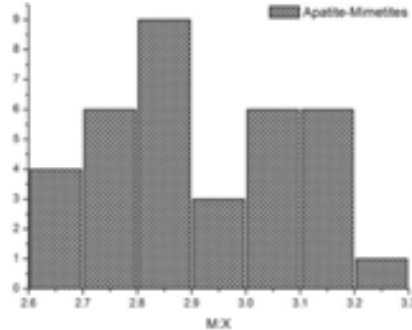
Group of apatites					
I. The vanadate–svabites		II. The apatite–mimetites		III. The pyromorphites	
Composition	M:X	Composition	M:X	Composition	M:X
La ₈ [GeO ₄] ₆	1.89	Ca ₆ Nd ₄ (SiO ₄) ₈	2.62	Pb ₁₀ (GeO ₄) ₂ (PO ₄) ₄	3.33
Ca ₁₀ (CrO ₄) ₆ (OH) ₂	1.94	Ca ₄ Nd ₆ (SiO ₄) ₆ (OH) ₂	2.65	Pb ₁₀ (SiO ₄)(GeO ₄)(PO ₄) ₄	3.44
Pb ₈ Na ₂ (VO ₄) ₆	2.13	Ca ₈ Ca ₂ La ₂ (SiO ₄) ₆	2.68	Pb ₁₀ (PO ₄) ₄ (SiO ₄) ₂	3.49
Ca ₄ Ce ₆ [GeO ₄] ₆ Cl ₂	2.18	Ca ₈ Ce ₂ (GeO ₄) ₂ (PO ₄) ₄	2.68	Pb ₈ Na ₂ (SO ₄) ₂ (PO ₄) ₂ (SiO ₄) ₂	3.50
Ca ₆ La ₄ [GeO ₄] ₆	2.18	Pb ₈ Na ₂ (AsO ₄) ₆	2.71	Sr ₁₀ (PO ₄) ₆ (OH,F) ₂	3.51
Ca ₄ La ₃ Ce ₃ [GeO ₄] ₆ (OH) ₂	2.20	Pb ₁₀ (GeO ₄) ₂ (AsO ₄) ₄	2.71	Ca ₄ Na ₆ (SO ₄) ₆ F ₂	3.52
Pb₁₀[VO₄]₆(F,Cl,Br,I)₂	2.21	Ca ₁₀ La ₅ Ce ₅ (SiO ₄) ₁₂ (OH) ₂	2.71	Pb ₉ Na(PO ₄) ₅ (SiO ₄)	3.59
Pb ₈ Tl ₂ [VO ₄] ₆	2.22 ^{a)}	Ca ₆ La ₄ (SiO ₄) ₆	2.72	Pb ₈ Na ₂ (PO ₄) ₆	3.62
Ca ₄ La ₆ [GeO ₄] ₆ (OH) ₂	2.24	Ca ₄ La ₈ Ce ₈ (SiO ₄) ₆ (OH) ₂	2.74	Pb ₈ KNa(PO ₄) ₆	3.73
Pb ₈ K ₂ [VO ₄] ₆	2.26	Ca ₅ La ₅ (SiO ₄) ₆ OH	2.76	Pb₁₀(PO₄)₆(F,Cl,Br,OH)₂	3.76
Sr ₄ Dd ₆ [SiO ₄] ₆ (OH) ₂	2.26	Ca ₄ La ₆ (SiO ₄) ₆ (OH) ₂	2.80	Pb ₈ Tl ₂ (PO ₄) ₆	3.80 ^{c)}
Pb ₁₀ [GeO ₄] ₂ (VO ₄) ₄	2.30	Ca ₄ La ₆ (SiO ₄) ₆ F ₂	2.80	Pb ₈ K ₂ (PO ₄) ₆	3.85
Sr ₄ a ₆ (GeO ₄) ₈ (OH) ₂	2.34	Pb ₈ KNa(AsO ₄) ₆	2.80	Pb ₈ Rb ₂ (PO ₄) ₆	3.94
Ca₁₀(AsO₄)₆(F,Cl)₂	2.34	Pb₁₀(AsO₄)₆(F,Cl,Br,I)₂	2.82	Pb ₈ Cs ₂ (PO ₄) ₆	4.06
Ca ₄ Ce ₆ (GeO ₄) ₄ (SiO ₄) ₂ Cl ₂	2.34	Pb ₈ Tl ₂ (AsO ₄) ₆	2.82 ^{b)}	Ba ₁₀ (PO ₄) ₆ (F,OH) ₂	4.24
La ₈ (SiO ₄) ₆	2.36	Tl ₂ La ₈ (SiO ₄) ₆ (OH) ₂	2.85	Pb ₁₀ (SiO ₄) ₂ (BO ₃) ₄	4.43

⁸ Latin phrase (abbreviated as s.l.) used, which means “in the broad sense.”

Group of apatites			
$\text{Ca}_6\text{Ce}_4(\text{GeO}_4)_4(\text{PO}_4)_2\text{Cl}_2$	2.41	$\text{Ba}_{10}(\text{MnO}_4)_6(\text{OH})_2$	2.86
$\text{Ca}_4\text{Y}_6(\text{SiO}_4)_6(\text{OH})_2$	2.45	$\text{Ba}_{10}(\text{CrO}_4)_6(\text{OH})_2$	2.86
$\text{Ba}_2\text{La}_8(\text{GeO}_4)_6\text{O}_2$	2.45	$\text{Pb}_8\text{K}_2(\text{AsO}_4)_6$	2.89
$\text{Ba}_3\text{La}_7(\text{GeO}_4)_6\text{O}_{1.5}$	2.49	$\text{Pb}_{10}(\text{SiO}_4)_2(\text{AsO}_4)_4$	2.91
$\text{Ca}_4\text{Ce}_6(\text{GeO}_4)_2(\text{SiO}_4)_4\text{Cl}_2$	2.49	$\text{Sr}_4\text{La}_6(\text{SiO}_4)_6(\text{OH})_2$	2.93
$\text{Ba}_{10}(\text{VO}_4)_6(\text{OH})_2$	2.50	$\text{Pb}_8\text{Rb}_2(\text{AsO}_4)_6$	2.96
$\text{Pb}_{10}(\text{SiO}_4)_2(\text{VO}_4)_4$	2.51	$\text{Pb}_{10}(\text{SiO}_4)_2(\text{VO}_4)_2(\text{PO}_4)_2$	3.02
$\text{Sr}_{10}(\text{MnO}_4)_6(\text{OH})_2$	2.52	$\text{Ca}_9\text{Mg}(\text{PO}_4)_6\text{Cl}_2$	3.02
		$\text{Ca}_9\text{Ni}(\text{PO}_4)_6\text{O}$	3.03
		$\text{Ca}_{10}(\text{SiO}_4)_8(\text{SO}_4)_3(\text{OH})_3$	3.03
		$\text{Pb}_{10}(\text{SiO}_4)(\text{GeO}_4)(\text{PO}_4)_2(\text{AsO}_4)_2$	3.05
		$\text{Ca}_5\text{Cd}_5(\text{PO}_4)_6\text{F}_2$	3.09
		$\text{Ba}_3\text{La}_7(\text{SiO}_4)_6(\text{OH})_2$	3.11
		$\text{Ca}_9\text{Cd}(\text{PO}_4)_6\text{F}_2$	3.11
		$\text{Ca}_{10}(\text{PO}_4)_6(\text{F},\text{Cl},\text{Br},\text{OH})_2$	3.12
		$\text{Pb}_8\text{Bi}_2(\text{SiO}_4)_4(\text{PO}_4)_2$	3.16
		$\text{Ca}_9\text{Sr}(\text{PO}_4)_6\text{O}$	3.16
		$\text{Ca}_9\text{Pb}(\text{PO}_4)_6(\text{O},\text{Cl}_2)$	3.18
		$\text{Ca}_9\text{Ba}(\text{PO}_4)_6(\text{O},\text{Cl}_2)$	3.23







a) 2.13–2.32

b) 2.70–2.95

c) 3.66–3.94

Table 1. The classification of synthetic (marked by bold) and natural apatites into three groups [15].

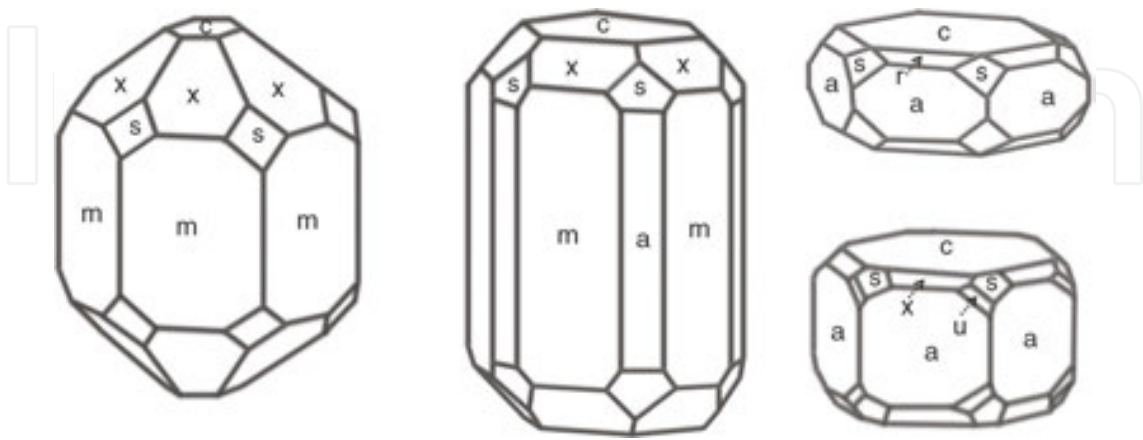


Fig. 1. Some of known forms of apatite crystals: c (0001), m ($11\bar{1}0$), a ($11\bar{2}0$), x ($10\bar{1}1$), s ($11\bar{2}1$), r ($10r2$) and u (2131).

Some examples of morphology of apatite crystals are shown in **Fig. 1**. The most abundant crystal faces of apatite possess the Miller–Bravais indices⁹ [21],[22],[23],[24],[25] (0001), i.e. basis (or basal pinacoid¹⁰), (11 $\bar{1}$ 0),¹¹ i.e. protoprism (or the prism of the first order), (10 $\bar{1}$ 1) and (20 $\bar{2}$ 1), i.e. the first-order dipyrramids, but the faces such as (11 $\bar{2}$ 0), i.e. deuteroprisms (or the prism of the second order), (11 $\bar{2}$ 1), i.e. dipyrramid of the second order as well as (10 $\bar{1}$ 2), i.e. the dipyrramids of the first order, and (21 $\bar{3}$ 1), i.e. dipyrramid of the third order, are also common. Other faces such as (31 $\bar{4}$ 1), (31 $\bar{4}$ 2), (21 $\bar{3}$ 0), (12 $\bar{3}$ 2), etc., i.e. dipyrramids of the third order, are also possible but rare (**Fig. 2**).

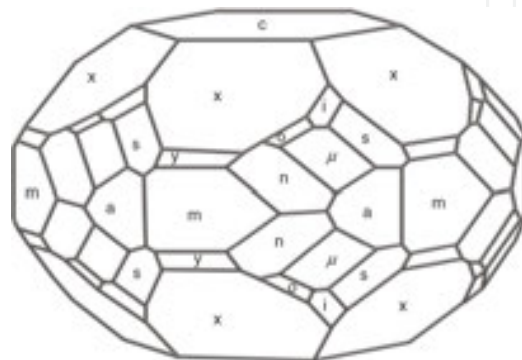


Fig. 2. Apatite from Gletsch (Switzerland): y (20 $\bar{2}$ 1), n (31 $\bar{4}$ 1), o (31 $\bar{4}$ 2), i (12 $\bar{3}$ 2) and μ (21 $\bar{3}$ 1).

This means that the shapes pinacoid {0001}, hexagonal prisms {10 $\bar{1}$ 0} and {11 $\bar{2}$ 0}, dihexagonal prism {21 $\bar{3}$ 0} and hexagonal dipyrramid¹² {10 $\bar{1}$ 1}, {10 $\bar{1}$ 2}, {20 $\bar{2}$ 1} and {11 $\bar{2}$ 1} are possible to be found on apatite crystals.

According to the crystal system, apatite minerals belong to the hexagonal¹³ dipyramid class (sometimes also termed as apatite type). The point group of apatite is 6/M (**HERMAN–MAUGUIN SYMBOLS**, H-M) or C_6h (**SCHÖNFLIES SYMBOLS**), and it is centrosymmetric [26],[27],[28], [29],[30], [31],[32]. The symmetry operation of this point group includes hexad perpendicular to mirror plane and the center of symmetry (**Fig. 3**).

⁹ The orientation of planes in crystal was determined by Miller indices, i.e. three integers (hkl), which refer to the plane (or planes $hb_1 + kb_2 + lb_3$, where b_1 , b_2 and b_3 are reciprocal lattice vectors). Negative integer, e.g. $-i$ is written as \bar{i} . The group of planes equivalent to (hkl) is written as $\{hkl\}$. The square brackets $[hkl]$ denote a direction on the basis of the direct lattice vectors instead of the reciprocal lattice and the set of equivalent planes ($ha_1 + ka_2 + la_3$, where a_1 , a_2 and a_3 are direct lattice vectors) is written as $\langle hkl \rangle$.

¹⁰ Pinacoid {0001} consists of two opposite faces perpendicular to the 6-fold axis. It commonly occurs in combination with hexagonal prism and hexagonal or dihexagonal truncated pyramids [25]. The single face is termed as pedion.

¹¹ The hexagonal (and rhombohedral) crystal system uses four (Miller–Bravais) indices ($hkil$), where i is termed as redundant index and $h + k + i = 0$, e.g. (20 $\bar{2}$ 1) is equivalent to (201) and (110) to (11 $\bar{2}$ 0).

¹² Hexagonal dipyrramids $\{h0\bar{h}l\}$ and $\{hh(2\bar{h})l\}$ consist of 12 isosceles faces which intersect in a point along the vertical axis. Those two dipyrramids differ only in their orientation with respect to three horizontal axes.

¹³ In hexagonal crystal system $a = b \neq c$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$. The hexagonal system is usually referred to four crystallographic axes designated a_1 , a_2 , a_3 , and c . The c -axis is vertical and the three a -axes lie in horizontal plane (c -axis is perpendicular to this plane) with the angle of 120° between their positive ends [25].

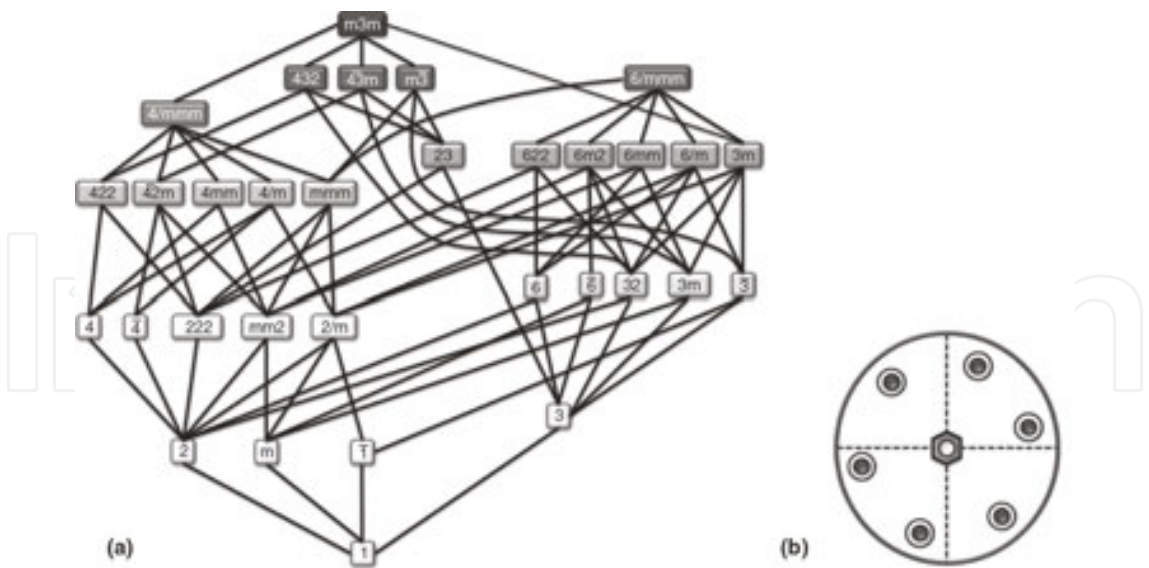


Fig. 3. Point group–subgroup relationship of point groups [31] (a) and stereogram of point group 6/M [36] (b) showing a sixfold rotation axis (hexad) plus the centre of symmetry and the mirror plane.

The projection of hexagonal crystal divided to twelve parts (dodecant) by the lateral axial planes is shown in **Fig. 4(a)**. The pole (\times) of each plane requires five other points above as well as six other located on the same place below the projection plane (b). This leads to the formation of hexagonal dipyramid. The cross section provides hexagon (c) inclined to right or left. Therefore, the right or right-handed form (d) and the left or left-handed form (e) of dipyramids were recognized. One is formed from the poles marked by sign (\times) and the second one is in the void dodecants of projections (b). The right form can be turned left by the rotation of 180° along one of the crystallographic axis a .

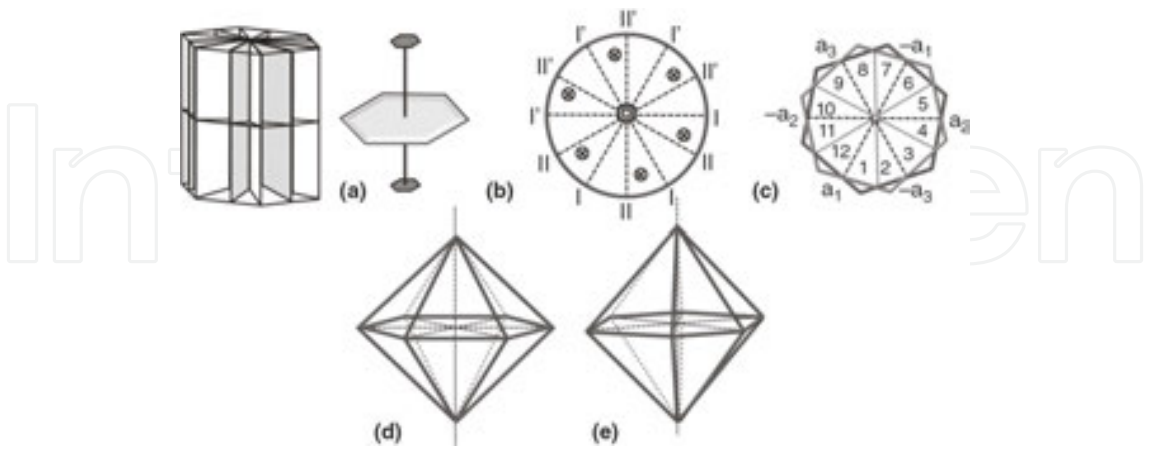


Fig. 4. Hexagonal dipyramidal crystal system: hexagonal lattice (a), stereographic projection (b), hexagon (c) and right (d) and left (e) dipyramids.

