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Other Minerals from the Supergroup of Apatite

Petr Ptáček

Additional information is available at the end of the chapter

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Abstract

The supergroup of apatite is divided into five groups of minerals. Therefore, minerals from the group of apatite were described in the first chapter, the second chapter of this book continues with description of minerals from the other four groups, i.e. minerals from the group of britholite, belovite, ellestadite and hedyphane. The structure, properties and known localities of these minerals were described. Although carbonate-apatite species are discredited from the IMA list of minerals, the chapter ends with description of structure and properties of carbonate-hydroxylapatite, carbonate-fluorapatite, and carbonate-rich varieties of apatite, i.e. francolite, dahlite, kurskite and collophane. The introduced three basic types of carbonate-apatites, i.e. type A, B and AB) are then discussed in Chapter 10 in depth.

Keywords: Apatite, Britholite, Belovite, Ellestadite, Hedyphane, Carbonate-apatite, Francollite, Dahlite

As was mentioned in **Section 1.1**, the supergroup of apatite is divided into five groups. The most important minerals form the group of britholite (**Section 2.3**), belovite (**Section 2.2**), ellestadite (**Section 2.4**) and hedyphane (**Section 2.1**), which are described in this chapter together with carbonate fluorapatite and hydroxylapatite (**Section 2.6**).

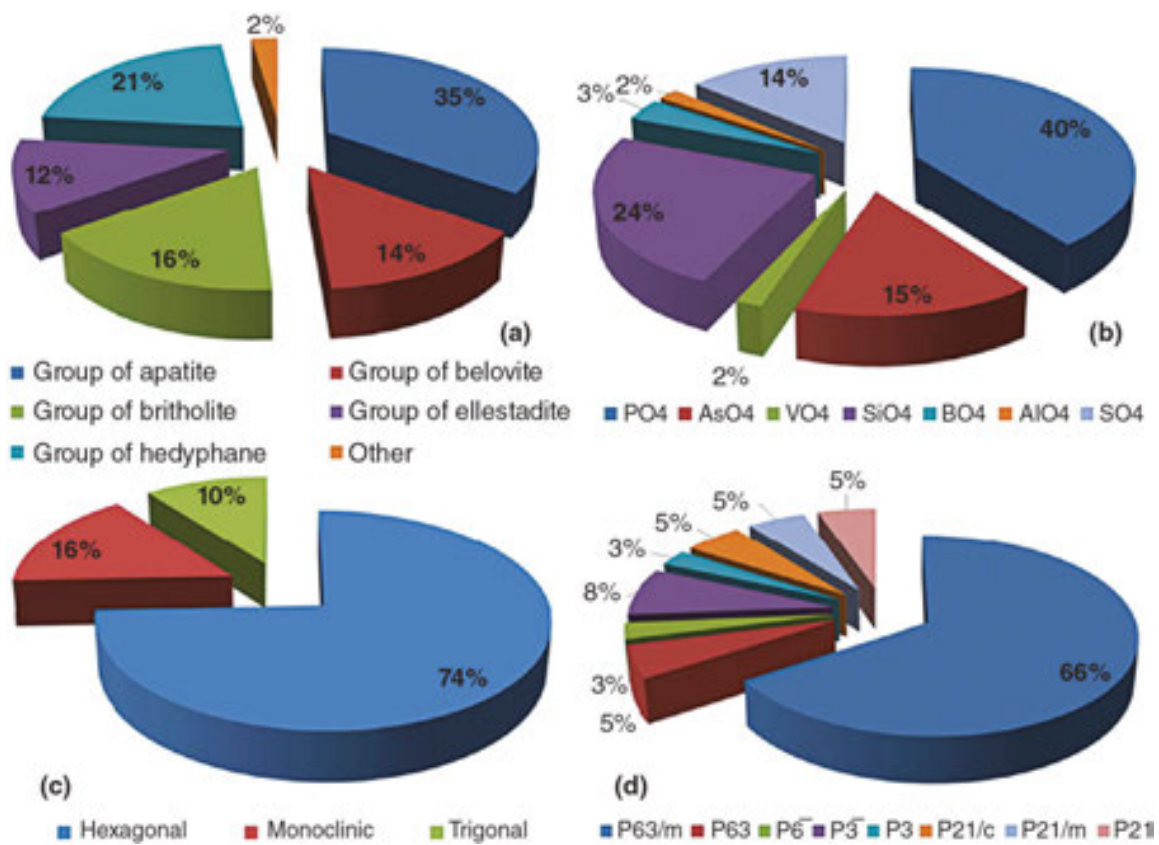


Fig. 1 Distribution of described minerals from the supergroup of apatite (discredited species are also included) among individual groups (a) and distribution of kind of XO₄ tetrahedra (b), crystal system (c) and space group (d) among these species.

Other minerals from the supergroup of apatite include 65%, i.e. 28 described mineral species **Fig. 1(a)**, which predominantly crystallize in hexagonal system (c) and in the space group P6₃/M (d). The [PO₄]³⁻ unit is the most frequent ortho-oxyanion for the supergroup of apatite in general (b), but its content in individual groups varies strongly (Fig. 2).

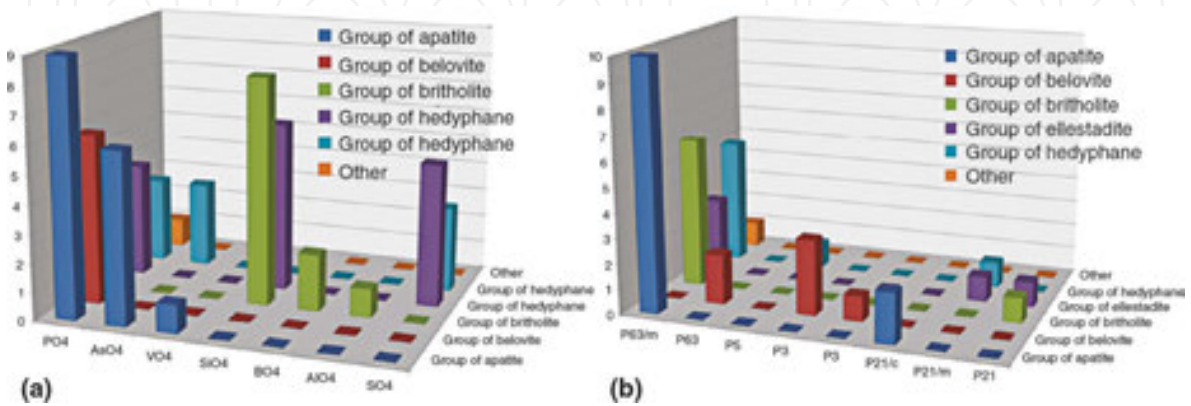


Fig. 2 Frequency of XO₄ ions and point groups for individual groups from the supergroup of apatite.

2.1. The group of hedyphane

2.1.1. Hedyphane

Hedyphane ($\text{Ca}_2\text{Pb}_3(\text{AsO}_4)_3\text{Cl}$), calcium-lead chloroarsenate [1],[2],[3],[4] is a mineral that was originally described from Langban, Sweden. It also occurs at the Harstig Mine, Pajsberg, Sweden and was moderately abundant at the Franklin Mine, Franklin, Sussex County, New Jersey. The mineral occurs in the localities introduced in Fig. 3. The mineral was named in 1830 by German mineralogist JOHANN FRIEDRICH AUGUST BREITHAUP [5] and its Greek name is usually translated as “pleasant appearance or beautifully bright.”