The crystal shaper related to the hexagonal–dipyramidal crystal system can be derived via extend or skip altering planes (the same up and down) according to **Table 2**.

1	2	3	4	5	6	7	8	9	10	11	12
1	2	3	4	5	6	7	8	9	10	11	12

Table 2. Derivation of shapes in hexagonal–dipyramidal crystal system.

The space group¹⁴ of apatite is $P6_3/M$ (**HERMAN–MAUGUIN SYMBOLS**¹⁵), where P denotes primitive type of Bravais lattice,¹⁴ 6_3 is sixfold ($360^\circ/6 = 60^\circ$) screw rotation axis parallel to (001) followed by a translation through a distance $3t/6$ (t is the magnitude of the shortest lattice vector along the axis), and the symbol /M refers to the mirror plane perpendicular to 6_3 screw axis (i.e. the mirror plane normal vector is parallel to the hexad¹⁶ that coincides with glide plane¹⁷ at $z = 1/4$ for the monoclinic variant in the space group $P2_1/B$ (**Fig. 9**, the structure of hexagonal and monoclinic apatite was described in **Section 1.2**) [28],[29],[30], [31],[32],[38],[39].

The composition of natural apatites ($\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})$) exhibits large variations in the content of F, Cl and OH. Pure end members, e.g. hydroxylapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) and chlorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{Cl}$), are uncommon in nature, but binary and ternary compositions are widely reported in igneous, metamorphic and sedimentary rocks. Petrologists proposed that the variations in OH–F–Cl ratio in apatites or between biotite and apatite may be used as a geothermometer [33],[34],[35] and an indicator of volatile fugacity of halogens and water in magmatic and hydrothermal processes [33],[36]. The concentration of OH, F and Cl also directly correlates with the properties such as etching rates, annealing characteristics of U fission track in apatite (**Section 7.3.3**) and investigation of paleoenvironment and diagenesis (**Section 6.5**) [33].

Apatite minerals represent a major class of ionic compounds [37] of interest to many disciplines, including medical and biomaterial sciences (**Section 10.9**), geology (**Chapter 7**), cosmology ([40], **Section 7.3.4**), environmental (**Chapters 7** and **9**) and nuclear sciences (**Chapter 10**). Apatite also represents an important source of inorganic phosphorus for natural ecosystems and may favor the establishment of microbial communities able to exploit it [42].

1.1. Nomenclature of apatite minerals and apatite supergroup

The mineral apatite was first recognized by German geologist ABRAHAM GOTTLOB WERNER (1950–1817) and named in 1786 from Greek word “*apatao*” (απατάω, which means to mislead, to cheat, or to deceive because the mineral was often mistaken for other species, e.g. mineral beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, space group P_6/MCC)) [43],[44],[45],[46].

¹⁴ There are 14 Bravais lattices, 32 point groups (crystal classes), and 230 crystallographic space groups in three dimensions [28]. The space groups were independently described by E.S. FEDEROV (1853–1919, Russian), A.M. SCHÖNFLIES (1853–1928, German), and W. BARLOW (1845–1934, English) [32].

¹⁵ The corresponding Schönflies symbol is C_{6h}^2 . The number of group is 176.

¹⁶ Hexad denotes the sixfold rotation axis. The 4-, 3-, 2-, and 1-fold rotation axes are termed as tetrad, triad, diad, and monad [27].

¹⁷ Glide plane combines a reflection with a translation parallel to the plane.

Since 1856–1860, these minerals have been named fluorapatite, chlorapatite, and hydroxylapatite, depending on the dominant Z^- anion. The increasing number of new discovered species¹⁸ resulted in a revision of the mineralogical nomenclature, which was initiated by the chairman of the IMA Commission on New Minerals, Nomenclature and Classification, E.A.J. BURKE, and aimed at adopting, as far as possible, modified Levinson suffixes¹⁹ (or Levinson modifier [47],[49]) instead of adjectival prefixes such as fluor-, chlor- and hydroxyl. The above-mentioned minerals were renamed to apatite-(CaF), apatite-(CaCl) and apatite-(CaOH).²⁰

One of the rationales for that change was the benefit of having the names of these minerals appear consecutively in alphabetical listings and databases. These changes did not fully consider the structural complexity of minerals with the apatite structure [45],[49],[50]. The name of these minerals was currently changed back from apatite-CaF) apatite-(CaOH), apatite-(CaCl) to fluorapatite, hydroxylapatite and chlorapatite. Furthermore, the monoclinic variants²¹ [51] fluorapatite-M, hydroxylapatite-M and chlorapatite-M are not considered to be distinct species [45].

The recently approved nomenclature scheme [49] could logically be extended to other minerals from the group of apatite, e.g. pyromorphite [52] should be named as apatite-(PbCl) or alforsite [53],[54] as apatite-(BaCl). It is also possible to include various tetrahedral cations (P, As, or V) into the extended suffix, e.g. apatite-(PbAsCl) instead of mimetite [55]. The results would be the mineral names, which are more similar to chemical formula [45]. The name mimetite-M is used for the polymorphic variant of mimetite. The mineral was previously known as clinomimetite and currently is not considered a distinct species [45].

The “apatite group” traditionally includes phosphate, arsenate and vanadate minerals. Other minerals belonging to different chemical classes, namely, silicates (e.g. britholite-(Ce) [56],[57] or britholite-(Y) [57],[58]), silicate-sulfates (e.g. hydroxyllellstadite [45],[59], fluorellstadite [45],[60] and chlorellstadite²² [45]) and sulfates (e.g. cesanite [61]) display the structural

¹⁸ The concept of mineral species is defined mainly on the basis of its chemical composition and crystallographic properties. For example, hydroxylapatite and fluorapatite both crystallize in the hexagonal system, with the same space group and have similar unit-cell parameters. They are considered as the separate species because the relevant structural site is predominantly occupied by OH⁻ in hydroxylapatite and by F⁻ in fluorapatite [4].

¹⁹ The nomenclature system based on chemical-symbol suffixes described by LEVISON [47] and originally applied only to rare-earth mineral species, which are defined to have the total atomic percentage of rare-earth elements and Y greater than any other element within a single set of crystal-structure sites, e.g. (~REE, Ca). A species name is related to a rare-earth mineral whenever the presence of rare-earth element distribution is determined. The chemical symbol for the predominant rare-earth element is appended, in parentheses, by means of a hyphen to the group name; this results in mineral species names such as monazite-(Ce), monazite-(La), and monazite-(Nd) [48]. If a rare-earth mineral appears together with considerable quantities of another rare-earth element which is unusual, or for any reason deserving the notice, two or more chemical symbols may be placed in the parentheses [47]. For example, a monazite-(Ce) with a considerable amount of samarium would be written as monazite-(Ce,Sm).

²⁰ Another examples are strontium apatite named as apatite-(SrOH) and clinohydroxylapatite named as apatite-(CaOH)-M.

²¹ In essence, the polytypes are distinguished by alphanumerical symbols appended to the root name and joined to by a hyphen, for example, wollastonite-3T or graphite-2H. The numerical part of the symbol represents the layering periodicity and the alphabetical part, rendered in italic print represents the crystallographic system as follows: cubic (C), hexagonal (H), rhombohedral (R), trigonal (T), orthorhombic (O), monoclinic (M), and triclinic (A).

²² The names of ellestadite-(OH), ellestadite-(F), and ellestadite-(Cl) minerals were changed back to hydroxyllellstadite, fluorellstadite, and chlorellstadite, respectively [45],[49].

morphology of apatite. In accordance with the newly approved standardization of mineral group hierarchies, all of these minerals can be included in the broader apatite supergroup [45].

The valid IMA-accepted mineral species within the apatite supergroup can be divided into five groups [45]:

- a. **Apatite group:** hexagonal and pseudo-hexagonal phosphates, arsenates and vanadates containing the same prevailing (species-defining) cations at both **M(1)** and **M(2)** sites.
- b. **Hedyphane group:** hexagonal and pseudo-hexagonal phosphates, arsenates and sulfates containing different prevailing (species-defining) cations at **M(1)** and **M(2)** sites. Minerals from the group of hedyphane are described in **Section 2.1**.
- c. **Belovite group:** hexagonal and trigonal phosphates with **M(1)** site split into the **M(1)** and **M(1')** sites containing different prevailing (species-defining) cations. Minerals from the group of belovite are described in **Section 2.2**.
- d. **Britholite group:** hexagonal and pseudo-hexagonal silicates, typically with partially ordered **M(1)** and **M(2)** cations. Minerals from the group of britholite are described in **Section 2.3**.
- e. **Ellestadite group:** hexagonal and pseudo-hexagonal sulfato-silicates with ideal ratio $[\text{SiO}_4]^{4-}:[\text{SO}_4]^{2-} = 1:1$. Minerals from the group of ellestadite are described in **Section 2.4**.

All of valid species within the apatite supergroup are listed in **Table 3**. There are also other minerals with the apatite structure [45]:

- i. Borosilicates with REEs atoms strongly prevalent over calcium in M sites, including three valid minerals: tritomite-(Ce), $\text{Ce}_5(\text{SiO}_4\text{BO}_4)_3(\text{OH},\text{O})$ [57], melanocerite-(Ce), $\text{Ce}_5(\text{SiO}_4\text{BO}_4)_3(\text{OH},\text{O})^{23}$ [45],[57] and tritomite-(Y), $\text{Y}_5(\text{SiO}_4\text{BO}_4)_3(\text{O},\text{OH},\text{F})$ [62],[63]. These minerals could be formally included as REE silicates in the britholite subgroup.
- ii. Carbonate-fluorapatite and carbonate-hydroxylapatite: Although the carbonate-fluorapatite names are extensively used in literature to denote the mineral portion of bones a teeth of vertebrates, their validity as distinct mineral species belonging to the group of apatite remains disputable. CO_3^{2-} anion is known to occur as subordinate component in the members of apatite group [64],[65], but both minerals mentioned above are discredited.

Group	Existing name (IMA list of minerals)	Approved name	End-member formula
Apatite group	Apatite-(CaF)	Fluorapatite	$\text{Ca}_5(\text{PO}_4)_3\text{F}$
	Apatite-(CaCl)	Chlorapatite ^a	$\text{Ca}_5(\text{PO}_4)_3\text{Cl}$
		Chlorapatite-M ^b	

²³ Melanocerite-Ce and tritomite-(Ce) are probably the same mineral, and tritomite-(Y) could be the Y-dominant analogue [45].

Group	Existing name (IMA list of minerals)	Approved name	End-member formula
Hedyphane group	Apatite–(CaOH)	Hydroxylapatite ^a	Ca ₅ (PO ₄) ₃ OH
	Apatite–(CaOH)–M	Hydroxylapatite–M ^b	
	Svabite	Svabite	Ca ₅ (AsO ₄) ₃ F
	Turneaureite	Turneaureite	Ca ₅ (AsO ₄) ₃ Cl
	Johnbaumite	Johnbaumite ^a	Ca ₅ (AsO ₄) ₃ OH
	Fermorite	Johnbaumite–M ^b	
	2008-009 ^c	Stronadelphite	Sr ₅ (PO ₄) ₃ F
	Pyromorphyte	Pyromorphyte	Pb ₅ (PO ₄) ₃ Cl
	Mimetite	Mimetite ^a	Pb ₅ (AsO ₄) ₃ Cl
	Clinomimetite	Mimetite–M ^b	
	Alforsite	Alforsite	Ba ₅ (PO ₄) ₃ Cl
	Vanadinite	Vanadinite	Pb ₅ (VO ₄) ₃ Cl
	Hedyphane	Hedyphane	Ca ₂ Pb ₃ (AsO ₄) ₃ Cl
	–	“Hydroxylhedyphane”^d	Ca ₂ Pb ₃ (AsO ₄) ₃ OH
	Phosphohedyphane	Phosphohedyphane	Ca ₂ Pb ₃ (PO ₄) ₃ Cl
	Phosphohedyphane–(F)	Fluorphosphohedyphane	Ca ₂ Pb ₃ (PO ₄) ₃ F
	–	“Hydroxylphosphohedyphane”^d	Ca ₂ Pb ₃ (PO ₄) ₃ OH
	–	New root name^d	Ca ₂ Sr ₃ (PO ₄) ₃ F
	Morelandite	Morelandite	Ca₂Ba₃(AsO₄)₃F,Cl
	–	New root name^d	Mn ₂ Ca ₃ (PO ₄) ₃ Cl
Belovite group	Cesanite	Cesanite	Ca ₂ Na ₃ (SO ₄) ₃ OH
	Caracolite	Caracolite	Na ₂ (Pb ₂ Na)(SO ₄) ₃ Cl
	Aiolosite	Aiolosite	Na ₂ (Na ₂ Bi)(SO ₄) ₃ Cl
	Fluorcaphite	Fluorcaphite	SrCaCa ₃ (PO ₄) ₃ F
	Apatite–(SrOH)	Fluorstrophite	SrCaSr ₃ (PO ₄) ₃ F ^e
	Deloneite–(Ce)	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}) (PO₄)₃F_{0.5}(OH)_{0.5}
	Belovite–(Ce)	Belovite–(Ce)	NaCeSr ₃ (PO ₄) ₃ F
	Belovite–(La)	Belovite–(La)	NaLaSr ₃ (PO ₄) ₃ F
	Kuannersuite–(Ce)	Kuannersuite–(Ce)	NaCeBa ₃ (PO ₄) ₃ F _{0.5} Cl _{0.5}
	Britholite–(Ce)	Britholite–(Ce)	(Ce,Ca) ₅ (SiO ₄) ₃ OH
Britholite group	Britholite–(Y)	Britholite–(Y)	(Y,Ca) ₅ (SiO ₄) ₃ OH

Group	Existing name (IMA list of minerals)	Approved name	End-member formula
Ellestadite group	Fluorbritholite-(Ce)	Fluorbritholite-(Ce)	$(\text{Ce,Ca})_5(\text{SiO}_4)_3\text{F}$
	2009-005 ^c	Fluorbritholite-(Y)	$(\text{Y,Ca})_5(\text{SiO}_4)_3\text{F}$
	Fluorcalciobricholite	Fluorcalciobricholite	$(\text{Ca,REE})_5(\text{SiO}_4)_3\text{PO}_4$
	Melanocerite-(Ce)	— ^f	
	Tritomite-(Ce)	Tritomite-(Ce)	$\text{Ce}_5(\text{SiO}_4)_3\text{BO}_3(\text{OH},\text{O})$
	Tritomite-(Y)	Tritomite-(Y)	$\text{Y}_5(\text{SiO}_4)_3\text{BO}_3(\text{O},\text{OH},\text{F})$
	Ellestadite-(OH)	Hydroxylellestadite	$\text{Ca}_5(\text{SiO}_4)_3(\text{SO}_4)_2\text{OH}$
	Ellestadite-(F)	Fuorellestadite	$\text{Ca}_5(\text{SiO}_4)_3(\text{SO}_4)_2\text{F}$
	Ellestadite-(Cl)	— ^g	—
	Mattheddleite	Mattheddleite	$\text{Pb}_5(\text{SiO}_4)_3(\text{SO}_4)_2\text{Cl}$
	—	“Hydroxylmattheddleite” ^d	$\text{Pb}_5(\text{SiO}_4)_3(\text{SO}_4)_2\text{OH}$

^a The suffix -H could be used to denote the hexagonal polymorph.

^b The name of monoclinic polymorph that should no longer to be considered as distinct species.

^c Mineral approved by the IMA CNMNC without a name.

^d Potentially new mineral species.

^e A mistake in the IMA list of minerals, please see PASERO et al [45] for further details. Since the mineral was initially considered to be the Sr-dominant analogue of fluorapatite with simplified formula $(\text{Sr,Ca})_5(\text{PO}_4)_3(\text{F},\text{OH})$, it was named as strontium apatite. Later structural study determined the idealized formula of mineral as $\text{SrCaSr}_3(\text{PO}_4)_3\text{F}$. Recently, the mineral was renamed as apatite-(SrOH) [45],[49]. However, the name should have been changed to apatite-(SrF) given that fluorine is the dominant Z⁻ anion.

^f Mineral to be potentially discredited (= tritomite-(Ce)).

^g Mineral be discredited (a mineral with ideal end-member formula $\text{Ca}_5(\text{SiO}_4)_3(\text{SO}_4)_2\text{Cl}$ is assumed not to exist).

Table 3. Existing (IMA) approved names and end-member formulas for the minerals within the apatite supergroup. Approved changes are marked by bold and names in quotes are the most appropriate for potential new minerals.

The nomenclature of minerals from the apatite group is very confusing because many of the names are initially used to ill-defined varieties, which did not deserve specific status. There are many historical names,²⁴ which still appear in literature [10],[67],[68]:

- **Apatite:** is currently used as a generic name for apatite group of minerals (**Section 1.5**).
- **Dahllite:** is an obsolete name for carbonate-hydroxylapatite²⁵ (soluble in HCl with the evolution of CO₂) of the composition of $\text{H}_2\text{Ca}_{14}\text{P}_8\text{C}_2\text{O}_{39}$ or $2\text{Ca}_3\text{P}_2\text{O}_8 \cdot \text{CaCO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$. Dahllite was described by BRÖGGER AND BÄCKSTRÖM [69] as a mineral which occurs in crusts with fibrous structure on apatite, and also in a pure state as nodular masses and concretions. The mineral is pale yellowish white, greenish, or colorless, has white streak, the hardness on the Mohs scale is 5 and the density is $3.053 \text{ g}\cdot\text{cm}^{-3}$ [70].
- **Francolite:** is an obsolete name for carbonate-fluorapatite²³.

²⁴ These names are no longer accepted by IMA/CNMMN.

²⁵ Described deeply in **Section 2.6** and **Chapter 7**.

- **Staffelite:** is an obsolete name for a variety of carbonate–fluorapatite from Staffel, Germany, which form nodular-stalactitic aggregates and crusts, of the composition of $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2 \cdot \text{CaCO}_3$ [71],[72].
- **Voelckerite:** the modern equivalent is oxyapatite ($3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaO}$) named according to agricultural chemist J.A. VOELCKER [73], who proved the fact that apatite is often deficient in fluorine and chlorine (**Section 1.4**). Voelckerite is a white, subtranslucent mineral with imperfect cleavage and faint luster. The specific gravity is 3.06, and the hardness on the Mohs scale is about 5. In a thin basal section, a negative uniaxial interference figure was obtained [74].
- **Kurskite:** is an obsolete name for carbonate–fluorapatite²³ [75],[76].
- **Quercyite:** is an obsolete name for carbonate–hydroxylapatite applied to mixtures of amorphous collophanite (collophane) and crystalline dahllite, francolite, etc. Quercyite is often composed of alternating layers α -quercyite (optically negative) and β -quercyite (optically positive). The density of quercyite ranges from 2.83 to 2.87 g·cm⁻³ [70].
- **Wilkeite:** siccatian strontian apatite [67]. Wilkeite is a former name (EAKLE AND ROGERS [77] in 1914) for a variety of mineral fluorellestadite (**Section 2.4.1**).
- **Manganapatite:** (manganoan fluorapatite, Mn-bearing fluorapatite) was named by SIEWERT [78] in allusion to its chemical relationship to fluorapatite.
- **Lasurapatite:** sky blue variety, it occurs in crystals with lapis-lazuli at Bucharei in Siberia [79].
- **Moroxite:** greenish-blue variety of conchoidal apatite (the green varieties are named as asparagus stone). The name moroxite was given to this mineral by Karsten and is borrowed from the morochites of Pliny, according to author's statement: "*Est gemma, per se porrcea viridisque, trita autem candicans*" [81].
- **Foliated apatite:** according to the system of mineralogy of JAMESON [81] in which minerals are arranged according to the natural history method, rhomboidal apatite (first specie) is divided in three subspecies, including (1) foliated apatite, (2) conchoidal apatite and (3) phosphorite described below.

The most frequent color of foliated apatite is snow-white, yellowish-whiter, reddish-white and greenish-white. Several of these colors occur frequently in the same piece. It sometimes occurs also as massive and disseminated in distinct concretions, which are large and small angulo-granular, and sometimes thin and straight lamellar, generally crystallized. The crystals are small, very small and middle-sized and occur sometimes single, sometimes many irregularly superimposed on each other. It is brittle and easily fragile. Foliated apatite becomes electric by heating and by being rubbed with woolen cloth. On glowing coals, it emits a pale grass-green phosphoric light [79]
- **Conchoidal apatite or asparagus-stone:** a yellow-green variety of apatite. The name of asparagus stone has been given to this variety in allusion to asparagus green color, which

it frequently exhibits. It was distinguished from the apatite partly by its crystalline form, and more particularly by tendency to phosphoresce on hot coals. It presents either the primitive or the perfect form, or it occurs with truncated lateral edges, but most frequently, the hexahedral prism is terminated by six-sided pyramids, the faces of which correspond with the sides of the prism and form with them the angle of $129^{\circ}14'$. These prisms are usually longer than in case of apatite. It sometimes occurs in small crystalline masses [80],[81]. This variety was former described also as a kind of schorl ($\text{NaFe}_3^{2+}\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3\text{OH}$ [82],[83]), afterwards as a variety of beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ [84][85]) [86].

In Europe, asparagus stone occurs as a porous iron-shot limestone near Cape de Gate, in Murcia in Spain, in granite near Nantes and is basalt at Mont Ferrier, in France, imbedded in green talc, in the Zillertal in Salzburg, in beds of magmatic ironstone, along with sphere or rutilite (the name is used for almandine, rutile, titanate, or rutilized quartz), calcareous-spar, hornblende, quartz and augite, at Arendal in Norway. In America, it was found imbedded in granite at Baltimore, and in mica-slate in West Greenland [86].

- **Phosphorite:** the third subspecies in JAMESON'S [86] system of mineralogy. There are two kinds of phosphorites (described in **Section 7.1.1**): (1) common phosphorite and (2) earthy phosphorite.
- **Naurite:** a colloidal variety of apatite from Nauru Island, Pacific. The mineral was considered as a mineral species of carbonate–hydroxyl–fluorapatite from the group of collophane [87].
- **Eupychroite:** a fibrous mammillary variety of apatite (carbonate–fluorapatite) from Point Crown, Essex County, New York, United States [88].
- **Podolite:** carbonate–fluorapatite (soluble in HCl with the evolution of CO_2) of the composition of $\text{Ca}_{10}\text{P}_6\text{CO}_{27}$ or $3\text{Ca}_3\text{P}_2\text{O}_5 \cdot \text{CaCO}_3$. The mineral was described by TSCHIRWINSKY [89] and occurs as crystalline masses or in prismatic crystals on phosphorite, in spherulites of prismatic crystals. The color of the mineral is yellowish, and its density is $3.077 \text{ g}\cdot\text{cm}^{-3}$. A comparison of the properties and chemical composition of podolite and dahllite shows they are essentially identical [70].
- **Dehrnite:** a varietal name for sodian hydroxylapatite, i.e. apatite where a part of calcium is replaced by alkali metals and the content of $\text{Na} > \text{K}$. Originally, it was described from Dehrn, Germany, by LARSEN AND SHANNON as a potassium sodium calcium phosphate that belongs to the apatite group [90],[91],[92].
- **Lewistonite:** a varietal name for alkali bearing [93]²⁶ hydroxylapatite where a part of calcium is replaced by alkali metals and the content of $\text{K} > \text{Na}$. The mineral was described from Fairfield, Utah [90],[91],[92].

²⁶ Adjectival modifier that gives some information on the chemistry of the mineral, for example, “sodian,” “sodium-rich,” “sodium-bearing,” or “sodium equivalent of” [93].

- **Saamite**: a rare earth element–strontian or calcium variety of fluorapatite of the composition of $(\text{Ca}, \text{Sr}, \text{REE})_5(\text{PO}_4)_3(\text{F}, \text{O})$ [40],[94]. According to VOLKOVA AND MELENTIEV [95], it is a saamite variety of apatite containing 5.58–11.42% SrO. Currently, the mineral name saamite refers to IMA approved mineral of the composition of $\text{Ba}\square\text{Na}_3\text{Ti}_2\text{Nb}(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ from the Kirovskii mine, Mount Kukisvumchorr, Khibiny alkaline massif, Kola Peninsula, Russia [96].
- **Collophane**: a varietal name for massive cryptocrystalline carbonate-rich apatite²³ $(\text{Ca}_5(\text{PO}_4, \text{CO}_3, \text{OH})_3(\text{F}, \text{OH})$ [97]). It is often used when the specific phase of apatite cannot be identified. The deposits of collophane are often associated with fossilized bone or coprolites. The term is sometimes used also in the context of bone composition and structure [98], [99]. Most of the collophane occurs as pelletal phosphorite, but some occurs as a collophane mudstone and as cement in sedimentary breccia²⁷ [100],[101].

The list of calcium phosphate species accepted by Commission on New Minerals and Mineral Names (CNMMN)²⁸ of International Mineralogical Association (IMA) [67] is given in **Table 3**.

1.2. The crystal structure of apatite minerals

The stoichiometric end-member formula for phosphate-bearing apatites is $\text{M}_{10}(\text{PO}_4)_6\text{Z}_2$ ($\text{Z} = 2$) (reduced formula $\text{M}_5(\text{PO}_4)_3\text{Z}$ ($\text{Z} = 2$) can be used [45]), where M and Z represent divalent cations and monovalent anion, respectively. In the case of oxyapatites ($\text{M}_{10}(\text{PO}_4)_6\text{O}$), 2Z^- ions are replaced by O^{2-} [37]. Various representations of orthophosphate ion are introduced in **Fig. 5**.

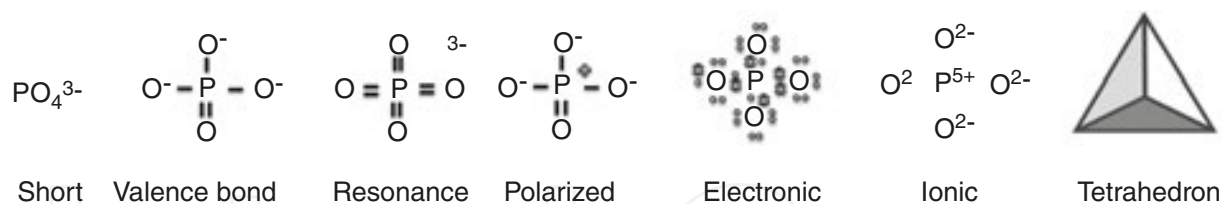


Fig. 5. Representation used for orthophosphate anion [106].

The PO_4 unit in the apatite structure can be partially substituted by AsO_4 (e.g. hedyphane $(\text{Ca}_2\text{Pb}_3(\text{AsO}_4)_3\text{Cl})$ [102] and minerals from the group of pyromorphite $(\text{Pb}_5(\text{PO}_4)_3\text{Cl})$ [17],[52], etc.), SiO_4 , SO_4 , VO_4 (vanadinite $(\text{Pb}_5(\text{VO}_4)_3\text{Cl})$ [103] and CO_3 ²⁹ [104],[105]. **Table 4** compares the properties of orthophosphate anion with other isoelectronic ortho-oxyanions [106].

²⁷ Breccias are among the most common features in ore deposits. They are associated with numerous types of ores, of either endogenic or supergenetic origin, and in both subsurface and submarine environments. Breccia is a rock composed of angular fragments of preexisting rocks embedded in fine-grained matrix cement [101].

²⁸ The Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) was formed in July 2006 by a merger between the Commission on New Minerals and Mineral Names (CNMMN) and the Commission on Classification of Minerals, at the request of both commissions.

²⁹ Please see the discussion dedicated to the nomenclature of other minerals with the structure of apatite in **Section 1.1**.


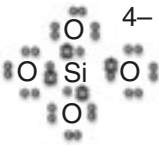
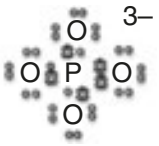
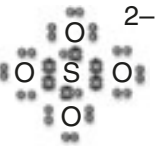
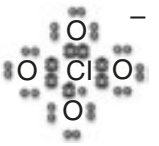
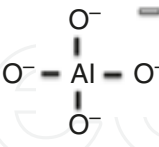
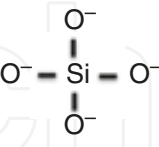
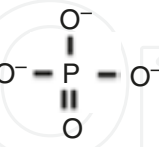
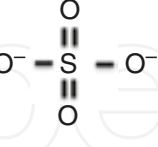
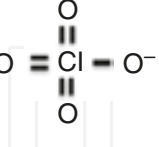
Anion	AlO ₄ ⁵⁻	SiO ₄ ⁴⁻	PO ₄ ³⁻	SO ₄ ²⁻	ClO ₄ ⁻
Electron formula					
Valence bonds					
Electrostatic formula	$\text{O}^{2-} \text{ Al}^{3+} \text{ O}^{2-}$	$\text{O}^{2-} \text{ Si}^{4+} \text{ O}^{2-}$	$\text{O}^{2-} \text{ P}^{5+} \text{ O}^{2-}$	$\text{O}^{2-} \text{ S}^{6+} \text{ O}^{2-}$	$\text{O}^{2-} \text{ Cl}^{7+} \text{ O}^{2-}$
Electrostatic strength	2/3	2/4	2/5	2/6	2/7
Observed length [Å]	1.77	1.62	1.54	1.49	1.46
Sum of covalent radii	1.92	1.83	1.76	1.70	1.65
Corrected sum	1.74	1.68	1.63	1.61	1.60
Ionic character of bond [%]	63	51	39	22	6
Acid strength (K ₁)	10 ⁻¹	10 ⁻¹⁰	10 ⁻²	10 ³	10 ⁸
Sodium salt	Na ₅ AlO ₄	Na ₄ SiO ₄	Na ₃ PO ₄	Na ₂ SO ₄	NaClO ₄
Density [g·cm ⁻³]	2.57	–	2.54	2.66	2.50
Melting point [°C]	–	1018	1530	884	468
Solubility [g/100 g H ₂ O]	–	5.0	12.1	19.5	201.0

Table 4. The comparison of properties of isoelectric ortho-oxyanions [106].

The crystal structure of apatite (*sensu stricto* fluorapatite) was first independently solved in 1930 by MEHMEL [107] and NÁRAY-SZABÓ [108]. The archetype crystalline³⁰ structure of apatite is hexagonal with the space group P6₃/M and the unit-cell parameters *a* = 9.3–9.6 and *c* = 6.7–6.9 Å. The above-mentioned generic crystal-chemical formula can be also written as follows [45], [109],[148]:

$$\text{}^{\text{IX}}\text{M}(1)_4 \text{}^{\text{VII}}\text{M}(2)_6 \left[\text{}^{\text{IV}}\text{XO}(1)\text{O}(2)\text{O}(3)_2 \right]_6 \text{}^{\text{Z}}_2;$$

³⁰ The term crystalline means atomic ordering on the scale that can produce an “indexable” (i.e. with Mille indices) diffraction pattern when the substance is traversed by a wave with suitable wavelength (X-ray, electrons, neutrons, etc.). However, some amorphous substances (e.g. georgeite, calciouranoite) were also accepted as minerals by the CNMMN.

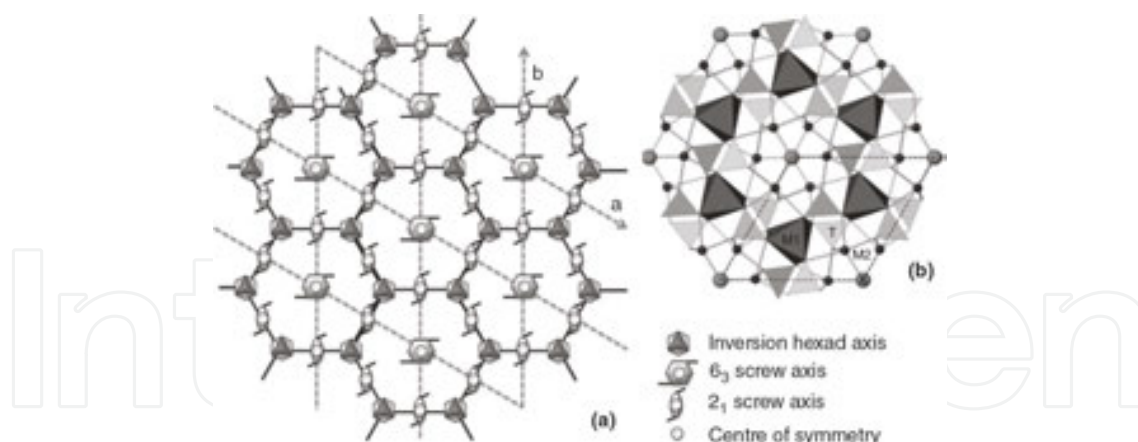


Fig. 6. Vertical symmetry elements of the space group $P6_3/M$ (a) [38] and the crystal structure of apatite as seen along c -axis (b) [45].

where left superscripts indicate ideal coordination numbers. **M** represents large cations, **X** represents metal or metalloids and **Z⁻** represents anion (sometimes termed as column anion) [109].

Minerals from apatite group belong to the hexagonal–dipyramidal crystal system with the space group $P6_3/M$ (fluorapatite, hydroxylapatite and chlorapatite [45]), to trigonal–pyramidal system with the space group $P3$ (belovite–Ce [110]), also to trigonal–rhombohedral system with the space group $P\bar{3}$ (belovite–La [45],[111]) and to hexagonal–pyramidal system with the space group $P6_3$ (fluorcapthite [45],[112],[113]).

Fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, FA), chlorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$, ClA) and hydroxylapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_2$, HA) are the most important end members of apatite groups of minerals (**Table 7**). The hexagonal ($P6_3/M$) and monoclinic ($P2_1/B$) polymorphs³¹ of apatite were described in literature [45],[104],[114].

The $P6_3/M$ space group **Fig. 6(a)** has three kinds of vertical symmetry elements [37]:

1. Sixfold screw axes passing through the corners of the unit cells. These symmetry elements are equivalent to a threefold rotation axis with a superimposed twofold screw axis.
2. Threefold rotation axes passing through $2/3, 1/3, 0$ and $1/3, 2/3, 0$.
3. Twofold screw axes passing through the midpoints of the cell edges and its center.

There are also mirror planes perpendicular to the c -axis and $z = 1/4, z = 3/4$ and numerous centers of symmetry.

³¹ Polymorphic minerals are those that have essentially the same chemical composition but different crystal structures. The polymorphic forms of minerals are considered as different species if their structures are topologically different. For example, graphite and carbon are polymorphs of crystalline carbon; both have the same composition, but their structures are topologically different and therefore the minerals such as these are considered as separate species [4].



Fig. 7. The nearest neighbor of Ca(1)O₉ and Ca(2)O₅Z(O) cationic polyhedral sites in the apatite structure (a) [115] and in the structure of [PO₄]³⁻ tetrahedra (b) [33].

The P6₃/M structure of calcium apatites **Fig. 6(b)** consists of isolated PO₄ (in general XO₄) tetrahedra centered at $z = \frac{1}{4}$ and $\frac{3}{4}$ are linked by **Ca(1)** (**M(1)**) in ninefold (6+3, 3 × O₁, 3 × O₂ and 3 × O₃ atoms) coordinated cation polyhedron (**M(1)O₉**) with a **Ch** site symmetry and **Ca(2)** (**M(2)**) in irregular sevenfold (6+1, O₁, O₂ and 4 × O₃ + **Z**) coordinated polyhedron (**M(2)O₅Z(O)**) with **Cs** site symmetry (**Fig. 7**). The **M(1)O₉** polyhedra share (0001) pinacoid¹⁰ faces to form channel parallel to *c*-axis. In some cases, the **M(1)** sites are split into pairs of nonequivalent sites, which correspond to lowering of space group symmetry. The **M(2)** sites may be more irregular and the central cation may be considered to be eightfold (**M(2)O₅Z**) or ninefold (**M(2)O₅Z(O)**) coordinated. A prominent feature of the structure is large *c*-axis channels (apatitic channels [105] or anionic columns), which accommodate **Z** anion (**Fig. 8**). In other words, the **M(1)₄(XO₄)₆** framework creates tunnels with the diameter adjusted to filling characteristics of **M(2)O₅Z(O)** components [33],[109],[115],[116].