- 1) Reward Mine (Brown Monster Mine; Ruth; Hirsch and Telescope group; Brown Monster-Reward; Graham-Jones; Eclipse; Golden West claims; Hidden Treasure group; F. D. Roosevelt claims), Reward, Russ District, Inyo Mts (Inyo Range), Inyo Co., California, USA (a), Bagdad-Chase Mine (Barstow mill; Camp Rochester; Pacific Mine; Pacific Mines; Roosevelt Consolidated Mine; Buckeye-Stedman-Bagdad Chase Mine), Stedman, Stedman District, San Bernardino Co., California, USA (b), Rowley Mine (Rawley Mine; Reliance Mine; Reliance Copper Mine; Rainbow Mine; Theba Mine; San Carlos patented claim #4524), Theba, Painted Rock District, Painted Rock Mts, Maricopa Co., Arizona, USA (c) and Glove Mine (Sunrise Mine), Glove Mine group (Zombie & Zeco claims; Festago-Franklin; Blacksmith adit), Devil's Cash Box ridge, Amado, Cottonwood Canyon, Tyndall District, Santa Rita Mts, Santa Cruz Co., Arizona, USA (d).
- 2) Potosi Mine (El Potosi Mine), Francisco Portillo, West Camp, Santa Eulalia District, Mun. de Aquiles Serdán, Chihuahua, Mexico (a), Ojuela Mine, Mapimi, Mun. de Mapimi, Durango, Mexico (b) and Bilbao Mine, La Blanca, Mun. de Ojo Caliente, Zacatecas, Mexico (c)
- 3) Franklin Mine, Franklin, Franklin Mining District, Sussex Co., New Jersey, USA
- 4) Tynagh Mine, Killimor, Co. Galway, Ireland (a), Brandy Gill Mine, Carrock Fell, Caldbeck Fells, North and Western Region (Cumberland), Cumbria, England, UK (b) and Torr Works Quarry (Merehead Quarry), Cranmore, Somerset, England, UK (c)
- 5) Jakobsberg Mine, Jakobsberg ore field, Nordmark district, Filipstad, Värmland, Sweden (a), Långban, Filipstad, Värmland, Sweden (b), Harstigen Mine, Pajsberg, Persberg district, Filipstad, Värmland, Sweden (c) and Sjögruvan, Grythyttan, Hällefors, Västmanland, Sweden (d)
- 6) Alexander Shaft (Alexander Mine), Vrančice, Příbram, Central Bohemia Region, Bohemia (Böhmen; Boehmen), Czech Republic
- 7) Poggio San Vittore asbestos mine, Balangero, Lanzo Valleys, Torino Province, Piedmont, Italy
- 8) Maffei Mine, Botro al Marmi, Campiglia Marittima, Livorno Province, Tuscany, Italy (b)
- 9) Kombat Mine (Klein Otavi; Asis), Kombat, Grootfontein District, Otjozondjupa Region, Namibia
- 10) Aroona Mine, Beltana Mine (E.Z. Mine; Beltana deposit; Beltana-Aroona deposit; Puttapa mine), Puttapa, Leigh Creek, North Flinders Ranges, Flinders Ranges, South Australia, Australia (a) and Beltana Mine (E.Z. Mine; Beltana deposit; Beltana-Aroona deposit; Puttapa mine), Puttapa, Leigh Creek, North Flinders Ranges, Flinders Ranges, South Australia, Australia (b)

Fig. 3 Known localities for the mineral hedyphane.

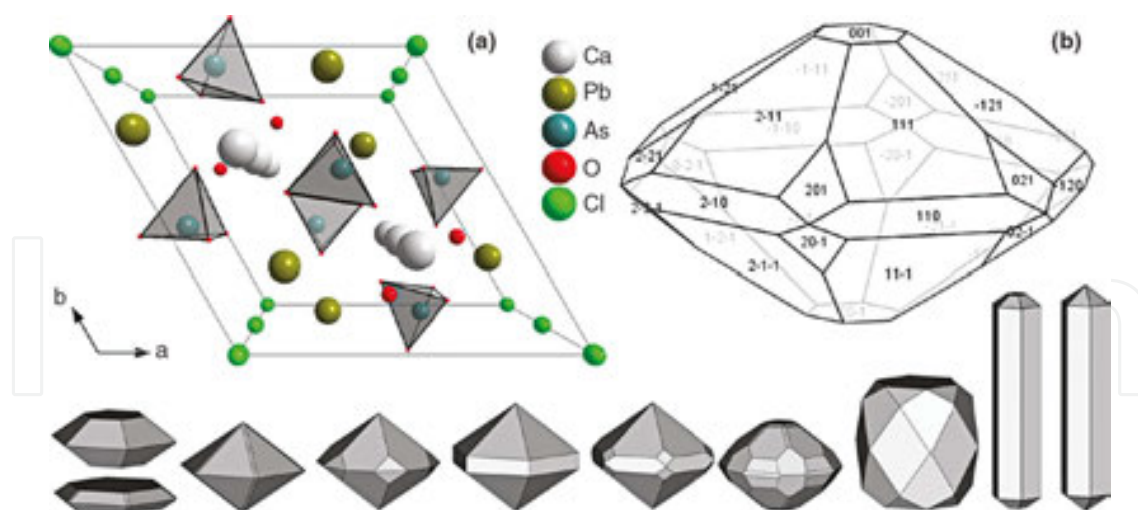


Fig. 4 The structure (perspective view according to the c -axis; a) and the crystal habit of hedyphane crystals (b).

The neotype (refer to **Footnote 48** in **Chapter 1**) hedyphane occurs as light yellow or white¹ euohedral crystal² approximately 1 mm in maximum dimension. Hedyphane is translucent with white streaks and has greasy to vitreous or (sub)resinous luster on crystal faces and fracture surfaces. The cleavage is indiscernible, the fracture is even, and the mineral is moderately brittle. Hedyphane is isostructural (arsenate analogue) with phosphohedyphane (**Section 2.1.3**) [3]. The structure and the crystal habit of hedyphane are shown in **Fig. 4**.

The unit cell parameters of hedyphane are $a = 10.14$, $c = 7.185$ Å, $Z = 2$ and $V = 639.78$ Å³. The average density of mineral is 5.81 g·cm⁻³. Hedyphane is optically uniaxial and positive. The hardness of the mineral on the Mohs scale is in the range from 4 to 5. Despite the fact that the formal charges of Ca²⁺ and Pb²⁺ are the same, the Pb²⁺ ion predominantly occupies M(2) sites in the structure of hedyphane. The exclusive presence of Pb in the M(2) site is probably due to the presence of stereoactive lone pair of electrons (please see **Fig. 7** and **Fig. 9**), which is characteristic for the Pb²⁺ ion in many compounds [6],[3],[7].

The average length of Ca-O(n), bond where $n = 1, 2$ and 3 , in CaO₉ polyhedron is 2.60 Å. The structure of PbO₅Cl₂ polyhedron with interatomic distances is shown in **Fig. 5**. The average value of O(n)-Pb-O(3) angle, where $n = 2$ and 3 , is 99.3°. The average interatomic distance and O-As-O angle in AsO₄ tetrahedron are 1.69 Å and 109°, respectively [3].

¹ Also described as “white variety” of “green lead ore” [4], i.e. the mineral mimetite (**Section 1.6.7**). It should be noted that “white lead ore” (grayish-white color, glassy luster and crystallized in small prisms) is related to the mineral cerussite (PbCO₃).

² Crystal habit shows well-formed and easily recognized faces. On the contrary, crystal faces that are not well formed are termed as anhedral. The intermediate texture between euohedral and anhedral is called subhedral.