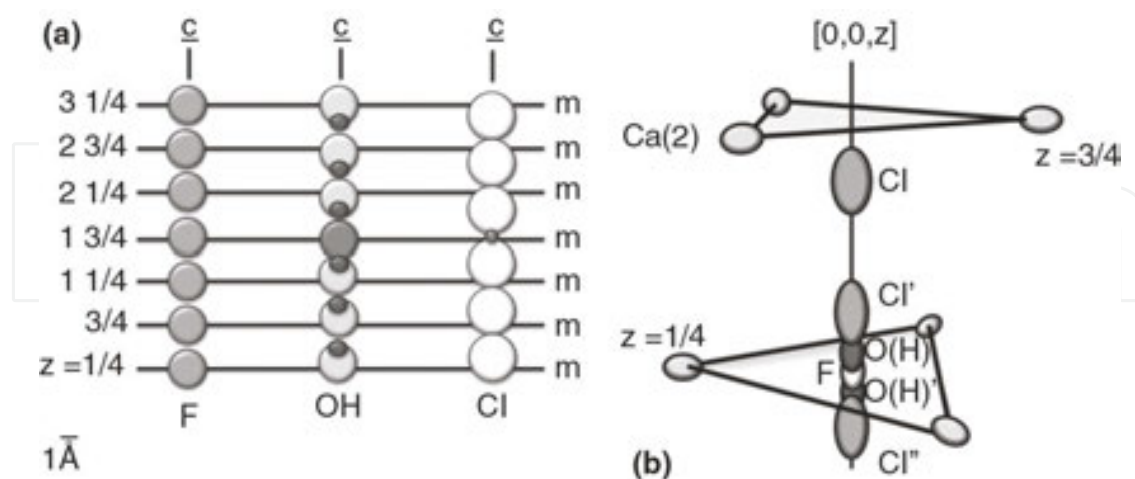


Fig. 8. Anion column in the hexagonal structure of fluor-, hydroxyl- and chlorapatite (a) [33] and depiction of triangle formed by Ca(2) atoms: Z' and Z'', which denotes atoms disordered above and below the mirror plane (b) [116].

Adjacent Ca(1) and Ca(2) polyhedra are linked through oxygen atoms shared with PO₄ tetrahedra. The relationships among ionic sites and multiplicity and Wyckoff positions in all

known space groups of apatite supergroup mineral are shown in **Table 5** [33],[38],[45], [66], [104],[117],[118].

Site	P6 ₃ /m	P6 ₃	P6̄	P3̄	P3	P2 ₁ /m	P2 ₁
M(1)	4f ³²	2 × 2b	2i, 2h	2 × 2d	2 × 1b, 2 × 1c	4f	2 × 2a
M(2)	6h	6c	3k, 3j	6g	2 × 3d	2a, 2 × 2e	3 × 2a
X	6h	6c	3k, 3j	6g	2 × 3d	3 × 2e	3 × 2a
O	2 × 6h, 12i	4 × 4c	2 × 3k, 2 × 3j, 2 × 6l	4 × 6g	8 × 3d	6 × 2e, 3 × 4f	12 × 2a
Z	2a or 2b or 4e (×0.5)	2a	1a, 1b or 2g	1a, 1b	2 × 1a	2a or 2e	2a

Table 5. Structure site multiplicities and Wyckoff positions for all known space groups of apatite supergroup minerals [45].

The anion column in fluorapatite **Fig. 8(F)** shows fluoride anion located on the mirror plane at $z = \frac{1}{4}$ and $\frac{3}{4}$ in successive unit cells. Three successive hydroxyls in hydroxylapatite (column **OH**) are disordered 0.35 Å above the mirror planes and three successive hydroxyls are below the mirror planes, with the sense of disordering reversed by an impurity of fluoride anion (stippled circle at the position $z = 1\frac{3}{4}$). In the column “**Cl**” of chlorapatite, there are three successive anions disordered about 1.2 Å above and three below the mirror planes. The vacancy (□) at $z = 1\frac{3}{4}$ in chlorapatite must exist in order to reverse the sense of ordering, as F and OH species are prohibited [33],[116].

Each F is bonded to three Ca(2) atoms, which form a triangle within the mirror plane **Fig. 8(b)** and **Fig. 16(b)**. Because of its larger size and longer Ca–Cl bond length as compared to Ca–OH and Ca–F, Cl anions in chlorapatite are displaced from the (0,0, $\frac{1}{4}$) special position on the mirror plane to two equivalent half-occupied positions at (0,0,0.4323) and (0,0,0.0677). In chlorapatite, Cl anion is displaced so far from the mirror plane (1.2 Å) that a weak bond (0.09 valence units) forms between Ca(2) and the second Cl anion, Cl', located one-half unit cell away along *c* (Ca(2)-Cl' bond distance is 3.27 Å). Slight overbonding of Ca(2) because of this weak Ca(2)-Cl' interaction is balanced through reduced bonding between Ca(2) and, O(1) in chlorapatite [33].

The species-forming substitutions at the **Z** anionic site are limited to the monovalent anions F⁻, Cl⁻ and OH⁻. This implies 50 negative charges per unit cell (i.e. 24 O²⁻ + (F,Cl,OH)⁻) for all known apatite minerals. In addition, many studies of synthetic compounds with the apatite structure show that Z site is occupied by O²⁻, which increases total negative charges, vacancies and water molecules. The M site can be occupied by Cd, Co, K and by almost all REE. The X site can be occupied by Be, Cr, Ge and Mn [45].

³² Consists of Wyckoff letter (f) and multiplicity (4). The multiplicity of the Wyckoff position is equal to the number of equivalent points per unit cell.

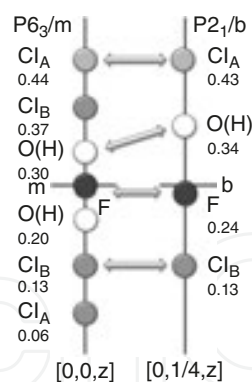


Fig. 9. Correlation between $P6_3/m$ and $P2_1/b$ sites in ternary apatites [116].

The difference between hexagonal and monoclinic polymorphs (e.g. apatite-(CaOH) and apatite-(CaOH)-M, see **Table 3**) lies in the position of Z^- anions along large c -axis channels³³ (apatitic channels or anionic columns). This gives the rise (or not) to a mirror plane but does not correspond to a large ion rearrangement [37]. As the average ionic radii increases, i.e. the size of the tunnel ion increases through the series $F > OH > Cl > Br$, the metaprism untwists to accommodate larger anion [45],[119]. The correlation between the column-anion sites is introduced in **Fig. 9**.

Monoclinic symmetry of mineral with the space group $P2_1/b$ named as clinohydroxylapatite [120] and subsequently renamed as apatite-(CaOH)-M [49] has typical axial setting of apatites resulting from the orientation ordering of OH^- anions within $[00z]$ anionic columns, with consequent doubling periodicity along $[010]$ (b -axis). The following unit-cell parameters are given: $a = 9.445 \text{ \AA}$, $b = 18.853 \text{ \AA}$, $c = 6.8783 \text{ \AA}$ and $\gamma = 120^\circ$ [33],[45],[116].

The structure of minerals from the family of apatite allows to formulate seven requirements, including the following [109]:

1. Cation ordering in chemically complex members with minimal $M(1)_4(XO_4)_6$ framework distortion (metaprism twist angle $< 25^\circ$) that is accommodated in the $P6_3$, $P\bar{6}$ and $P\bar{3}$ maximal isomorphic subgroup of $P6_3/M$.
2. Intra- and inter-tunnel anion ordering that leads to $P2_1/B$ varieties, possible modulation and extension of the (001) basal plane.
3. Framework topological tuning where the $M(2)Z_2$ tunnel contents are sufficiently small or substoichiometric so that the framework must constrict by increasing $M(1)O_6$ metaprism twist angle to $> 25^\circ$, which is accompanied by a reduction to $P2_1/M$, $P2_1$, or P symmetry.
4. Framework hybrid intergrowth in which oxygen super- and substoichiometry leads to partial or complete replacement of BO_4 tetrahedra by BO_5 and BO_3 polyhedra, sometimes accompanied by a reduction in symmetry.

³³ The positions of noncolumn atoms in $P2_1/B$ ternary apatite are similar to those in $P6_3/M$ ternary apatite [116].

- Polymorphic transformations initiated by the application of temperature/pressure that changes ionic sizes to drive the framework tuning.
- Pseudomorphism whereby quite compositional adjustments lead to breaches in the critical limit of the metaprism twist angle and to the change in symmetry.
- Polysomatism that arises by rotational twinning of $M_5X_3O_{18}Z_8$ modules in ordered and disordered sequences [109].

1.3
Polysomatic apatites

Less known polysomes of apatite are **ganomalite**³⁴ ($Pb_3Ca_2(SiO_4)(Si_2O_7)$ [121],[122],[123]) and **nasonite**³⁵ ($Ca_4Pb_6(Si_2O_7)_3Cl_2$ [124]) [109],[125],[126]. The concept of polysomatism was extensively developed by THOMPSON [127] and VEBLEN [128] for the crystallochemical analysis of rock-forming silicates and is a widely applied taxonomic principle for the description of condensed matter. Numerous polysome families include perovskite derivatives such as layered high T_c superconductors [129],[130],[131],[132], fluorite superstructures found in high-level nuclear ceramics [133] and β -alumina-hibonite ($CaAl_{12}O_{19}$) materials [134],[135],[136], which are encountered in superionic conductivity [109].

N	Crystallochemical formulae	Chemical formulae	Stacking sequence
2	$M_{10}(XO_4)_6Z_{28}$	$M_{10}X_6O_{24}Z_{28}$ ¹⁾	$\dots\beta(\alpha\beta)\alpha\dots$
3	$M_{15}(X_2O_7)_3(XO_4)_3Z_{36}$	$M_{15}X_9O_{33}Z_{36}$ ²⁾	$\dots\beta(\alpha\alpha\beta)\alpha\dots$
4	$M_{20}(X_3O_{10})_3(XO_4)_3Z_{48}$	$M_{20}X_{12}O_{42}Z_{48}$	$\dots\beta(\alpha\alpha\alpha\beta)\alpha\dots$
	$M_{20}(X_2O_7)_6Z_{48}$	$M_{20}X_{12}O_{42}Z_{48}$ ³⁾	$\dots\beta(\alpha\alpha\beta\beta)\alpha\dots$
5	$M_{25}(X_4O_{13})_3(XO_4)_3Z_{56}$	$M_{25}X_{15}O_{51}Z_{56}$	$\dots\beta(\alpha\alpha\alpha\alpha\beta)\alpha\dots$
	$M_{25}(X_3O_{10})_3(X_2O_7)_3Z_{56}$		$\dots\beta(\alpha\alpha\alpha\beta\beta)\alpha\dots$
6	$M_{30}(X_5O_{15})_3(XO_4)_3Z_{66}$	$M_{30}X_{18}O_{60}Z_{66}$	$\dots\beta(\alpha\alpha\alpha\alpha\alpha\alpha)\alpha\dots$
	$M_{30}(X_4O_{13})_3(X_2O_7)_3Z_{66}$		$\dots\beta(\alpha\alpha\alpha\alpha\beta\beta)\alpha\dots$
	$M_{30}(X_3O_{10})_6Z_{66}$		$\dots\beta(\alpha\alpha\alpha\beta\beta\beta)\alpha\dots$
7	$M_{35}(X_6O_{19})_3(XO_4)_3Z_{78}$	$M_{35}X_{21}O_{69}Z_{78}$	$\dots\beta(\alpha\alpha\alpha\alpha\alpha\alpha\beta)\alpha\dots$
	$M_{35}(X_5O_{16})_3(X_2O_7)_3Z_{78}$		$\dots\beta(\alpha\alpha\alpha\alpha\alpha\beta\beta)\alpha\dots$
	$M_{35}(X_4O_{13})_3(X_4O_{10})_3Z_{78}$		$\dots\beta(\alpha\alpha\alpha\alpha\beta\beta\beta)\alpha\dots$
8	$M_{40}(X_7O_{22})_3(XO_4)_3Z_{88}$	$M_{40}X_{24}O_{78}Z_{88}$	$\dots\beta(\alpha\alpha\alpha\alpha\alpha\alpha\beta\beta)\alpha\dots$
	$M_{40}(X_5O_{16})_3(X_3O_{10})_3Z_{88}$		$\dots\beta(\alpha\alpha\alpha\alpha\alpha\beta\beta\beta)\alpha\dots$
	$M_{40}(X_4O_{13})_6X_{66}$		$\dots\beta(\alpha\alpha\alpha\alpha\beta\beta\beta\beta)\alpha\dots$

³⁴ Greek name reflecting luster appearance of mineral.

³⁵ Mineral is named according to American geologist LEWIS NASON.

N Crystallochemical formulae	Chemical formulae	Stacking sequence
∞ $M_5(X_3O_9)X_6$	$M_5X_3O_9Z_6$	$\dots\alpha(\alpha)\alpha\dots$
¹⁾ Apatite	²⁾ Ganomalite	³⁾ Nasonite

Table 6. Staking sequence and compositions of polysomic apatites [109].

Certain complex structures are logically considered as intergrowths of chemically or topologically discrete modules. When the proportions of these components vary systematically, a polysomatic series is created. Certain complex structures are logically considered as intergrowths of chemically or topologically discrete modules. When the proportions of these components vary systematically a polysomatic series is created, the creation of which provides a basis for understanding the defects, the symmetry alternation and the trends in physical properties. The composition of polysomic family, which is formed by the condensation of N -modules of apatite (where N is the number of modules in the crystallographic repeat, **Table 6**) units of $M_5X_3O_{18}X_6$, can be described by the formula [109]:

$$M_{6N}X_{3N}O_{9N+6}X_N.$$

The apatite modules condense in a configuration to create B_nO_{3n+1} , where the values of n vary in range: $1 \leq n \leq \infty$. For $N = 2$, the composition of polysome corresponds to the hydroxylapatite, e.g. $Ca_{10}(PO_4)_6(OH)_2$ if $M = Ca$, $X = P$ and $Z = OH$.

Based on the value of parameter N , the following polysomes of apatite are recognized [109]:

1. Apatite: the value of $N = 2$ and the general composition corresponds to the formula $M_{10}X_6O_{24}Z_2$. Although, there are an infinite number of possible arrangements ($2 \leq N \leq \infty$), the ideal composition of apatite has the value of N from 2 to 8.
2. Ganomalite: the value of $N = 3$ and the general composition corresponds to the formula $M_{15}(X_2O_7)_3(XO_4)_3Z_3$.
3. Nasonite: the value of $N = 4$ and the general composition corresponds to the formula $M_{20}(X_2O_7)_6Z_4$.

The Z site could be vacant or partially occupied as required from the charge balance, and the $M:X$ ratio must be maintained 5:3 (**Table 7**).

The apatite modules, while topologically identical, are often compositionally or symmetrical-ly distinct and an infinite number of polysomes are feasible. The end members are the $N = 2$ polysome with all tetrahedra separated, and $N = \infty$ polysome, in which the hypothetical compound $M_5X_3O_9Z$ contains infinite, corner connected tetrahedral strings [109].

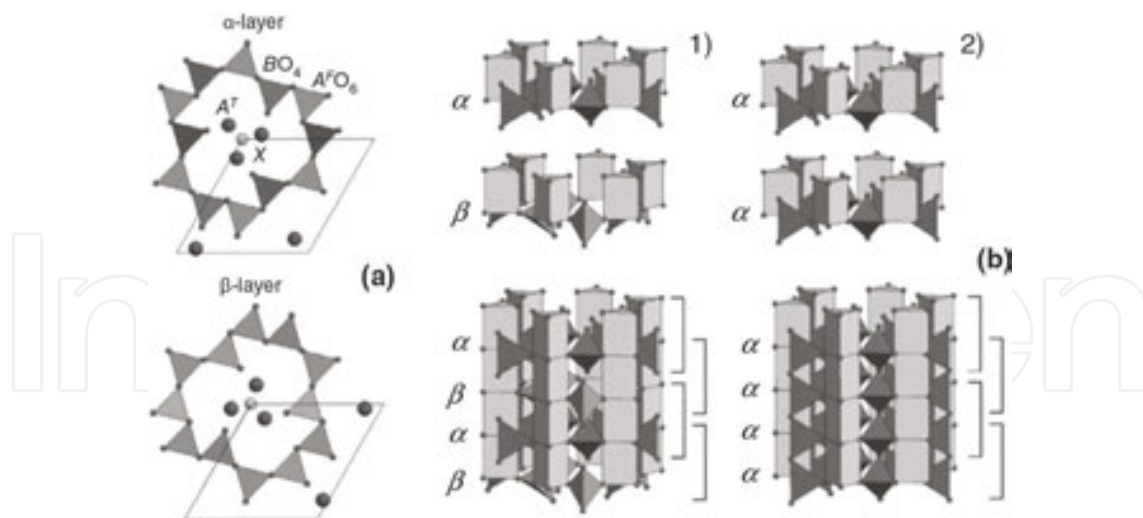


Fig. 10. Schematic representation of α and β , $M_5X_3O_{18}Z_2$ apatite modules (assuming a hexagonal basal plane), which are related by $[0001]_{\text{hex}}$ 60° rotation twinning. The principal idealization is that the M^FO_6 polyhedron is represented as a trigonal prism, but in real polysomes, twisting of the triangular faces through an angle φ creates a metaprism (a). Stacking of a and b modules show the construction of ... $\beta(\alpha\beta)\alpha$... apatite-2H $M_{10}(XO_4)_6Z_2$ (1) and the hypothetical structure ... $\alpha(\alpha)\alpha$... apatite-1H $M_5(X_3O_9)Z$ polysome end members (2). The coincident lattice where the condensation and elimination of oxygen take place is emphasized by brackets (M^T and Z ions are not included) (b) [109].

An idealized polysome module of apatite has the composition of $M(1)_2M(2)_3X_3O_{18}Z$ and the thickness of $\sim 3.5\text{\AA}$. These modules can occupy a hexagonal unit cell in two orientations, designated α and β layers **Fig. 10(a)**, which are rotated by 60° with respect to each other, with the condensation leading to the elimination of oxygen from coincident lattice position. The layers joint without the rotation create corner-connected B_nO_{3n+1} ($n = \infty$) tetrahedral strings,

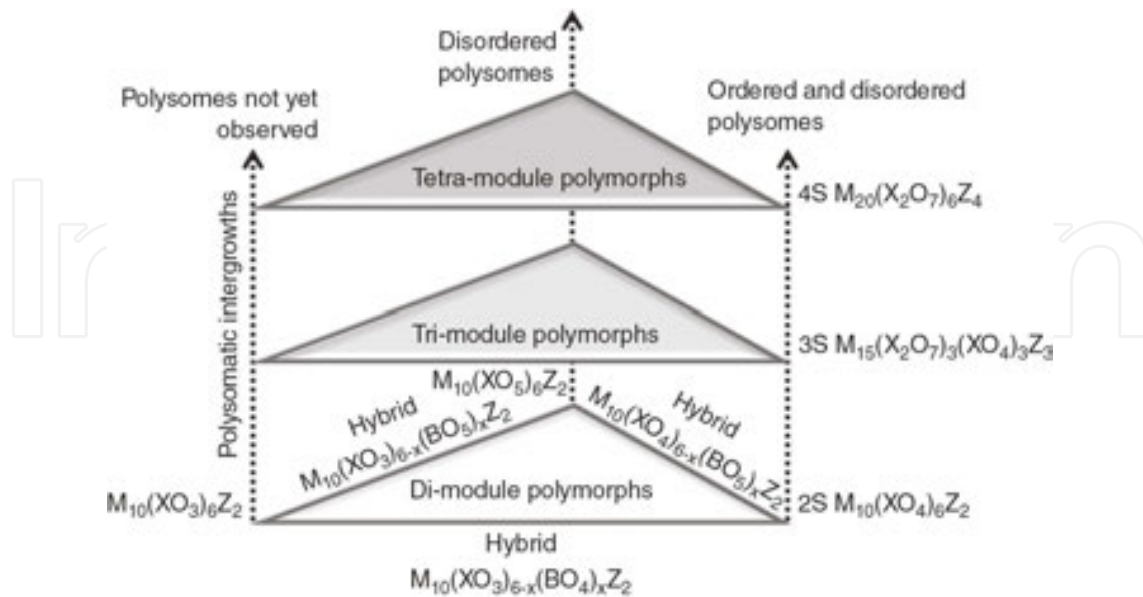


Fig. 11. Expanded apatite phase space containing all permutations of polymorphs, pseudomorphs, polysomes and hybrid structures, which may be feasible [109].

which can be broken through the introduction of a rotated layer. The case when the modules are placed directly upon one another in the sequence ... $\alpha(\alpha)\alpha$... (**Fig. 10(b)**), of the composition that corresponds to the hypothetical compounds $M(1)_2M(2)_3X_3O_9Z$ with continuous chains of corner connected tetrahedral is created. Alternatively, if every module is rotated by 60° (rotationally twinned) with respect to the order ... $\beta(\alpha\beta)\beta$..., six oxygens per layer pair are duplicated in the trigonal prisms and overall composition of polysome is $M(1)_4M(2)_6X_6O_{24}Z_2$. This motive can be found in the mineral mattheddleite $(Pb(1)_4Pb(2)_6[Si/SO_4]_6(Cl,OH)_2)$ [109].