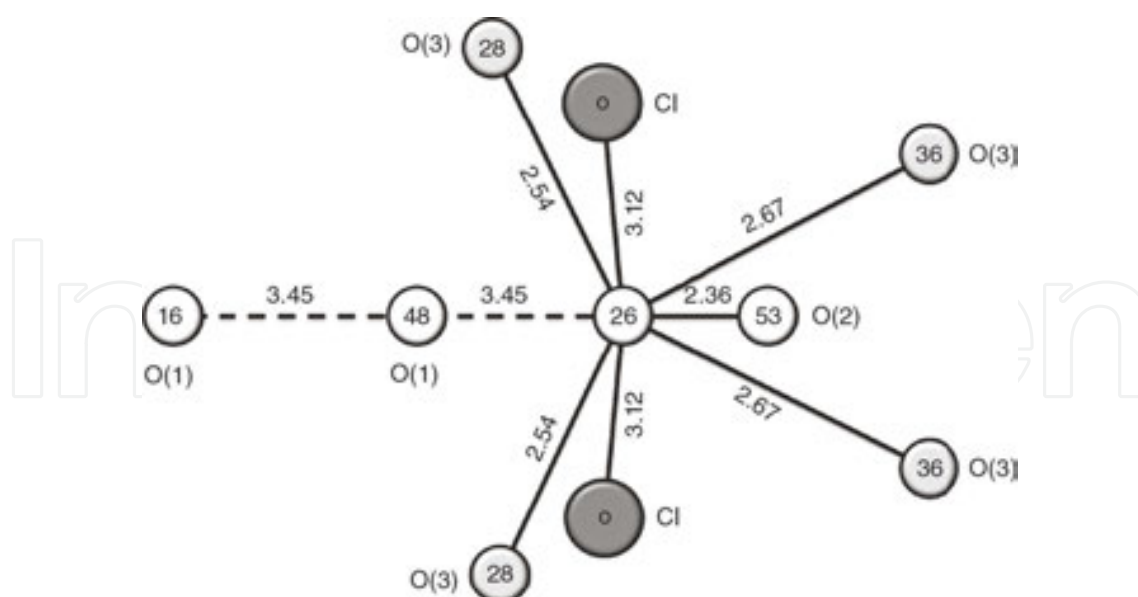


Fig. 5 The coordination polyhedron around the Pb site in hedyphane (projection on 001). The number within the circle denotes x coordinates of atoms [3].

2.1.2. Fluorophosphohedyphane

Fluorophosphohedyphane ($\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{F}$, [1],[8]): occurs in the oxidation zone of a small Pb-Cu-Zn-Ag deposit in the Blue Bell claims, about 11 km west from Baker, San Bernardino County, California (**Fig. 6**). Fluorophosphohedyphane is a fluor-analogue of phosphohedyphane, forms subparallel intergrowths and irregular clusters of transparent, colorless, highly lustrous, hexagonal prisms with pyramidal terminations.



Fig. 6 The locality for the mineral phosphohedyphane.

Fluorphosphohedyphane is found in cracks and narrow veins in highly siliceous hornfels³ [9] in association with cerussite¹, chrysocolla⁴ ($(\text{Cu}_{2-x}\text{Al}_x)\text{H}_{2-x}\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ [10]), fluorite, fluorapatite, goethite, gypsum, mimetite, opal ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$ [11],[12]), phosphohedyphane, plumbogummite ($\text{PbAl}_3(\text{PO}_4)(\text{PO}_3\text{OH})(\text{OH})_6$ [13],[14],[15]), plumbophyllite ($\text{Pb}_2\text{Si}_4\text{O}_{10} \cdot \text{H}_2\text{O}$ [16]), plumbotsumite ($\text{Pb}_5\text{Si}_4\text{O}_8(\text{OH})_{10}$ [17],[18],[19]), pyromorphite (**Section 1.6.4**), quartz and wulfenite (PbMoO_4 [20]). The streak of the new mineral is white; the luster is subadamantine [8]. The structure and the crystal habit of fluorphosphohedyphane hedyphane are shown in Fig. 7.

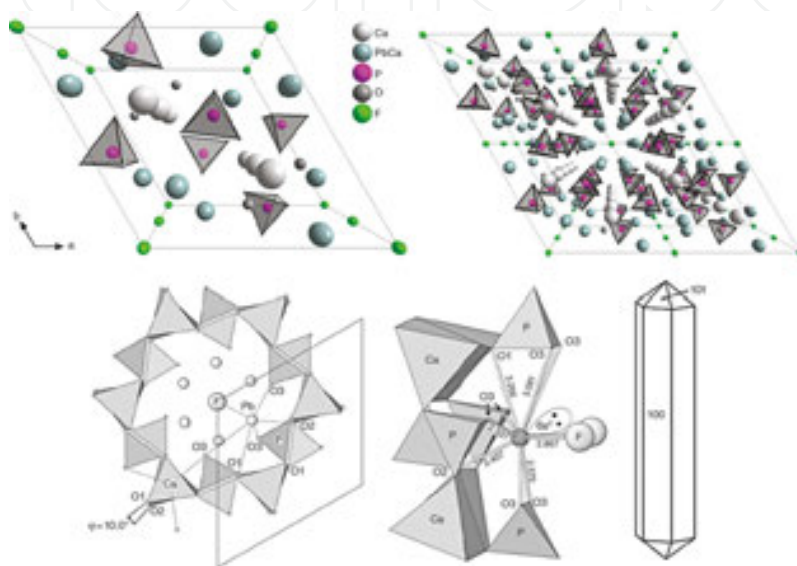


Fig. 7 The structure (perspective view along the *c*-axis), the coordination of Pb with likely approximate location of lone-electron pair and the crystal habit of fluorphosphohedyphane in clinographic projection⁵ [8].

Fluorphosphohedyphane has the apatite structure with the ordering of Ca and Pb in two cation sites, as in hedyphane and phosphohedyphane. The Pb^{2+} cation exhibits a stereoactive $6s^2$ lone electron pair⁶ [21] (**Fig. 7**). The Z anion site at $(0, 0, \frac{1}{2})$ is fully occupied by F forming six bonds of 2.867 Å to Pb atoms, in contrast to six Pb-Cl bonds of 3.068 Å in phosphohedyphane. For

³ The name for this type of contact metamorphic rock was given by K. VON LEONHARDT. The name originates from the designation of the highest peaks in the Alps but it can be also derived from ancient mining term from Saxony (Germany) which was used to describe hard, compact metamorphic rock developed at the margin of an igneous body. These rocks possess outstanding toughness due to fine-grained nonaligned crystals of platy or prismatic habit. Hornfels are sometimes banded, but their texture can be also porphyroblastic, i.e. they occur as large crystals within fine ground groundmass of metamorphic rock [9].

⁴ The name of the mineral comes from the Greek words *chyrosos* (gold) and *kolla* (glue). The mineral is also named as bisbeeite (blue mineral of the composition of $(\text{Cu},\text{Mg})\text{SiO}_3 \cdot n\text{H}_2\text{O}$ named after Bisbee Cochise County, Arizona).

⁵ In the clinographic projection the crystal is turned by angle Θ around a vertical axis in order to make the front- and the right-hand faces visible. Other forms are orthographic projection and perspective projection.

⁶ The electronic configuration for Pb is $[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^2$. Cations with formal $ns^2 np^6$ electronic configuration usually display novel properties and it is widely believed that the so-called ns^2 lone pair is responsible for the stereochemical activity that causes the Jahn–Teller geometry distortion, specific optical properties, and ferroelectricity. Lone electron pair is also used for the explanation of anisotropies of thermal expansion coefficient, piezoelectric and elastic properties, and optoelectronic properties [21].

fluorophosphohedyphane, phosphohedyphane and hedyphane in which Ca^{2+} occupies the M(1) site and Pb^{2+} occupies the M(2) site, the M(1) metaprisms twist angles are notably smaller, 10.0° , 8.6° and 5.2° , respectively [8].