The prism of expanded apatite space (**Fig. 11**) enables to formulate new derivatives via the creation of $M(1)_4M(2)_6(XO_3/XO_4/XO_5)_6Z_2$ hybrids, which may display the polysomatic character [109].

1.4. Chemical composition of apatite supergroup minerals

The general formula of apatite compounds several times mentioned above $(Ca_{10}(PO_4)_6(F,Cl,O)_2)$ or $3Ca_3(PO_4)_2 \cdot Ca(F_2,Cl_2,O)$ was given by VOELCKER [74] and HOSKYNS-ABRAHALL [137]. RAMMELSBERG [138] assumed the existence of compound $Ca_{10}P_6O_{25}$ (equivalent to $3Ca_3(PO_4)_2 \cdot CaO$) to explain the chemical composition of various apatites, although he thought the presence of this molecule was due to alteration. GROTH [139] substituted hydroxyl for oxygen and gave the formula $(PO_4)_3(Cl,F,OH)Ca_5$. He was followed by LACROIX, NAUMANN-ZIRKEL and others [73]. Many minerals of the apatite group are deficient in combined fluorine and chlorine [73],[74],[140]. This deficiency was generally explained by assuming the compound $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$ [73].

Based on the results of chemical analysis, the calculation of apatite formula $(M_5(XO_4)_3Z)$ can be determined according to the following criteria [45]:

- a. Calculation on the basis of 13 total anions
- b. Calculation on the basis of 8 total (M+X) cations
- c. Calculation on the basis of 3X cations

In principle, criterion a is preferable to criteria b and c. In fact, the calculation based on any subset of all atoms does not affect the stoichiometric ration between them but automatically shifts the analytical error to the atoms not belonging to that subset. Criteria b and c would be best to use in cases in which structural vacancies are possible at some sites, but this does not seem to be the case for any apatite supergroup minerals [45].

Cations P^{5+} , As^{5+} , V^{5+} , Si^{4+} and S^{6+} can be assumed to be in tetrahedral coordination and assigned to X site in the formula of apatite. The total sum of these cation should be equal to 3 apfu³⁶ (in the single formula $M(1)_2M(2)_3(XO_4)_3Z$). All remaining cations enter **M(1)** and **M(2)** sites. The elucidation of partitioning between these two sites is almost impossible without an accurate evaluation of the electron density at each of them, which makes the structural study manda-

³⁶ The abbreviation for atoms per formula unit (apfu).

tory. Generally, **M**(1) sites (Wyckoff positions *4f* in $P6_3/M$ structure, **Table 5**) are occupied by smaller cations (in particular Ca) and **M**(2) sites (Wyckoff positions *6h*) accommodate larger cation³⁷ such as Ba^{2+} or Pb^{2+} [45].

1.5. Apatite group minerals

The apatite group includes minerals listed in **Table 3**. The most important are three minerals with ideal apatite formula $Ca_5(PO_4)_3F$, $Ca_5(PO_4)_3OH$ and $Ca_5(PO_4)_3Cl$ known as fluorapatite, hydroxylapatite and chlorapatite, respectively. They are recently renamed as apatite-(CaF), apatite-(CaOH) and apatite-(CaCl). The origin of those three distinct names to denote the F^- , OH^- and Cl^- variants and their distinction with respect to the “original apatite” *sensu lato* is uncertain [41],[45]. The composition and the cell dimension of major end members of apatite group minerals are listed in **Table 7**.

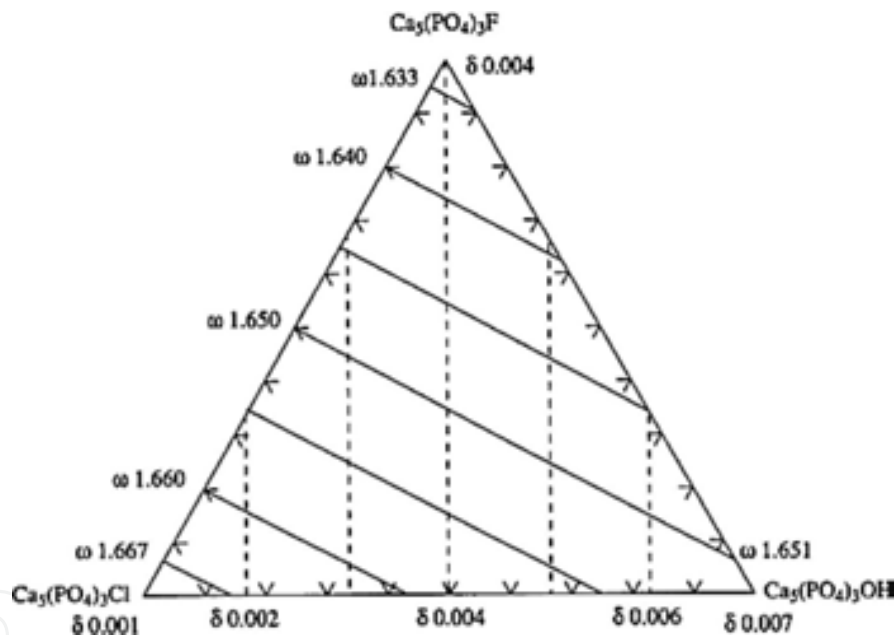


Fig. 12. Optical properties of fluoro-, hydroxyl- and chlorapatite series based on the values of end-member apatites [39].

Apatite is optically negative and normally uniaxial, although biaxial varieties with optic angle up to 20° are known. Carbonate bearing apatites (e.g. francolite), in particular way, have anomalous optics. Large variations in the composition within the apatite group make the accurate correlation of optical data difficult. The refractive index is the highest for chlorapatite (**Fig. 12**) and decreases by the substitutions of OH and F [39].

³⁷ The distribution of atoms at cationic sites can be affected also by Coulombic effect as was recognized for the structure of mineral aiolosite (**Section 2.1.5**) and cesanite (**Section 2.1.7**).

Mineral	Hydroxylapatite ³⁸ Apatite–(CaOH)	Fluorapatite Apatite–(F)	Chlorapatite Apatite–(Cl)	Carbonate–apatite –
Formula	Ca ₅ (PO ₄) ₃ OH	Ca ₅ (PO ₄) ₃ F	Ca ₅ (PO ₄) ₃ Cl	Ca ₅ [(PO ₄) _{3–x} (CO ₃ F) _x](F,OH,Cl)
Abbreviation ³⁹	HAP, OHAp, HAp	FAP, FAp	CLAP	CHAP, CFAP, CCLAP
M [g mol ^{–1}]	502.31	504.30	520.76	483.30 ⁴⁰
Crystal system	Hexagonal–bipyramidal, space group P6 ₃ /M			
a [Å]	9.42	9.39	9.60	9.36–9.32
c [Å]	6.87	6.88	6.78	6.89
a:c	1:0.73	1:0.73	1:0.71	1:0.73–0.74
V [Å ³]	527.59	526.03	540.59	520.97–529.06
Z	2			
CaO [%]	55.82	55.60	53.84	57.83 (CHAP) 57.60 (CFAP)
P ₂ O ₅ [%]	42.39	42.22	40.89	36.66 (CHAP) 36.45 (CFAP)
X [%]	1.79	3.77	6.81	4.54(CO ₂),1.86(H ₂ O) 4.52(CO ₂),3.90(F)
Ca:P ratio	1.67 (5/3, ideal Ca:P ratio in the stoichiometric apatite ⁴¹)			
density ⁴² [g·cm ^{–3}]	3.10–3.21/3.16	3.10–3.25/3.18	3.17–3.18/3.17	3.04 (CHAP) 3.12 (CFAP)
Hardness	5 (Mohs scale)			
Refractive index, $\omega - \varepsilon = \delta$	Negative uniaxial (–)			
	1.651 - 1.644 = 0.007	1.633 - 1.1.629 = 0.004	1.677 - 1.676 = 0.001	1.603 - 1.598 = 0.005 1.628 - 1.619 = 0.009

Table 7. Composition and properties of calcium apatite end-member Ca₅(PO₄)₃Z.

1.5.1. Fluorapatite (Apatite–CaF))

Fluorapatite (Ca₁₀(PO₄)₆F₂, F-rich apatite, FAP and FAp) [45],[141] is the most common member in the group of apatite that can be found mainly in igneous rocks (fluorapatite is a common accessory mineral in syenites [39] and metamorphic environments, for example, in carbona-

³⁸ In some works termed as hydroxylapatite.

³⁹ The symbol Ap, e.g. in HAp, reflects the abbreviation of mineral in rocks and ores, i.e. apatite = Ap.

⁴⁰ Depends on the type of carbonated apatite (Section 2.6), Table 7 provides data for Ca₅(PO₄CO₃)₃OH (ideal composition of TYPE-B).

⁴¹ Apatite is known to be often nonstoichiometric, especially on the surface [41].

⁴² Measured/calculated density of mineral.

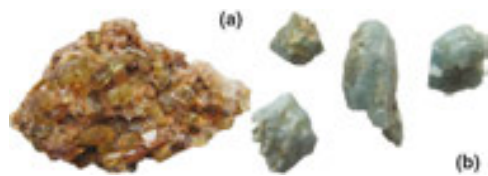


Fig. 13. Fluorapatite from (a) Cerro de Mercado Mine, Victoria de Durango, Mexico and (b) Sljudjanka, Bajkal, Russia.

tites and mica-pyroxenites [142]. The mineral crystallizes in the form of well-formed hexagonal crystals elongated on [0001], forms tabular to discoidal crystals flattened on {0001} or occurs as granular, globular to reniform, nodular and massive. The properties and chemical composition of fluorapatite mineral are listed in **Table 7**.

The color of fluorapatite mineral (**Fig. 13**) is pale green, green, light blue, yellow, purple, or white. Some varieties are colorless. Very brittle mineral gets broken to small fragments showing conchoidal fractures. Apatite shows poor cleavage on {0001} and {10 $\bar{1}$ 1}. Fluorapatite is the most insoluble from the phosphate minerals [143],[144]. Apatite forms rare contact twins on {11 $\bar{2}$ 1} or {10 $\bar{1}$ 3}. Some examples of fluorapatite crystals morphology are introduced in **Fig. 14**.



Fig. 14. Habit of fluorapatite crystals.

As was mentioned above (**Section 1.2**), fluorapatite was the first apatite with established structure [107],[108]. There is slight disagreement on the position of fluoride anion [145] Fluorapatite crystallizes in hexagonal dipyramidal crystal system with the parameters listed in **Table 7**. Atomic parameters including the number of atoms (N , where $\Sigma N = 42$) with equivalent site symmetry, their positions (coordinates x , y and z) in fractional coordinate system and equivalent isotropic temperature factor (B) for fluorapatite by HUGHES et al [33] are listed in **Table 8**.

Atom	N	Site symmetry	x	y	z	B [Å ²]
Ca(1)	4	C_{3h}	$2/3$	$1/3$	0.0010	0.91
Ca(2)	6	C_3	-0.00712	0.24227	$\frac{1}{4}$	0.77
P	6	C_s	0.36895	0.39850	$\frac{1}{4}$	0.57

Atom	N	Site symmetry	x	y	z	$B [\text{\AA}^2]$
O ₁	6	C _s	0.4849	0.3273	¼	0.99
O ₂	6	C _s	0.4667	0.5875	¼	1.19
O ₃	12	C _s	0.2575	0.3421	0.0705	1.32
F	2	E	0	0	¼	1.93

Table 8. Positional parameters and equivalent isotropic factor for fluorapatite [33],[148].

The lengths of bonds in the fluorapatite structure are listed in **Table 9**.

Bond	Length [Å]	Bond	Length [Å]
P-O(1)	1.537	Ca(2)-F	2.3108
P-O(2)	1.539	Ca(2)-O(1)	2.701
P-O(3)	1.532	Ca(2)-O(2)	2.374
Ca(1)-O(1)	2.399	Ca(2)-O(3)	2.349
Ca(1)-O(2)	2.457	Ca(2)-O(3)	2.501
Ca(1)-O(3)	2.807	–	–

Table 9. Bond lengths in the structure of fluorapatite [33].

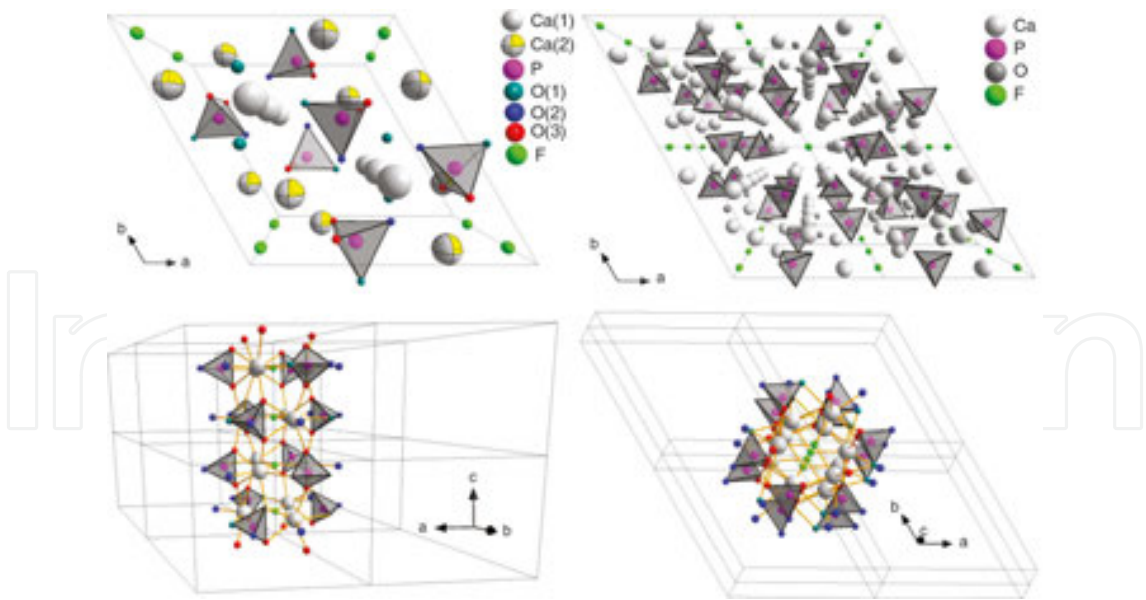


Fig. 15. Primitive unit cell of fluorapatite ($C_{10}(PO_4)_6F_2$) with atoms labeled according to symmetric type of element (a). The crystal structure of apatite (b, perspective view along the c -axis) and structure of columns (c, d).

The hexagonal crystal structure of fluorapatite of $P6_3/M$ space group is shown in **Fig. 15**. The atoms of Ca occupy two distinct sites [146], [147]:

- i. $\text{Ca(I)}\text{O}_9$ polyhedra in sevenfold coordination
- ii. $\text{Ca(II)}\text{O}_5\text{Z(O)}$ polyhedra in ninefold coordination

The length of $\text{Ca(2)}\text{-F}$ bond is 2.311 Å (**Table 7**). As was described in **Section 1.2**, each fluoride anion is surrounded by three Ca atoms (**Fig. 16(a)**) at one level, and in addition, Ca-O columns are linked with PO_4^{3-} groups forming hexagonal networks. This arrangement gives very stable structure to fluorapatite while the structure of hydroxylapatite is lightly expanded and less stable to compare with fluorapatite. F anions lie in special position at the intersections of hexads with mirror planes at $z = \frac{1}{4}$ and $\frac{3}{4}$ (**Fig. 16(b)**) [39],[147],[148].

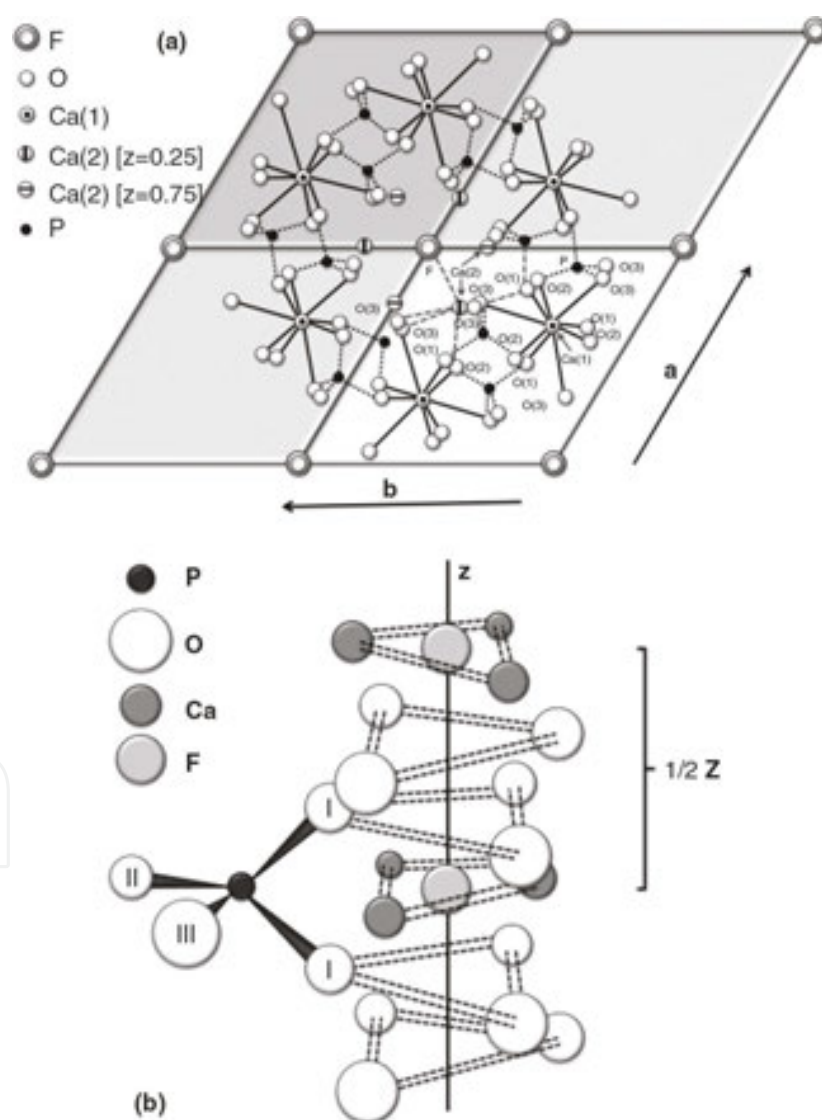


Fig. 16. Schematic depiction of a portion of four unit cells of the fluorapatite structure projected onto the (0001) plane. (a) Solid, dashed and dotted lines indicate bonds in different polyhedra. (b) The arrangement of Ca- and O-triangles on the screw axis (Z anion column) and attached PO_4^{3-} group [39].