The mineral is brittle with subconchoidal fracture and no cleavage. Based on the empirical formula, the calculated density is $5.45 \text{ g}\cdot\text{cm}^{-3}$. Fluorophosphohedyphane is hexagonal with the space group $\text{P6}_3/\text{M}$ and the cell parameters $a = 9.6402$, $c = 7.0121 \text{ \AA}$, $a:c = 1:0.727$, $V = 564.4 \text{ \AA}^3$ and $Z = 2$. The hardness of the mineral on the Mohs scale is 4.

2.1.3. Phosphohedyphane

Phosphohedyphane ($\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}$ [1],[22]): the mineral from the Capitana mine, Copiapó, Atacama Province, Chile, discovered in 2004. Known localities for the mineral phosphohedyphane are introduced in Fig. 8. Phosphohedyphane is brittle with subconchoidal fracture and no cleavage. Phosphohedyphane is hexagonal with the space group $\text{P6}_3/\text{M}$ and the cell parameters $a = 9.857$, $c = 7.13 \text{ \AA}$, $V = 599.94 \text{ \AA}^3$ and $Z = 2$. The hardness of the mineral on the Mohs scale is 4. The mineral is closely associated with quartz, duftite ($\text{PbCuAsO}_4(\text{OH})$ [23]) and bayldonite ($\text{Cu}_3\text{PbO}(\text{AsO}_3\text{OH})_2(\text{OH})_2$ [24]).



- 1) Silver Coin Mine, Valmy, Iron Point District, Humboldt Co., Nevada, USA (a), Reward Mine (Brown Monster Mine; Ruth; Hirsch and Telescope group; Brown Monster-Reward; Graham-Jones; Eclipse; Golden West claims; Hidden Treasure group; F. D. Roosevelt claims), Reward, Russ District, Inyo Mts (Inyo Range), Inyo Co., California, USA (b), Library Mine, Otto Mountain, Baker, San Bernardino Co., California, USA (c), Tonopah-Belmont Mine (East Vulture Mine; Belmont-McNeil Mine; Economy Mining Co. Mine), Belmont Mountain, Tonopah, Osborn District, Big Horn Mts, Maricopa Co., Arizona, USA (d), C and B Mine (C & B Mine; C. and B. Mine; C & B Group Mine; Vanadium Mine; Vanadium property; International property; Cutler and Bywater Mine), Christmas, Christmas area, Banner District, Dripping Spring Mts, Gila Co., Arizona, USA (e), Mammoth-Saint Anthony Mine (Mammoth-St Anthony Mine; Mammoth Mine; St. Anthony Mine), St. Anthony deposit, Tiger, Mammoth District, Pinal Co., Arizona, USA (f), Hardshell Mine (Manto Mine; Eagle-Picher properties), Hardshell Gulch, Harshaw, Harshaw District, Patagonia Mts, Santa Cruz Co., Arizona, USA (g), Reef Mine (Tungsten Reef Mine; Exposed Reef Mine; Silric Mine; Reef group of claims), Carr Canyon, Hartford District (Huachuca Mountains District), Huachuca Mts, Cochise Co., Arizona, USA (h) and Marila Mine, Tombstone District, Tombstone Hills, Cochise Co., Arizona, USA (ch)
- 2) Bilbao Mine, La Blanca, Mun. de Ojo Caliente, Zacatecas, Mexico
- 3) Maria Catalina mine, Pampa Larga district, Tierra Amarilla, Copiapó Province, Atacama Region, Chile
- 4) Wilsons Vein, Whytes Cleuch, Warrlockhead, Dumfries & Galloway (Dumfriesshire), Scotland, UK (a), Higher Roughton Gill (Ballway Rigg), Roughton Gill, Caldbeck Fells, North and Western Region (Cumberland), Cumbria, England, UK (b), Whitwell Quarry, Whitwell, Derbyshire, England, UK (c), Wheal Mary Ann, Menheniot, Liskeard District, Cornwall, England, UK (d) and Wheal Mexico (Trebellan Mine; incl. Trenworthy Mine), Wheal Cobert (Cubert United Mine), Cubert, St Agnes District, Cornwall, England, UK (e)
- 5) La Paloma Mine, Zarza la Mayor, Cáceres, Extremadura, Spain (a) and Preguiça Mine, Sobral da Adilça, Moura, Beja District, Portugal (b)
- 6) Nulzière (Nulzière Mine), Chenelette, Rhône, Rhône-Alpes, France
- 7) Pilbram, Central Bohemia Region, Bohemia (Böhmen; Boheimen), Czech Republic
- 8) Sa Duchessa Mine, Oridda, Domusnovas, Carbonia-Iglesias Province, Sardinia, Italy
- 9) Djebel Sekama Mine (Sekama deposit), Djebel Sekama, Silana, Silana Governorate, Tunisia
- 10) Berezovskoe Au Deposit (Berezovsk Mines), Berezovskii (Berezovskii Zavod), Ekaterinburg (Sverdlovsk), Sverdlovskaya Oblast', Middle Urals, Urals Region, Russia
- 11) Kyzylspe (Kyzyl-Spe), Balkhash Region (Balkash; Karatas; Prebalkhashie), Karagandy Province (Karagandy Oblasty; Karagandia Oblast'), Kazakhstan
- 12) Tennant Creek, Barkly Region, Northern Territory, Australia
- 13) Broken Hill, Yancowinna Co., New South Wales, Australia (a) and Cave Hill (David Mitchell Limestone Quarry), Lilydale, Victoria, Australia (b)

Fig. 8 Known localities for the mineral phosphohedyphane.

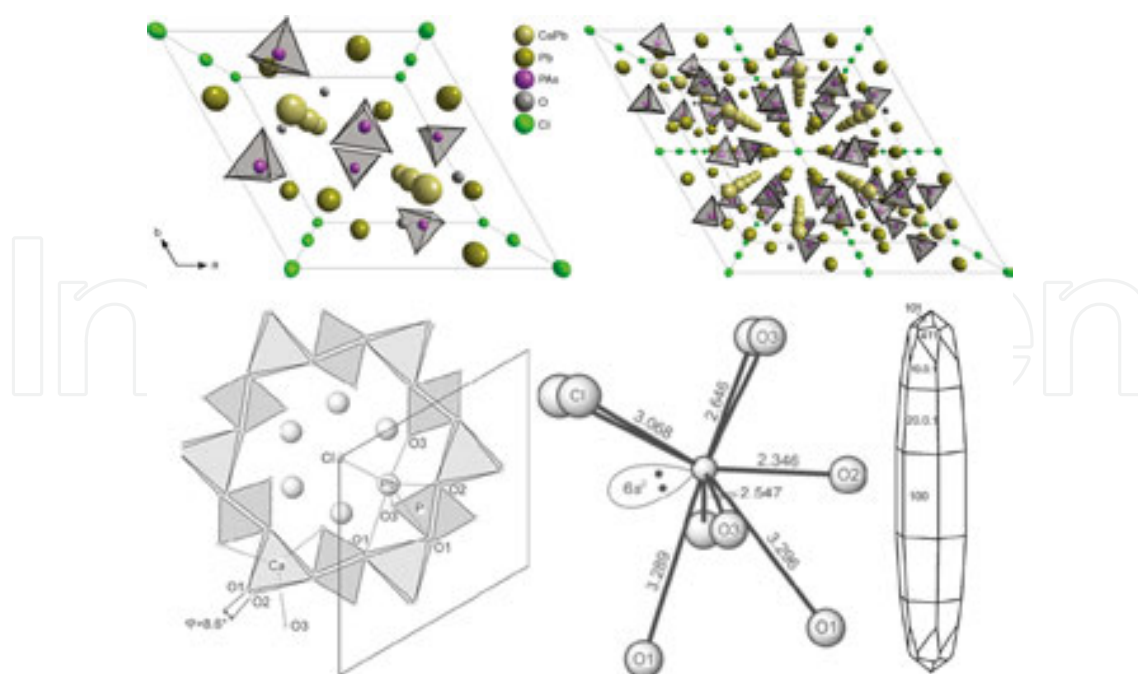


Fig. 9 The structure (perspective view along the *c*-axis), the coordination of Pb with approximate location of lone-electron pair and the crystal habit of phosphohedyphane [22].

The mineral is a phosphate analogue of hedyphane and possesses an apatite structure with the ordering of Ca and Pb in two nonequivalent large cation sites. The structure refinement indicates that the Ca(2) sites are completely occupied by Pb and the Ca(1) sites contain 92% Ca and 8% Pb. The tetrahedral site refines to 91% P and 9% As. The refinement indicates the 0,0,0 position to be fully occupied by Cl. The structure and the crystal habit of phosphohedyphane are shown in **Fig. 9**.

Other secondary minerals identified in the oxidized zone together with phosphohedyphane are: anglesite (PbSO_4 [25]), arsentsumebite ($\text{Pb}_2\text{Cu}(\text{AsO}_4)(\text{SO}_4)(\text{OH})$ [26],[27]), azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ [28]), beaverite⁷ ($\text{PbCu}^{2+}\text{Fe}^{3+}_2(\text{SO}_4)_2(\text{OH})_6$ [29],[30],[31]), calcite (CaCO_3 , hexagonal with the space group $R\bar{3}c$ ⁸ [32]), cerussite, mimetite (**Section 1.6.7**), malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$ [33]), mottramite and perroudite ($\text{Ag}_4\text{Hg}_5\text{S}_5(\text{I,Br})_2\text{Cl}_2$ [34]) [22].

2.1.4. Morelandite

Morelandite ($\text{Ca}_2\text{Ba}_3(\text{AsO}_4)_3\text{Cl}$, $(\text{Ba}, \text{Ca}, \text{Pb})_5(\text{AsO}_4, \text{PO}_4)_3\text{Cl}$ [1],[35],[36]), is a mineral that was named in 1978 according to MORELAND. It occurs as small irregular masses associated with hausmannite ($\text{Mn}^{2+}\text{Mn}^{3+}_2\text{O}_4$ [37]) and calcite in the Jakobsberg mine, near Nordmark, Sweden (**Fig. 10**). The structure of morelandite is shown in **Fig. 11**.

⁷ The minerals beaverite-(Cu) and beaverite-(Zn), i.e. $\text{PbZnFe}^{3+}_2(\text{SO}_4)_2(\text{OH})_6$ [29], were recognized. Beaverite is an old name for the mineral beaverite-(Cu).

⁸ There is also an orthorhombic polymorph (PMCN) aragonite.



Fig. 10 Known locality of the mineral morelandite.

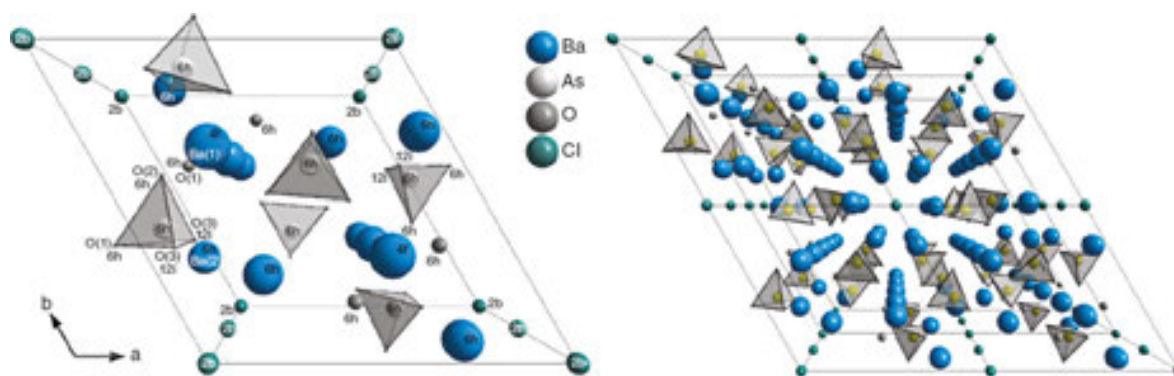


Fig. 11 The structure of morelandite (perspective view according to the c -axis).

The mineral is gray to light yellow with white streaks, greasy to vitreous luster, and shows poor cleavage on $\{001\}$. Morelandite is hexagonal with the space group $P6_3/M$ and the cell parameters $a = 10.169$, $c = 7.315$ Å, $V = 655.09$ Å³ and $Z = 2$. The hardness of the mineral on the Mohs scale is $4\frac{1}{2}$.

2.1.5. Aiolosite

Aiolosite ($\text{Na}_2(\text{Na}_2\text{Bi})(\text{SO}_4)_3\text{Cl}$, ideally $\text{Na}_4\text{Bi}(\text{SO}_4)_3\text{Cl}$ [7]): hexagonal mineral with the space group $P6_3/M$ and the cell parameters $a = 9.626$, $c = 6.88$ Å, $V = 552.09$ Å³ and $Z = 2$. The calculated density of the mineral is 3.59 g·cm⁻³. Aiolosite is a sulfate mineral isotopic with apatite, which was found in an active medium-temperature intracrater fumarole at La Fossa crater, Vulcano Island, Aeolian archipelago, Sicily, Italy (Fig. 12). It occurs as acicular to slender prismatic crystals up to 0.5 mm long in an altered pyroclastic breccia (refer to **Footnote 27** in **Section 1.1**), together with alunite, anhydrite (CaSO_4 [38]), demicheleite-(Br) (BiSBr [39]), bismuthinite (Bi_2S_3 [40]) and panichiite ($(\text{NH}_4)_2\text{SnCl}_6$ [41]). Aiolosite is colorless to white, with white streaks and nonfluorescent. The luster is vitreous.



Fig. 12 The locality of the mineral aiolosite.

The structure of the mineral aiolosite is shown in Fig. 13.

The structure of aiolosite shows two independent cationic sites M(1) and M(2). Due to close similarity in ionic radii of Na^+ and Bi^{3+} , Bi exclusively prefers the M(2) site instead of M(1), which can be ascribed mainly to the Coulombic effect, in view of the higher charge of Bi^{3+} compared to Na^+ , since the average M(2)-O distance (2.516 Å) is shorter than that of M(1)-O (2.617 Å). A similar effect also affects the distribution of Na^+ and Ca^{2+} sites in cesanite (Section 2.1.7) [7].

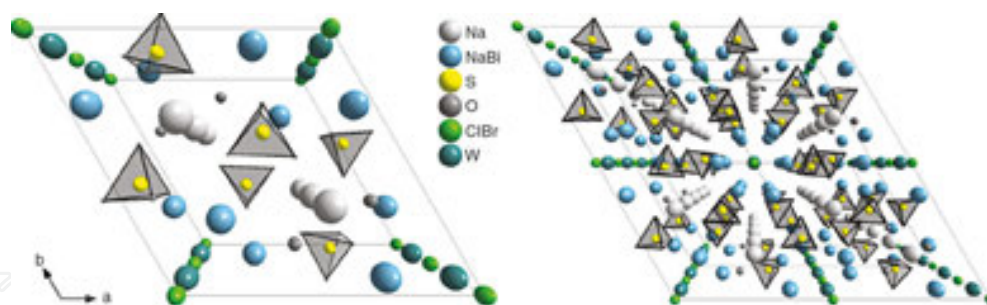


Fig. 13 The structure of aiolosite (perspective view according to the c -axis).

2.1.6. Caracolite

Caracolite ($\text{Na}_2(\text{Pb}_2\text{Na})(\text{SO}_4)_3\text{Cl}$, sodium lead hydroxylchlorosulfate [1],[42],[43],[44]), is a vitreous colorless or grayish mineral from Beatriz mine, Caracoles, Chile, which was reported by WEBSKY in 1886. Known localities and the structure of the mineral caracolite are shown in Fig. 14. It occurs as crystalline incrustations with imperfect pseudo-hexagonal crystals up to 1 mm large. The crystals have the form of hexagonal pyramids with the base and the prism, but they are supposed to be pseudo-hexagonal. The mineral exhibits complex polysynthetic twinning with rather large extinction angles.