The structure field of fluorapatite **Fig. 17** was investigated by KREIDLER and HUMMEL [149]. It is defined within the limits of radii of ions occupying the positions of phosphorus (R_p) and calcium (R_c) and is in the following range:

- i. $0.29 \leq R_p \leq 0.60 \text{ \AA}$
- ii. $0.95 \leq R_c \leq 1.35 \text{ \AA}$

The size limitations of ions occupying the calcium positions were less well defined because upper limit radius of ion was not found from the following reasons:

1. The only divalent cation larger than Ba^{2+} is Ra^{2+} .
2. Near the lower limit, apatites tended to have distorted structures, which no longer enabled hexagonal symmetry.

From practical proposes, the upper limit of R_c was set to 1.35 \AA , which is slightly greater than ionic radius of barium. The lower limit of R_c was set to 0.95 \AA so that both normal and distorted phases were included in the fluorapatite structure field.

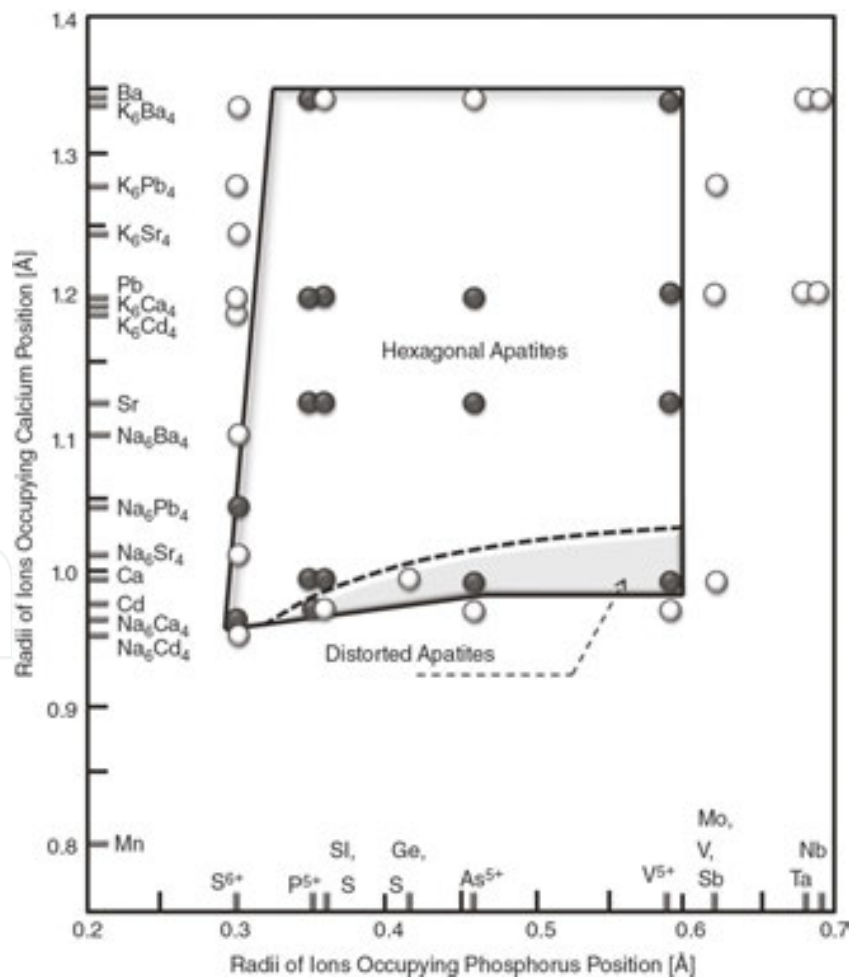


Fig. 17. The structure field of fluorapatite (Ahrens's radii): filled circles = apatite; open circles = no apatite [149].

The structure of monoclinic polymorph of fluorapatite is related to the space group $P2_1/B$ with the crystallographic parameters $a = 9.488$, $b = 18.963$, $c = 6.822\text{\AA}$, $\beta = 119.97^\circ$ and $Z = 6$ [145].

1.5.2. Hydroxylapatite (apatite-(CaOH))

Hydroxylapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAP, pentacalcium monohydroxyorthophosphate) can be found mainly in igneous and metamorphic environments but also in biogenic deposits, e.g. in bone deposits [38],[44],[142]. Hydroxylapatite is very rare mineral. Wax yellow crystals up to $6 \times 6 \times 11\text{ mm}$ have been described from talc schist⁴³ from the Old Verde Antique serpentine quarry near Holly Springs, Cherokee County, Georgia [38]. The properties of hydroxylapatite are summarized in Table 7. The structure of hydroxylapatite and the comparison of sizes of ions is shown in Fig. 18 and Fig. 19, respectively.

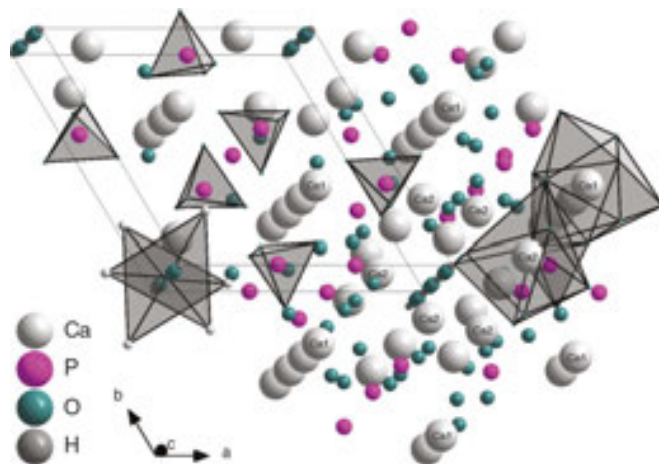


Fig. 18. The structure (view according to the c -axis) of hydroxylapatite showing the location of Ca(1) and Ca(2) sites.

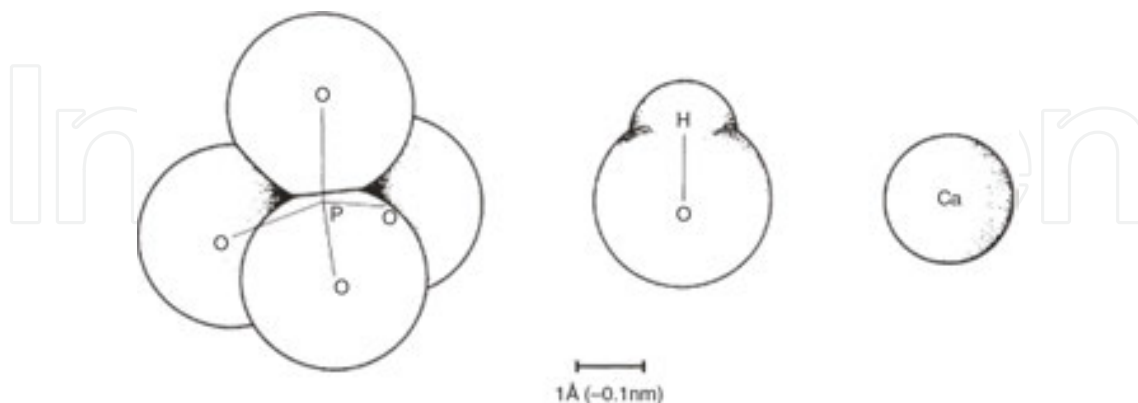


Fig. 19. The comparison of size of ions in the structure of hydroxylapatite [38].

⁴³ Medium-grade metamorphic rock occurred in almost infinite varieties, which was formed by the metamorphosis at high temperatures and pressure which leads to preferred orientation of flat (sheet-like) grains. The schist is medium to coarse grained.

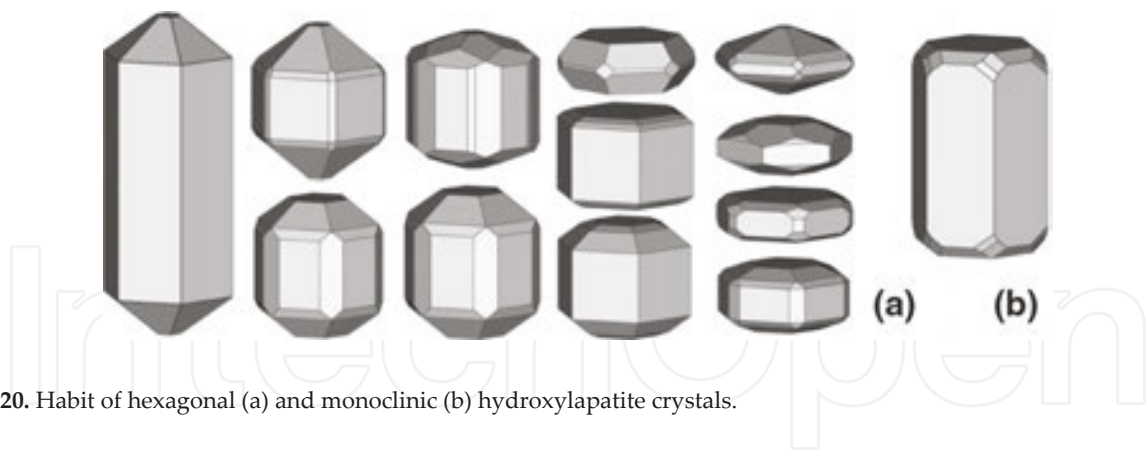


Fig. 20. Habit of hexagonal (a) and monoclinic (b) hydroxylapatite crystals.

The crystal habit and the structure of monoclinic polymorphs is show in **Fig. 20**. The monoclinic structure of hydroxylapatite (apatite–(CaOH)–M) appears to exist only in completely pure stoichiometric hydroxylapatite, and it is transformed to hexagonal form above about 250°C. The properties such as acid solubility and OH infusibility along the channels are related to the degree of disorder of OH positions. Hydroxyl anions lie in ordered positions in channels, whereas in hexagonal variety there is some disorder. Electrical properties are probably also dependent on exact channel position [106].

The atomic parameters (**Table 10**) and the length of bonds (**Table 11**) in the structure of hydroxylapatite were refined by POSNER et al [150] from the structural data collected on the crystal of synthetic hydroxylapatite specimen. The results of natural sample of near-end member hydroxylapatite were provided by HUGHES et al [33] and these data are also listed in **Table 10** and **Table 11**.

Hydroxylapatite is mainly used in the biomedical field for the preparation of bioceramics⁴⁴ [151],[152]. Since hydroxylapatite (HAp) is chemically similar to inorganic component of bone matrix and has excellent biocompatibility and surface active properties with living tissues, it has become one of the most important materials for artificial bone and bone regeneration [153], [154]. HA ceramics together with β -tricalcium phosphate have been the most extensively used substitution materials for artificial bone grafts for nearly three decades [153] (described in **Section 10.9**).

Atom	N	x	y	z	B [Å ²]
Ca(1)	4	0.333/2/3	0.667/1/3	0.001/0.00144	0.666/0.929
Ca(2)	6	0.246/-0.00657	0.993/0.24706	0.250/1/4	0.328/0.859
P	6	0.400/0.36860	0.369/0.39866	0.250/1/4	0.192/0.62
O1	6	0.329/0.4850	0.484/0.3289	0.250/1/4	0.295/1.00

⁴⁴ Bioceramics can be divided into two large groups: bioinert and bioactive ceramics. The bioinert ceramics have almost no influence on surrounding living tissues like ZrO₂ and Al₂O₃. In contrast, the bioactive ceramics like calcium phosphates are able to bond with living tissues (**Section 10.9**).

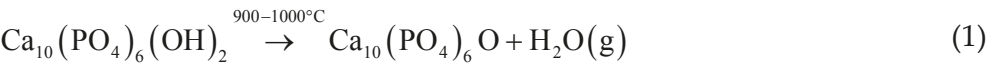
Atom	N	x	y	z	B [Å ²]
O2	6	0.589/0.4649	0.466/0.5871	0.250/1/4	0.496/1.25
O3	12	0.348/0.2580	0.259/0.3435	0.073/0.0703	0.632/1.57
OH		20.0/0.0	0.0/0.0	0.250/0.1979 O(H) -/0.04 H	0.875/1.31 -/3.3

Table 10. Atomic parameters for synthetic [150]/natural [33] hydroxylapatite: number of atoms per formula unit (N), positional parameters (x, y and z) and equivalent isotropic temperature factor (B).

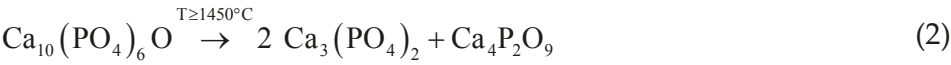
Bond	Length [Å]	Bond	Length [Å]
P-O1	1.533/1.534	Ca(2)-OH	2.354/2.3851
P-O2	1.544/1.537	Ca(2)-O1	2.712/2.711
P-O3	1.514/1.529	Ca(2)-O2	2.356/2.353
Ca(1)-O1	2.416/2.404	Ca(2)-O3	2.367/2.343
Ca(1)-O2	2.449/2.452	Ca(2)-O3	2.511/2.509
Ca(1)-O3	2.802/2.802	–	–

Table 11. Length of bonds in the structure of synthetic [150]/natural [33] hydroxylapatite based on the parameters from Table 10.

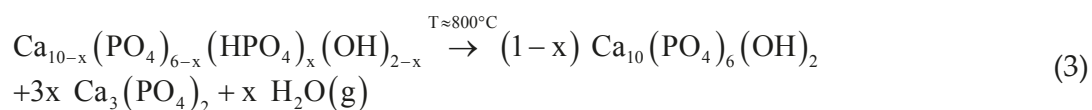
The dehydroxylation of stoichiometric hydroxylapatite to oxyapatite takes place within the temperature range from 900°C to 1200°C [114]:



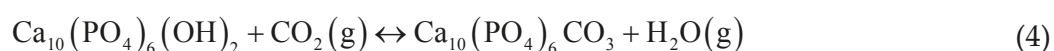
Further heating to temperatures higher than 1450°C leads to the thermal decomposition of oxyapatite into tricalcium phosphate (TCP, $\alpha\text{-Ca}_3(\text{PO}_4)_2$) and tetracalcium phosphate (TTCP, $\text{Ca}_4\text{P}_2\text{O}_9$):



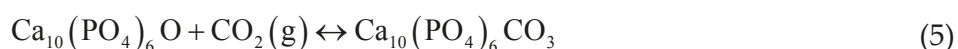
Calcium deficient hydroxylapatite decomposes at lower temperatures (at about 800°C) to stoichiometric hydroxylapatite and tricalcium phosphate according to their stoichiometry:



Another important option for utilization of hydroxylapatite is the preparation of porous high-temperature sorbent for carbon dioxide [155]. Apatite materials can be employed in discontinuous operations for removing CO₂ from gaseous streams in the form of structured monoliths or foams, with reduced pressure drops and enhanced refractory properties. High-temperature capture of carbon dioxide by hydroxylapatite proceeds via following reversible chemical reaction⁴⁵ [155]:



A similar reaction is also possible with oxy-apatites:



The highest CO₂ carrying capacity of HA macrogranules was detected at temperatures from 1000°C to 1100°C, achieving the values close to the theoretical limits. The changes in the HA microstructure induced during the thermal treatment (sintering) reduce the reactivity [155].

Since in the next decades the exploitation of fossil resources will continue and is expected to increase, rising the impact of fossil energy on the pollution and greenhouse effect, current technologies must be improved to become less harmful to the environment and more sustainable (zero emissions). The capture and the sequestration of CO₂ generated from the conversion of fossil fuels are being investigated as effective measures to reduce greenhouse gas emissions [156]. The apatite materials seem to be suitable sorbents for this purpose [155].

1.5.3. Chlorapatite (apatite–CaCl)

Calcium chlorapatite, as mineral, is relatively much less frequent than fluorapatite or hydroxylapatite and is formed primarily in flour-deficient environment [157]. The mineral crystallizes in the hexagonal system and the crystals are prismatic in habit, usually long, sometimes short and may have rounded ends or be terminated by pyramidal faces. Sometimes it occurs in granular massive to compact form [158]. The crystal habit and the structure of chlorapatite and monoclinic polymorphs chlorapatite–M are shown in **Fig. 21**. The crystallographic parameters and the properties are listed in **Table 7**.

⁴⁵ The preparation of carbonated apatites (**Section 4.6.1**) is based on the same principle as shows more general equation **Eq. 37**.

Chlorapatite mineral can be found as a mineral in calcium silicate marble, is an accessory mineral in layered mafic intrusions, occurs in veins such as “diabase,” and replaces “triphy-lite” in some granite pegmatites. Such deposits are found in the USA; Quebec, Canada; Bushveld complex of Transvaal, South Africa; Angarth-Sud Tazenekht Plain of Morocco; Rajagarth, India; Kurokura, Japan; and Snarum, Norway [157].

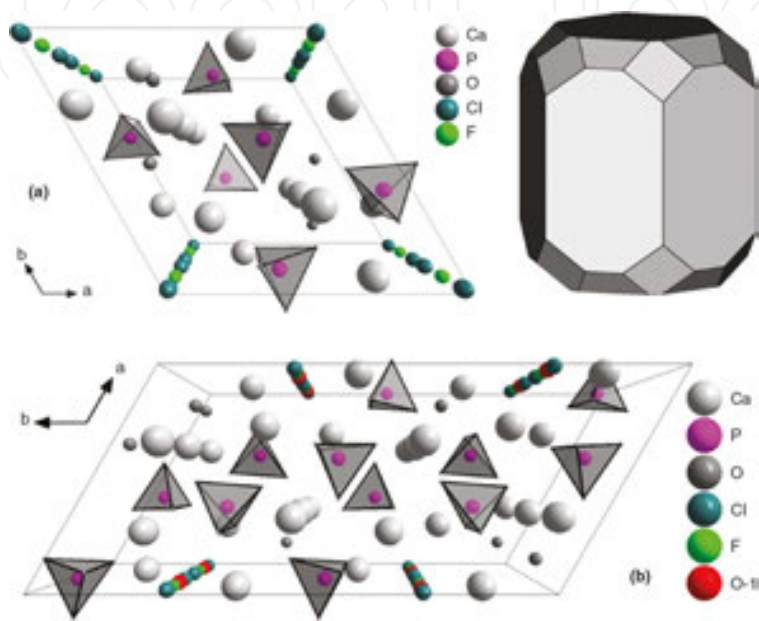


Fig. 21. Structure (perspective view according to the *c*-axis) and crystal habit of chlorapatite ([33], a) and chlorapatite-M ([116], b).

Atom	<i>N</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> [Å ²]
Ca(1)	4	2/3	1/3	0.0027	0.99
Ca(2)	6	0.00112	0.25763	1/4	1.14
P	6	0.37359	0.40581	1/4	0.77
O ₁	6	0.4902	0.3403	1/4	1.34
O ₂	6	0.4654	0.5908	1/4	1.47
O ₃	12	0.2655	0.3522	0.0684	1.88
Cl	2	0	0	0.4323	2.68

Table 12. Positional parameters and equivalent isotropic factor for chlorapatite [33].

The atomic parameters and equivalent isotropic temperature factor for chlorapatite by HUGHES et al [33] are listed in **Table 12**. The lengths of bonds in the chlorapatite structure are listed in **Table 13**.

Bond	Length [Å]	Bond	Length [Å]
P-O1	1.533	Ca(2)-F	2.759
P-O2	1.538	Ca(2)-O1	2.901
P-O3	1.524	Ca(2)-O2	2.306
Ca(1)-O1	2.407	Ca(2)-O3	2.331
Ca(1)-O2	2.448	Ca(2)-O3	2.254
Ca(1)-O3	2.793	—	—

Table 13. Bond lengths in the structure of chlorapatite [33].

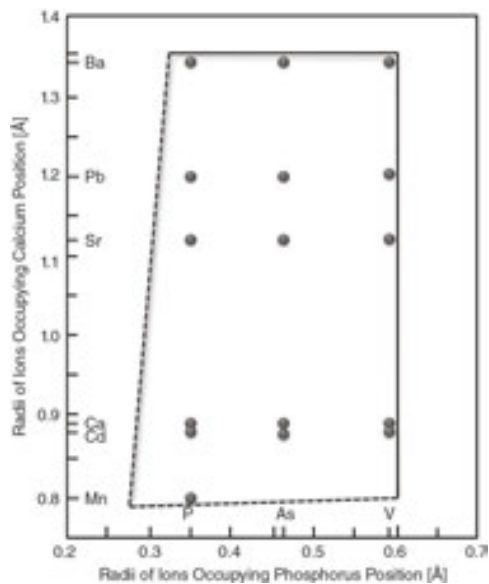


Fig. 22. The structure field of chlorapatite (Ahrens's radii) [149].

Together with fluorapatite, chlorapatite forms the solution⁴⁶ $[\text{Ca}_5(\text{PO}_4)_3\text{F}]_{1-x} \cdot [\text{Ca}_5(\text{PO}_4)_3\text{Cl}]_x$, where parameter x varies in the range from 0 to 1) on whole range of composition [157].

The chlorapatite structural field (**Fig. 22**) was investigated by KREIDLER and HUMMEL [149]. It has the boundaries of $0.19 \leq R_p \leq 0.60 \text{ Å}$ and $0.80 \leq R_c \leq 1.35 \text{ Å}$ differing from those of fluorapatite in two aspects:

1. Structurally distorted chlorapatite does not occur near the lower limit of R_c .
2. The chlorapatite structure could tolerate much smaller cations at the calcium sites than the fluorapatite structure.

Both of these differences are probably related to the difference in the position of halide ions in the fluor- and chlorapatite structure, but more detailed explanation of how the structural

⁴⁶ Activated by Sb^{3+} and Mn^{2+} , the resulting phosphor was used in fluorescent lamps until about 1990 when it was replaced by rare-earth activated alkaline earth aluminates [157].

difference enables chlorapatite to accept smaller cations without the distortion will not be attempted.

1.6. Other members of the apatite group

1.6.1. Svabite

Svabite is rare accessory mineral in calc-silicate skarns and arsenate analogue of fluorapatite [15] with the composition given by the formula $\text{Ca}_{10}(\text{AsO}_4)_6\text{F}_2$ (calcium fluorarsenate, CAAP). The mineral was named in 1981 by SJÖGREN [159] according to the Swedish chemist ANTON VON SWAB (1703–1768), who distilled zinc from calamine (smithsonite, ZnCO_3 [160]) [161]. Svabite has the same crystal habit as apatite, with rough hexagonal prisms, some of which show rounded pyramidal termination [162]. The structure of mineral svabite is shown in **Fig. 23**.

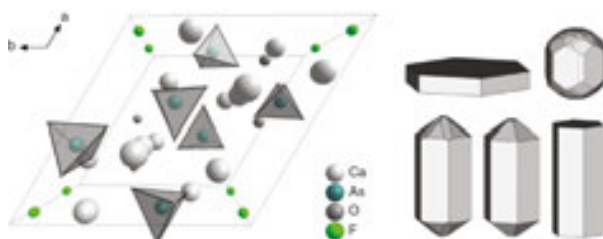


Fig. 23. The structure (perspective view along the *c*-axis) and examples of crystal habits of svabite.



Fig. 24. Known localities for the mineral svabite.

It is brittle mineral that can be white, gray, gray-green, or colorless and transparent. The mineral is considered to be the intermediate between the apatite and the pyromorphite series. Svabite has the average density of $3.7 \text{ g}\cdot\text{cm}^{-3}$, and the hardness on the Mohs scale ranges from 4

to 5. It is hexagonal mineral belonging to the space group $P6_3/M$, $a = 9.75 \text{ \AA}$ and $c = 6.92 \text{ \AA}$, $a:c = 1:0.71$, $V = 569.7 \text{ \AA}^3$, and $Z = 2$. The mineral occurs in the localities introduced in **Fig. 25**.

1.6.2. Turneaureite

Turneaureite ($\text{Ca}_5(\text{AsO}_4)_3\text{Cl}$, calcium chloroarsenate [7],[163]) is hexagonal mineral with the space group $P6_3/M$ with following crystallographic parameters $a = 9.81$ and $c = 6.868 \text{ \AA}$, $a:c = 1:0.700$, $V = 572.4 \text{ \AA}^3$ and $Z = 2$. The mineral is Cl analogue of svabite (**Section 1.6.1**) and OH analogue of johnbaumite (**Section 1.6.3**). The structure of turneaureite is shown in **Fig. 25**.

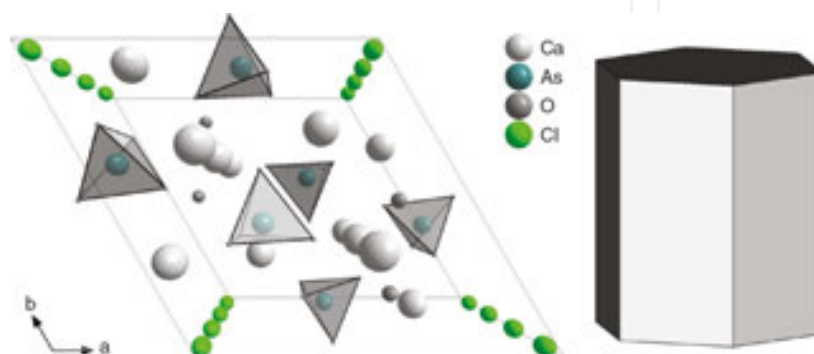


Fig. 25. The structure of turneaureite (perspective view along the c -axis) and examples of crystal habits of turneaureite.

The mineral occurs⁴⁷ in Franklin, New Jersey; Långban, Sweden (holotype⁴⁸); and Balmat, New York [164]. The name honors Dr. FREDERICK STEWART TURNEAURE, Professor Emeritus at the University of Michigan, in recognition of his contributions to the geology and mineralogy of ore deposits. The mineral occurring occasionally as colorless, slightly turbid, prismatic (only the forms $\{1010\}$ and $\{0001\}$ are present) crystals up to 1.5 mm long. The mineral is colorless with a vitreous to slightly greasy luster. The hardness on the Mohs scale is 5. Measured and calculated density of mineral is 3.60 and $3.63 \text{ g}\cdot\text{cm}^{-3}$, respectively [163], [164].

1.6.3. Johnbaumite

Johnbaumite ($\text{Ca}_5(\text{AsO}_4)_3\text{OH}$ [165],[166]) is a hexagonal mineral from the Franklin mine from Franklin, Sussex County, New Jersey, in 1944. The mineral is arsenate analogue of hydroxylapatite and hydroxyl analogue of svabite (**Section 1.6.1**). Johnbaumite was named in 1980 according to BAUM [164]. The structure and crystal habits of johnbaumite is shown in **Fig. 26**.

⁴⁷ Turneaureite was found at three localities, but only the sample from Långban, Varmland, Sweden, provided single crystals of a size and quality adequate for the characterization of the specie [163].

⁴⁸ Holotype is the definition for single specimen (designated by the author) from which all the data from the original description were obtained. If the portion of such a specimen was send to other museum for preservation, the author shall designate this portion as "part of holotype." Other types of specimen are the cotype and the neotype. The cotype is a specimen used to obtain quantitative data for the original description (specimen examined only visually should not be considered a cotype). The neotype is a specimen chosen by author for a redefinition or reexamination of a species to represent the species when the holotype or cotypes cannot be found [5].

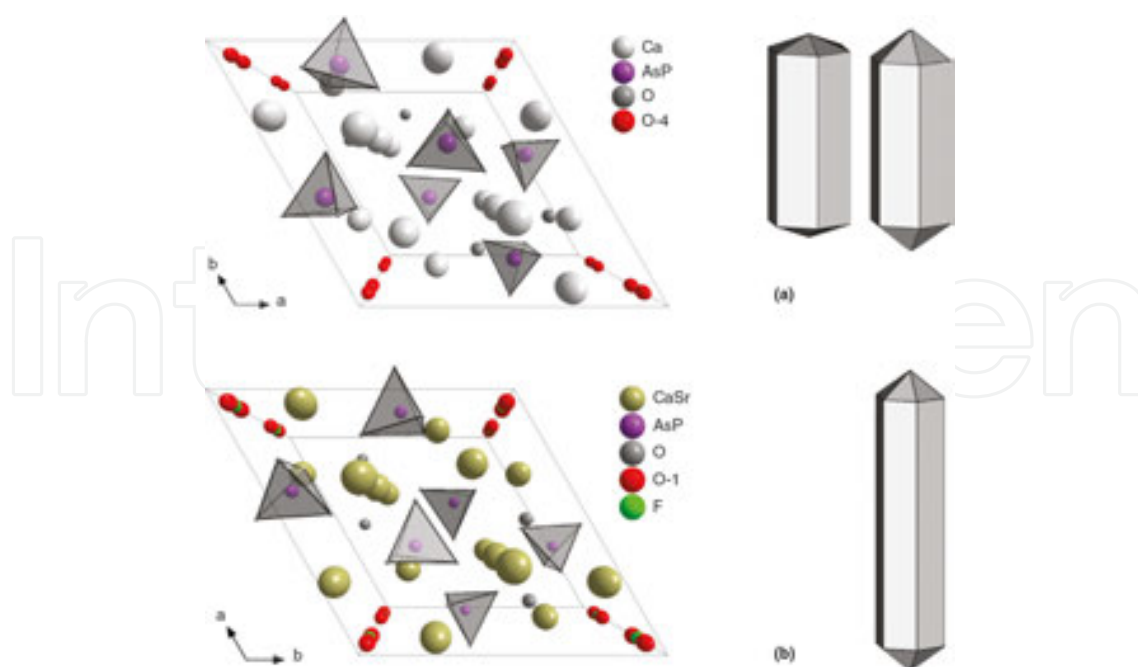


Fig. 26. The structure (perspective view along the c -axis) and the crystal habit of johnbaumite (a) and johnbaumite-M (b).

The space group of johnbaumite is $P6_3/M$ or $P6_3$ with $a = 9.70 \text{ \AA}$ and $c = 6.93 \text{ \AA}$, $a:c = 1:0.714$, $V = 564.96 \text{ \AA}^3$ and $Z = 2$. Johnbaumite occurs as massive anhedral grayish-white granular material with individual grains of approximately 8 mm or less in diameter and is white to colorless with vitreous luster. Johnbaumite is colorless in thin section and has white streaks. The Mohs hardness is approximately $4\frac{1}{2}$. The luster is vitreous on cleavage surfaces and slightly adamantine to greasy on fracture surfaces. The cleavage is distinct, parallel to $\{100\}$. Measured and calculated density of mineral is 3.68 and $3.73 \text{ g}\cdot\text{cm}^{-3}$, respectively. Johnbaumite is fluorescent in short-wave UV radiation with a medium pinkish orange response color [165].

The monoclinic variant of mineral, which was previously named strontiumarsenapatit and fermorite $3[(\text{Ca},\text{Sr})_3(\text{P},\text{As})_2\text{O}_8]\cdot\text{Ca}(\text{OH},\text{F})_2$ [74],[167], is now named johnbaumite-M and is not considered a distinct species [45]. The mineral crystallizes in the space group $P2_1/M$ with crystallographic parameters $a = 9.594 \text{ \AA}$, $b = 6.975 \text{ \AA}$ and $c = 9.579 \text{ \AA}$; $\alpha = \gamma = 90^\circ$ and $\beta = 119.97^\circ$; $V = 556.341 \text{ \AA}^3$; and $Z = 2$.

1.6.4. Pyromorphite

Pyromorphite (lead chlorophosphate, $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ [52],[168],[169],[170],[171],[172],[188], **Fig. 27**) was named by F.L. HAUSMANN in 1813. The name was derived from Greek words for “fire” and “form” to describe the recrystallization of a mineral from the melt. The structure and the example of shape of pyromorphite are shown in **Fig. 28**. Since the structures of vanadinite and pyromorphite are similar except for the tetrahedrally coordinated cations, it is described in **Section 1.6.8**.

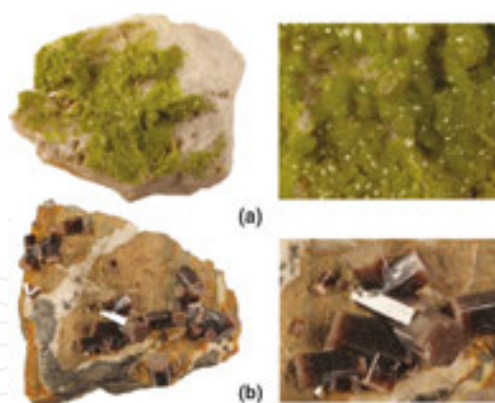


Fig. 27. Pyromorphite: (a) Brandy Gill Mine, Great Britain and (b) Friedrichsegen Mine, Bad Ems, Nassau, Germany.

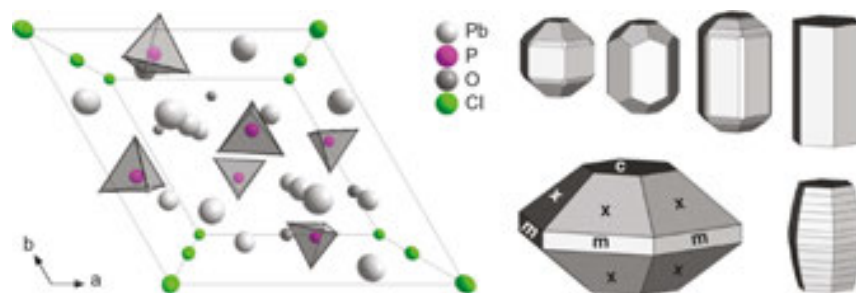


Fig. 28. The structure of pyromorphite mineral (perspective view according to the c -axis) (a) and the shape of crystal from Beaujeu (b): c (0001), m ($10\bar{1}0$) and x ($10\bar{1}1$).

Lead bearing minerals pyromorphite, mimetite (Section 1.6.7) and vanadinite (Section 1.6.8) occur independently or in great variety of isomorphous mixtures. All these species were prepared synthetically and pyromorphite is also known as a furnace product in slag [173], [174].

Pyromorphite is brittle hexagonal mineral that crystallizes in the space group $P6_3/M$ with the crystallographic parameters $a = 9.9764$, $c = 7.3511$ Å, $a:c = 1:0.737$, $V = 634.14$ Å³ and $Z = 2$. The mineral has the hardness from $3\frac{1}{2}$ to 4 (Mohs scale) and shows the density in the range from 6.5 to 7.1 g·cm⁻³. The luster is resinous and the color of mineral is commonly green, varying from grass green to the lighter and darker shades. It may be also pale brown. The secondary mineral formed together with limonite, cerussite ($PbCO_3$ [175]), hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$ [176],[177]) and smithsonite [160] in the upper oxidized portion of lead veins [178].

1.6.5. Stronadelphite

The mineral is named after the chemical element strontium and αδελφός, Greek word for “brother,” as the full strontium analogue of fluorapatite, the most widespread member of the apatite supergroup. The mineral chemically close to stronadelphite, found in peralkaline

pegmatite and Mt. Karnasurt, Lovozero alkaline complex, Kola Peninsula, Russia (**Fig. 29**), was first reported as “strontium-apatite.”



Fig. 29. Known localities for the mineral stronadelphite.

Stronadelphite ($\text{Sr}_5(\text{PO}_4)_3\text{F}$, strontium fluorophosphates, strontium apatite,⁴⁹ apatite-(SrF), SFAP [45],[179]) is a hexagonal mineral that crystallizes in the space group $P6_3/M$ and has the cell parameters $a = 9.845$ and $c = 7.383$ Å, $a:c = 1:0.75$, $V = 619.7$ Å³ and $Z = 2$. The brittle mineral is transparent and colorless with a pale greenish tint. There are no cleavages, and the hardness of mineral on the Mohs scale is 5 (apatite). Calculated and measured densities of the mineral are 3.98 and 3.92 g·cm⁻³, respectively. The structure of mineral stronadelphite is shown in **Fig. 30**.