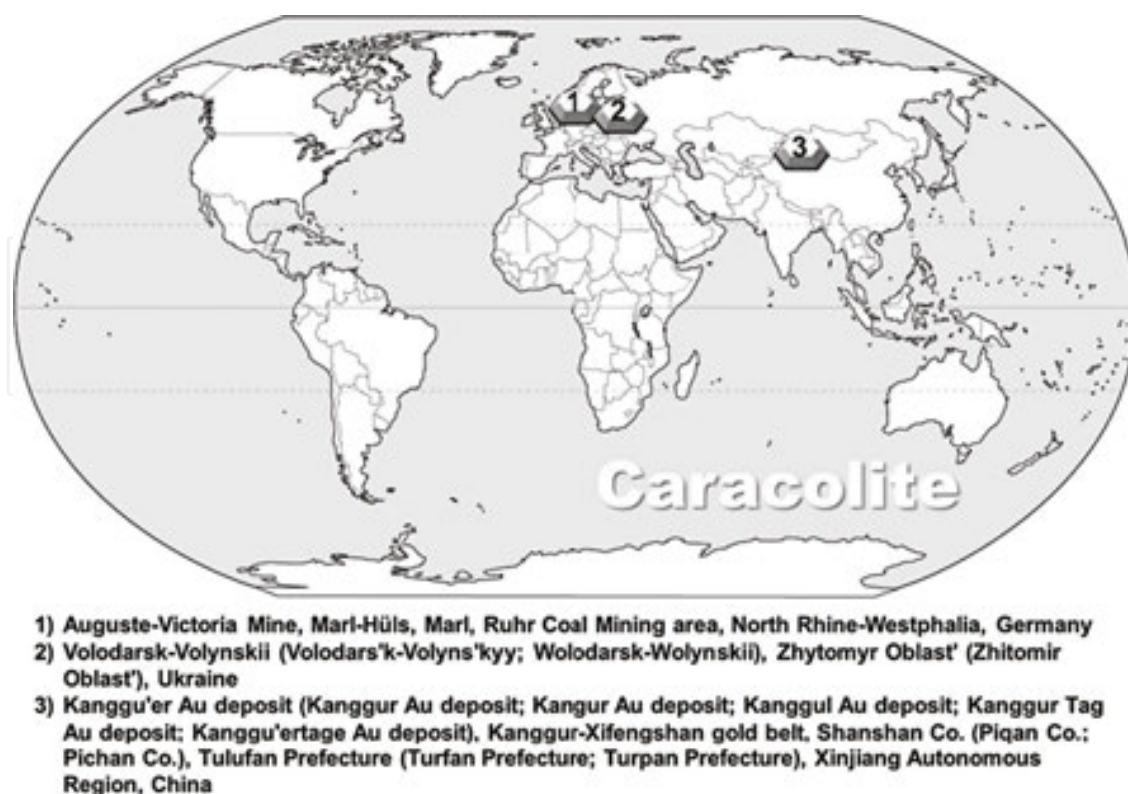


Fig. 14 The localities of the mineral aiolosite.

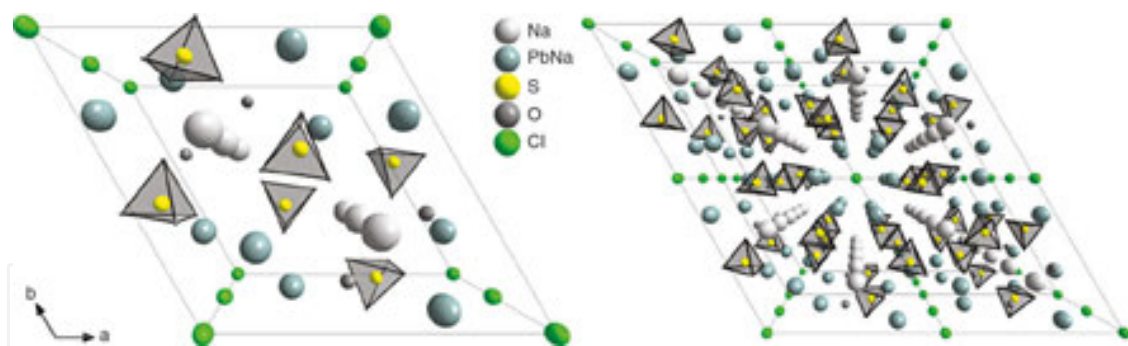


Fig. 15 The structure of caracolite (perspective view according to the c -axis).

Caracolite is monoclinic mineral with the space group $P2_1/M$ and the cell parameters $a = 19.62$, $b = 7.14$, $c = 9.81$ Å and $\beta = 120^\circ$, $V = 1190.14$ Å³, $Z = 4$. Calculated density is 4.50 g·cm⁻³. The hardness of the mineral on the Mohs scale is $4\frac{1}{2}$. The structure of caracolite is shown in Fig. 15.

2.1.7. Cesanite

Cesanite ($\text{Ca}_2\text{Na}_3(\text{SO}_4)_3\text{OH}$ [45],[46],[47]) is a colorless, medium to coarse-grained, soft mineral which occurs both as a solid vein (1 cm thick) and as cavity-filling of an explosive breccia in core samples of the Cesano-I geothermal well (Cesano area, Latium, Italy). Cesanite was

recognized as new mineral by CAVARRETA et al [47]. The crystal structure determination confirms that cesanite has to be considered a member of the apatite-wilkeite-ellestadite series, where $(\text{PO}_4)^{3-}$ is entirely substituted by $(\text{SO}_4)^{2-}$, the charge balance being made up by partial substitution of Na^+ for Ca^{2+} and H_2O for $(\text{OH}^-, \text{Cl}^-, \text{F}^-)$.

The general formula of this series, proposed by HARADA et al [48] and modified by CAVARRETA et al [47], is as follows:

$$\text{Ca}_{5-w}\text{Na}_w(\text{Si}_y\text{S}_z\text{P}_{3-y-z})\text{O}_{12}(\text{F}, \text{Cl}, \text{OH})_x n\text{H}_2\text{O};$$

where $w = 1 - x - y + z$ and $n \leq 1 - x$.

Cesanite is a hexagonal mineral with the space group $\text{P}\bar{6}$ and the cell parameters $a = 9.463$, $c = 6.9088 \text{ \AA}$, $V = 535.79 \text{ \AA}^3$ and $Z = 1$. Calculated density of the mineral is $2.75 \text{ g}\cdot\text{cm}^{-3}$. The hardness of the mineral on the Mohs scale ranges from 2 to 3.

The structure of cesanite is shown in **Fig. 16**. Synthetic and natural cesanite show typical elements of the apatite structure, but the reduction of symmetry from the centrosymmetric space group $\text{P6}_3/\text{M}$ to the noncentrosymmetric space group $\text{P}\bar{6}$ leads to a doubling of the number of crystallographically independent sites. Na and Ca cations are distributed over four independent sites. They are coordinated either by six O atoms and one hydroxyl ion or by water molecule (M(1), M(2)) or nine O atoms (M(3), M(4)) [46].