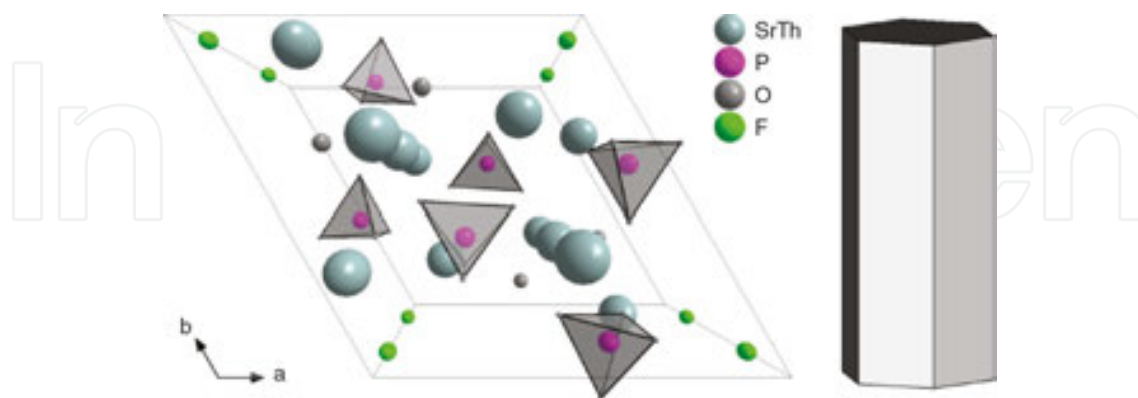


Fig. 30. Structure (view according to the c -axis) and crystal habit of stronadelphite mineral.

⁴⁹ Strontium apatite was also used as the old name for the mineral named apatite-(SrOH). The original name strontium-apatite was given before the structural study of the mineral and incorrectly reflects its relationship with apatite (please consult with **Table 3**). The name fluorostrophite (**Section 2.2.6**) was suggested by PASSERO et al [45].

1.6.6. Alforsite

Alforsite ($\text{Ba}_5(\text{PO}_4)_3\text{Cl}$, barium analogue of chlorapatite, barium chlorapatite, pentabarium tris[arsenate(V)] chloride [53],[54],[180]) is a colorless hexagonal mineral from the group of apatite named according to the geologist J.T. ALFORS. The mineral occurs in the localities introduced in **Fig. 31**.



Fig. 31. Known localities for the mineral alforsite.

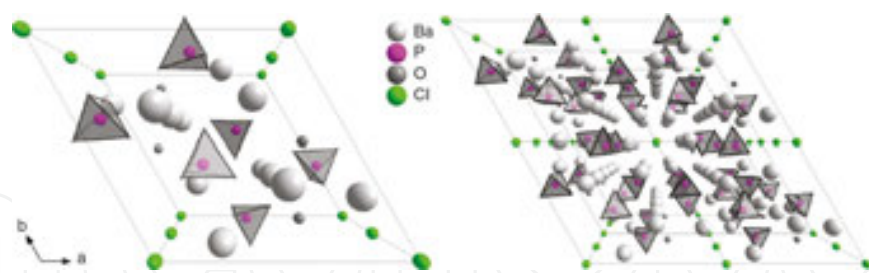


Fig. 32. The structure of mineral alforsite (perspective view along the c -axis).

Alforsite occurs as isolated small subhedral grains, generally less than 0.05 mm in diameter but rarely up to 0.2 mm. These colorless grains resemble typical fluorapatite, exhibiting low birefringence and high relief. This makes it difficult to distinguish alforsite from fluorapatite and from many of the associated high-relief barium minerals except by using the electron microprobe. Mineral is uniaxial and negative, with extremely low birefringence [53].

The structure of mineral alforsite is shown in **Fig. 32**. The space group of alforsite is $P6_3/M$ with the crystallographic parameters $a = 10.25 \text{ \AA}$, $c = 7.64 \text{ \AA}$, $a:c = 1:0.745$, $V = 700.77 \text{ \AA}^3$ and $Z = 2$.

The mineral hardness on the Mohs scale is equal to 5. Calculated and measured density of mineral are 4.81 and 4.77 g·cm⁻³, respectively [53],[54],[180].

1.6.7. Mimetite and clinomimetite

Mimetite (arsenopyromorphite, lead chloroarsenate, mimetite-H, Pb₅(AsO₄)₃Cl) [45],[55], [181],[182]), is the end member in the ternary system pyromorphite–vanadinite–mimetite. This is also the reason why the name of mineral is derived from Greek word “*mimethes*,” i.e. the imitator. Mimetite is also Pb₅ analogue of hedyphane (Section 2.1). Mimetite (Fig. 33) is an arsenate mineral; it usually forms as a secondary mineral in lead deposits through the oxidation of galena (PbS [183], Gn⁵⁰) and arsenates [184].



Fig. 33. Mimetite (Příbram, Czech Republic).

Mimetite usually crystallizes in oxidized zones of lead deposits as small hexagonal prism with colors ranging from pale to bright yellow, orange, yellowish-brown, white, translucent, to opaque [184]. In accordance with other hexagonal apatite-group minerals, it crystallizes in the space group P6₃/M. The unit cell parameters are $a = 10.46$, $c = 7.44$ Å, $a:c = 1:0.71$ $Z = 2$ and $V = 704.96$ Å³. The calculated density is 7.10 g·cm⁻³. The hardness of the mineral on the Mohs scale is in the range from 3½ to 4. The structure and the shape of mimetite crystal is shown in Fig. 34.

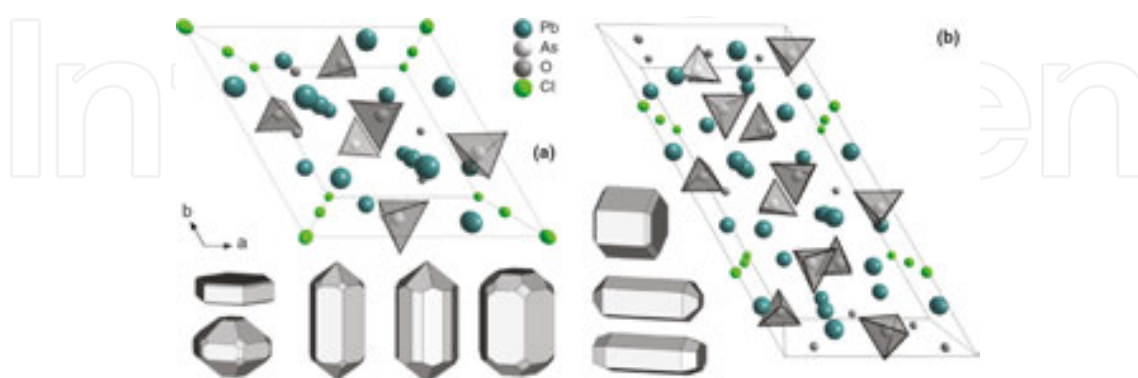


Fig. 34. The structure (perspective view along the c -axis) and the shape of mimetite crystal of hexagonal (a) and monoclinic polymorph (b).

⁵⁰ Symbol of mineral for rock- and ore-forming minerals.

The polymorphs of mimetite⁵¹ are the monoclinic mimetite-M formerly known as clinomimetite mineral [185],[186] and mimetite-2M [182]. Monoclinic mimetite-M crystallizes in the space group $P2_1/B$ with the crystallographic parameters $a = 10.189$, $b = 20.371$ and $c = 7.46$ Å; angles $\alpha = \beta = 90^\circ$ and $\gamma = 119.88^\circ$; $V = 1342.57$ Å³; and $Z = 4$. It is brittle mineral with the hardness of 4 (Mohs scale). The color of mimetite-M is pale greenish, yellow or white, and the mineral has white streak. Measured and calculated densities of the mineral are 7.36 and 7.37 g·cm⁻³, respectively. Monoclinic polymorphs of mimetite-2M crystallize in the space group of $P2_1$ with the crystallographic parameters $a = 20.422$, $b = 7.438$ and $c = 20.435$ Å; ratio $a:b:c = 2.746:1:2.747$; angles $\alpha = \beta = 90^\circ$ and $\gamma = 119.95^\circ$; $V = 2689.5$ Å³; and $Z = 8$.

1.6.8. Vanadinite

Vanadinite was named with regard to the content of vanadium⁵² ($Pb_5(VO_4)_3Cl$ or $3Pb_3(VO_4)_2 \cdot PbCl_2$ [103],[187],[188],[189]). Since simple vanadates⁵³ incorporate other ions in their lattices, several series are known, including descloizite [190],[191]–mottramite [192],[193] and mounanaite⁵⁴ [194],[195]–krettnichite⁵⁵ [196],[197].



Fig. 35. Vanadinite (Mibladén, Morocco).

⁵¹ Both monoclinic polymorphs were discredited from the IMA list of minerals in 2010.

⁵² The most common vanadinite minerals are vanadate, descloizite ($PbZnVO_4(OH)$, orthorhombic [191]), and mottramite ($PbCuVO_4(OH)$, orthorhombic [193]) [204]. Vanadium was discovered in 1891 within lead vanadate ore by a Mexican mineralogist ANDRES MANUEL DEL RIO (and named as erythronium), but it was mistaken as a form of chromium. The new element was recognized and named in 1830 by Swedish chemist NILS GABRIEL SEFTSTRÖM. Vanadium was named after the Norse goddess VANADIS, who represented beauty and fertility [199],[205]. About 80% of vanadium is used for the production of special steel and alloys. Other applications include catalysts (e.g. in the production of sulfuric acid), pigments, and the manufacture of batteries [210]. Vanadium is used as alloy with a number of metals, e.g. ferro-vanadium (40–80% of vanadium), nickel-vanadium, alumino-vanadium, etc. [189].

⁵³ There are about 65 vanadium minerals, the most important sources of vanadium are titaniferous magnetites, carnotite (potassium uranyl vanadate used for the extraction of uranium, vanadium and radium), vanadinite, roscelite ($K(V,Al,Mg)_2AlSi_3O_{10}(OH)_2$), patronite (VS_4), sylvanite ($Cu_3V^{2+}S_4$), uvanite ($U_2V^{5+}_6O_{21} \cdot 15H_2O$), bravoite, and davidite [210]. Vanadium is also found in clays, crude oil [189], and vanadium-rich variety of lignite (quisqueite).

⁵⁴ Monoclinic mineral (space group $C2/M$) of the composition $PbFe^{3+}_2(VO_4)_2(OH)_2$.

⁵⁵ Monoclinic mineral (space group $C2/M$) of the composition $PbMn^{2+}_2(VO_4)_2(OH)_2$.

Vanadinite mineral is the lead chlorovanadate (lead chloro orthovanadate) analogue of minerals mimetite (**Section 1.6.7**) and pyromorphite (**Section 1.6.4** [52]) and is considered as the end member in the ternary system pyromorphite–vanadinite–mimetite [198],[199]. The arseniferous variety of vanadinite was named as endlicheite (arsenian vanadinite, $\text{PbCl}_2 \cdot 3\text{Pb}_3(\text{V,As})_2\text{O}_8$ [200],[201],[202]).

Vanadinite is formed as the secondary product in oxidized zone of lead-bearing deposits⁵⁶ [203],[204],[205],[206] associated usually with galena, cerussite, or limonite [207]. It is known to form typically well-developed hexagonal prismatic crystals with smooth faces and sharp edges along [0001] [203]. It occurs frequently as acicular, hairlike, fibrous, rounded, globular, or hollow prismatic crystals. Synthetic vanadinite was first presented in 1957 by DURAND [208].

The structure of hexagonal vanadinite belongs to the space group $\text{P6}_3/\text{M}$. The unit cell parameters are $a = 10.33$, $c = 7.34$ Å, $a:c = 1:0.71$, $Z = 2$ and $V = 678.72$ Å³. Calculated and measured average densities are 6.93 and 6.94 g·cm⁻³, respectively. It is brittle mineral of brown, brownish yellow, brown red, orange or yellow color, and some varieties can be colorless. The hardness of vanadinite on the Mohs scale varies in the range from 3½ to 4 [207],[209]. The structure of vanadinite and the example of crystal habit is shown in **Fig. 36**.

Vanadinite and pyromorphite (**Section 1.6.4**) possess similar structure where Pb(1) bonds to six oxygen atoms ($3 \times \text{O}(1)$ and $3 \times \text{O}(2)$) in the form of an approximate trigonal prism, with three longer bonds to oxygen atoms ($3 \times \text{O}(3)$) through the prism faces. Adjacent Pb(1)-O₉ “prisms” share pinacoidal faces at the mirror planes ($z = \frac{1}{4}$ and $\frac{3}{4}$) to form Pb(1)-O₉ polyhedral chains parallel to the c -axis. Pb(2) lies in the mirror planes $z = \frac{1}{4}$ and $\frac{3}{4}$ and bonds to two oxygen atoms within the plane ($\text{O}(1)$ and $\text{O}(2)$), four oxygen atoms ($4 \times \text{O}(3)$) and two Cl atoms located on the hexad at $0,0,0$ and $0,0,\frac{1}{2}$ positions [188].

The major structural difference between vanadinite and pyromorphite occurs in XO₄ tetrahedra, which are occupied by V⁵⁺ (radius 0.59 Å) in vanadinite and by P⁵⁺ (0.35 Å) in pyromor-

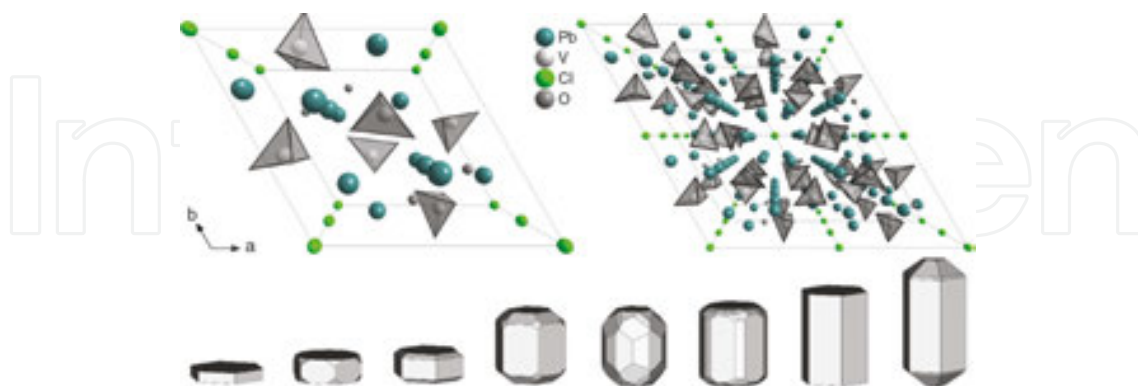


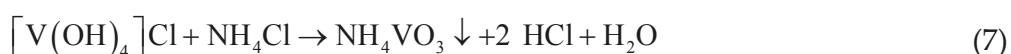
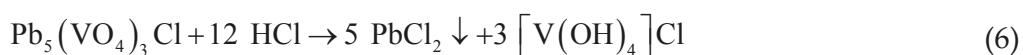
Fig. 36. The structure (perspective view along the c -axis) and the example of crystals habit of vanadinite.

⁵⁶ Almost all base-metal vanadate deposits occur in oxidized zones of the base-metal vein and replacement deposits. They also occur in other vanadium minerals in sediments. Vanadate deposits are largely restricted to tropical and temperature zones and to regions of dry climate [204],[206].

phite. The O-V-O and O-P-O angle in vanadate (VO_4^{3-}) and phosphate ion (Section 1.2) tetrahedron varies from 105.4 to 113.1° and from 107.1 to 111.8°, respectively. The most important structural features are the octahedral coordination of Pb(2) around Cl^- ions and the tetrahedral coordination of oxygen atoms around the vanadium atom. Each Cl^- ion is surrounded by six Pb(2) at the corner of a regular octahedron in which the Pb(2)-Cl distance is 3.17 Å and the shortest Pb(2)-Pb(2) distance (along an edge of the octahedron) is 4.48 Å [204], [210].

The production of vanadium metal from vanadinite ore consists of the following steps [188], [212]:

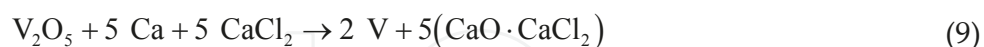
1. **Preparation of ammonium metavanadate** (NH_4VO_3) from powdered vanadinite ore, which is treated by concentrated HCl. This leads to the precipitation of PbCl_2 and to the solution of complex salt of $[\text{V}(\text{OH})_4]\text{Cl}$ (Eq. 6). Ammonium metavanadate precipitates when $[\text{V}(\text{OH})_4]\text{Cl}$ solution is boiled with NH_4Cl (Eq. 7).



2. **Conversion of ammonium metavanadate into V_2O_5** is reached by ignition. The process can be described by the following equation:



3. **Reduction of V_2O_5 to vanadium metal** via fluxing with Ca and CaCl_2 (Eq. 9) or by the aluminothermic process (Eq. 10):

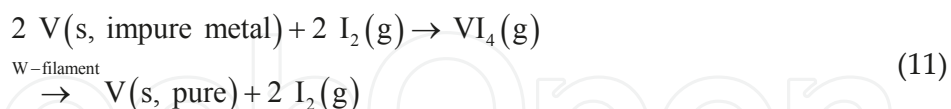


4. **Purification of vanadium metal** by *Van Arkel-de Boer method* [211],[216]⁵⁷ in which the impure vanadium metal is heated with a limited amount of I_2 under vacuum.⁵⁸ Formed

⁵⁷ The method of reactive distillation of metal compounds (or also the chemical vapor transport reactions [214] developed by Dutch chemists ANTON EDUARD VAN ARKEL AND JAN HENDRIK DE BOER in 1925. The process can be applied if volatile iodides (from that they are also termed as the iodine process) of metal were formed and if the metal has higher melting point than the dissociation temperature of formed iodide. This technique has practical importance for Ti, Zr, Hf, Th, Cr, and V. The method which uses CO reactive gas instead of I_2 is known as the carbonyl or **Mond-Langer process** [213], e.g. $\text{Ni(s)} + 4 \text{CO(g)} \leftrightarrow \text{Ni(CO)}_4\text{(g)}$.

⁵⁸ Chemical vapor transport (CVT) or vaporization reaction with iodine [214]. The investigation of the vaporization processes for several vanadium halide systems shown the existence of mixed halides $\text{VX}_{4-n}\text{Y}_n$ ($\text{X} = \text{Cl, Br; Y} = \text{Br, I}$) formed in reaction of Br_2 or I_2 with VX_2 or VX_3 solid phases at elevated temperature [215].

volatile iodide (VI_4 , vanadium tetraiodide or vanadium(IV) iodide) decomposes at a higher temperature on the wolfram filament into pure vanadium and I_2 , which becomes available to react with the impure vanadium, thus sustaining the process [189],[213],[214],[215],[216]:



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