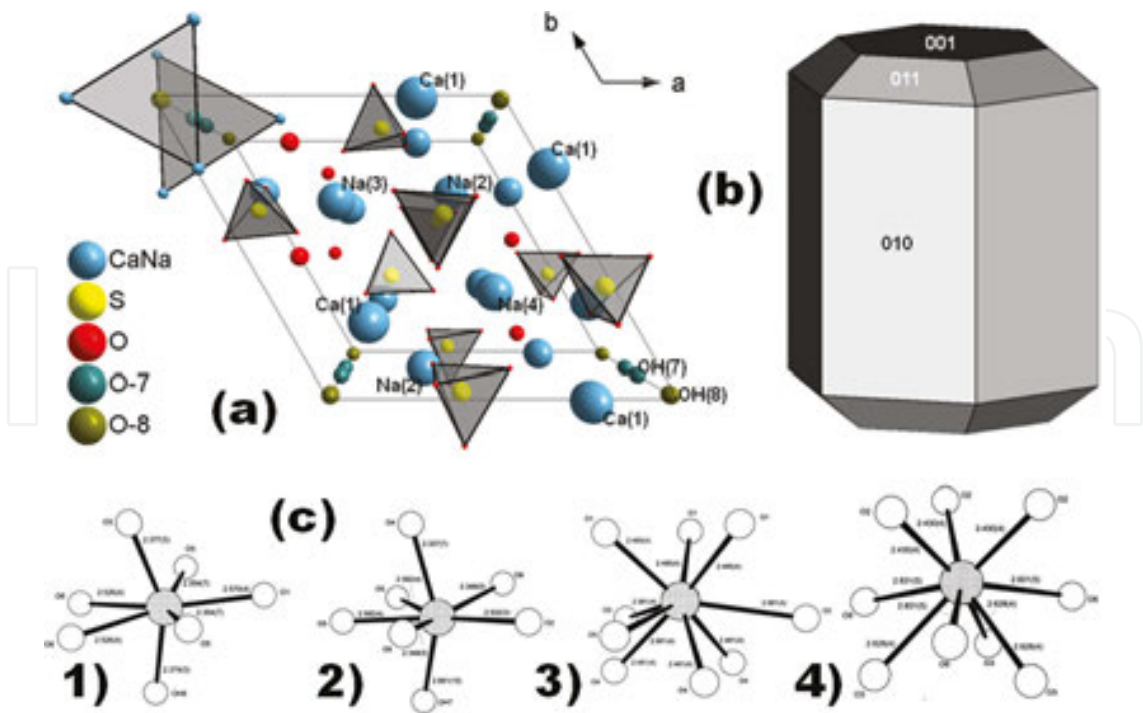


Fig. 16 The structure of cesanite (perspective view according to the c -axis; a), crystal habit (b) and the coordination polyhedra for M(1) (1), M(2) (2), M(3) (3) and M(4) (4) in synthetic analogue of the mineral cesanite (c) [47].

2.2. The group of belovite

The minerals from the group of belovite are cation ordered. Strontium substitutes for Ca in the M(2) site, and Na + REE substitute for Ca in the M(1) site. This results in lowering of symmetry from $P6_3/M$ (the space group of the apatite archetype structure) to $P6_3$ (fluorstrophite, fluorcaphite), $P\bar{3}$ (belovites), or $P3$ (deloneite) [1].

2.2.1. Belovite-(Ce)

Belovite-(Ce) ($\text{NaCeSr}_3(\text{PO}_4)_3\text{F}$ [49],[50],[51]), is a mineral from alkaline pegmatite in differentiated alkalic massifs which was named in 1954 by L.S. Borodin and M.E. Kazakova according to Russian mineralogist and crystallographer N.V. BELOV. The mineral is found in Russia, on Mts. Punkaruaiiv, Lepkhe-Nelm, Sengischorr, Karnasurt, Kedykvyrpakhk and Alluaiv, Lovozero massif; and on Mts. Kukisvumchorr and Koashva, Khibiny massif, Kola Peninsula. The localities of belovite-(Ce) are shown in Fig. 17.



Fig. 17 The localities of the mineral belovite-(Ce).

The mineral belovite-(Ce) is usually associated with ussingite ($\text{Na}_2\text{AlSi}_3\text{O}_8(\text{OH})$ [52]), natrolite ($\text{Na}_2(\text{Si}_3\text{Al}_2)\text{O}_{10}\cdot 2\text{H}_2\text{O}$ [53]), chkalovite ($\text{Na}_2\text{BeSi}_2\text{O}_6$ [54]), epistolite ($\text{Na}_4\text{TiNb}_2(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2\cdot 4\text{H}_2\text{O}$ [55]), tugtupite ($\text{Na}_4\text{BeAlSi}_4\text{O}_{12}\text{Cl}$ [56]), manganneptunite ($\text{Na}_2\text{KLi}(\text{Mn}^{2+}, \text{Fe}^{2+})_2\text{Ti}_2[\text{Si}_8\text{O}_{24}]$ and manganoneptunite [57] (the mineral is isostructural with neptunite [58],[59]), murmanite ($\text{Na}_2\text{Ti}_2(\text{Si}_2\text{O}_7)\text{O}_2\cdot 2\text{H}_2\text{O}$ [60]), gaidonnayite ($\text{Na}_2\text{ZrSi}_3\text{O}_9\cdot 2\text{H}_2\text{O}$ [61]), nordite-(La) ($\text{Na}_3\text{SrLaZnSi}_6\text{O}_{17}$), lamprophyllite ($\text{Na}_3(\text{Sr}, \text{Na})\text{Ti}_3(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_2$ [62]), fluorcaphite, lomonosovite, deloneite-(Ce), sitinakite ($\text{KNa}_2\text{Ti}_4\text{Si}_2\text{O}_{13}(\text{OH})\cdot 4\text{H}_2\text{O}$ [63]), aegirine ($\text{NaFe}^{3+}\text{Si}_2\text{O}_6$ [64]), sodalite ($\text{Na}_4\text{Si}_3\text{Al}_3\text{O}_{12}\text{Cl}$ [65]), microcline⁹ (KAlSi_3O_8 [66],[67]) and

⁹ Originally, the mineral was named as mikroklin [66],[67]: triclinic mineral, space group $C\bar{1}$ with the unit cell parameters: $a = 8.5784 \text{ \AA}$, $b = 12.9600 \text{ \AA}$, $c = 7.2112 \text{ \AA}$, $\alpha = 90.30^\circ$, $\beta = 116.03^\circ$, and $\gamma = 89.125^\circ$.

(NaAlSiO_4 [68]). The morphology of belovite-(Ce) crystals and its structure are shown in **Fig. 18**.

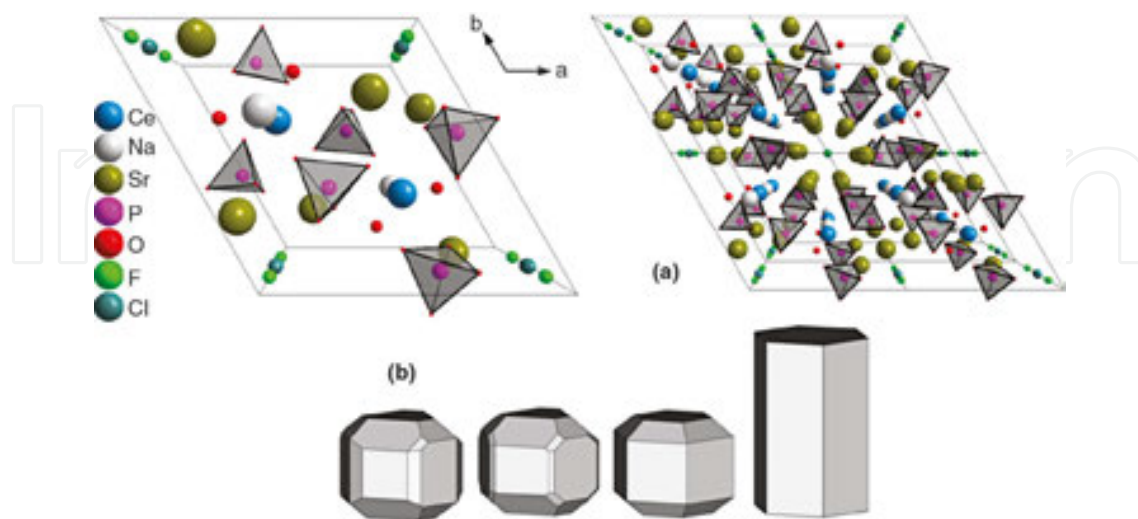


Fig. 18 The structure of belovite-(Ce) (perspective view according to the c -axis; a) and the shape of belovite-(Ce) crystals (b).

Belovite-(Ce) is the cerium analogue of belovite-(La) (**Section 2.2.2**) and the strontium analogue of kuannersuite-(Ce) (**Section 2.2.7**). The ideal formula of belovite-(Ce) is $\text{Sr}_6(\text{Na}_2\text{REE}_2)(\text{PO}_4)_6\text{O}_{24}(\text{OH},\text{F},\text{Cl})_2$, and it is equivalent to apatite *sensu stricto*¹⁰ with the following substitution of $\text{Ca}(2)_{-6}\text{Sr}_{+6}$ and $\text{Ca}(1)_{-4}\text{Na}_{+2}\text{REE}_{+2}$. Strontium overcomes the REE in the competition for Ca(2) sites of apatite. The sites equivalent to Ca(1) of apatite must respond to the occupation by essentially equal amounts of Na and REE. Unlike single Ca(1) site in apatite *sensu stricto*, low symmetry in the space group $P\bar{3}$ yields two Ca(1) subequivalents, one dominated by Na and the other one by REE [51].

Belovite-(Ce) is a brittle mineral with a honey-yellow or greenish color that crystallizes in trigonal system with the unit cell parameters $a = 9.692$ and $c = 7.201\text{\AA}$, $a:c = 1 : 0.743$, $V = 585.80\text{\AA}^3$ and $Z = 2$. It has white streaks, (sub-)vitreous, resinous or greasy luster and a hardness on the Mohs scale of 5. Calculated and measured densities of the mineral are 4.23 and 4.19 $\text{g}\cdot\text{cm}^{-3}$, respectively. It has imperfect prismatic and pinacoidal cleavage.¹¹

2.2.2. Belovite-(La)

Belovite-(La) ($\text{NaLaSr}_3(\text{PO}_4)_3\text{F}$ [1],[69]) was named according to N.V. BELOV (**Section 2.2.1**) with respect to higher content of La than Ce, i.e. the mineral is the lanthanum analogue of belovite-(Ce) described above and NaSr_3La analogue of fluorapatite (**Section 1.5.1**). It occurs as prismatic crystals, up to 3 cm large, and it may also be granular. The structure and the crystal habit of the mineral belovite-(La) are shown in **Fig. 19**.

¹⁰ Latin phrase (abbreviated as s.s.) used, which means "in exact sense."

¹¹ Cleavage that is parallel to the orientation $\{0001\}$, i.e. to the base of crystal.

Belovite-(La) can be found in natrolite veinlets¹² in pegmatites in a differentiated alkalic massif [70]), lamprophyllite, murmanite, aegirine, pectolite ($\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$ [71]), microcline and natrolite.

2.2.3. Carlgieseckeite-(Nd)

Carlgieseckeite-(Nd)¹³ ($\text{NaNdCa}_3(\text{PO}_4)_3\text{F}$ [31],[72],[73]) was named according to the mineralogist and polar explorer GIESECKE with respect to the content of Nd that is higher than the content of other REE. The mineral was found in Kuannersuit (formerly Kvanefjeld) Plateau, northern section of the Ilímaussaq alkaline complex, South Greenland, Denmark. It is associated with albite ($\text{NaAlSi}_3\text{O}_8$ [74]), analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ [75]) and fluorapatite in the cavities of albite vein cross-cutting augite syenite. Carlgieseckeite-(Nd) forms hexagonal tabular crystals up to $0.25 \times 1 \times 1.3$ mm, and their parallel intergrowth up to 0.7×1.3 mm is found epitactically overgrown on prismatic crystals of fluorapatite. A phase with idealized formula $\text{Na}_{1.5}\text{Nd}_{1.5}\text{Ca}_2(\text{PO}_4)_3\text{F}$ epitactically overgrows some crystals of carlgieseckeite-(Nd).

The structure of the mineral (Fig. 21) is representative of the structure type of belovite *sensu stricto*. In this structure, large M cations occupy three sites with different coordination numbers: 9-fold polyhedra M(1) (average distance $\langle \text{M}(1)\text{--O} \rangle$ is 2.522 Å), 6-fold polyhedral M(1)' (reduced 9-fold polyhedra, $\langle \text{M}(1)'\text{--O} \rangle$ with average interatomic distance 2.445 Å) and 7-fold polyhedra M(2) ($\langle \text{M}(2)\text{--O,F} \rangle > 2.486$ or 2.560 Å in the case of F1) [72].

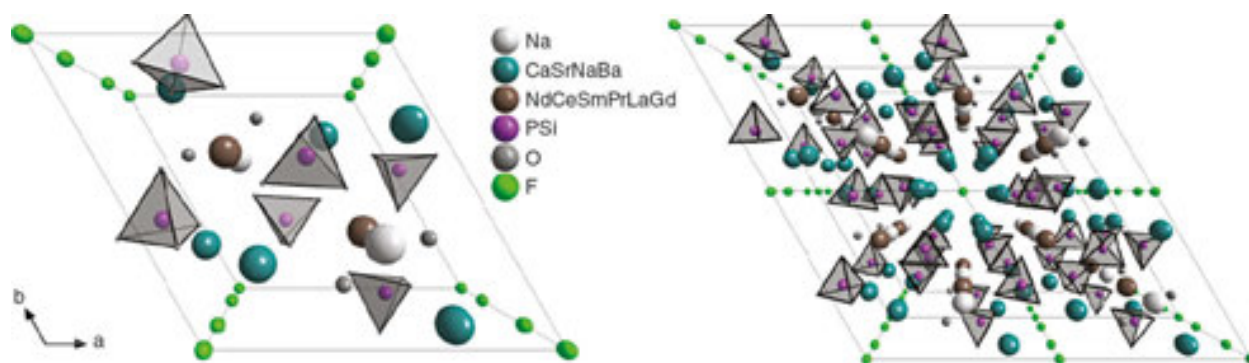


Fig. 21 The structure of carlgieseckeite -(Nd) (perspective view according to the *c*-axis).

Mineral carlgieseckeite-(Nd) is trigonal, from the space group $P\bar{3}$ with crystallographic cell parameters $a = 9.4553$, $c = 6.9825$ Å, $a:c = 1:0.738$, $V = 540.62$ Å³ and $Z = 2$. Carlgieseckeite-(Nd) is the isostructural Ca- and Nd-dominant analogue of belovite-(Ce) and belovite-(La). The mineral carlgieseckeite-(Nd) is colorless, transparent and shows a distinct color-change effect, from almost colorless with a greenish hue in daylight to pink in yellow electric light. The luster is vitreous. The Mohs hardness is about 5. The mineral is brittle with no observed cleavage [72].

¹² Sheetlike body of minerals which crystallize within the rock.

¹³ The holotype material is deposited in the Fersman Mineralogical Museum of Russian Academy of Sciences, Moscow [72].

2.2.4. Deloneite

Deloneite $((\text{Na}_{0.5}\text{REE}_{0.25}\text{Ca}_{0.25})(\text{Ca}_{0.75}\text{REE}_{0.25})\text{Sr}_{1.5}(\text{CaNa}_{0.25}\text{REE}_{0.25})(\text{PO}_4)_3\text{F}_{0.5}(\text{OH})_{0.5}$ [1],[76]): the name of the mineral was changed from deloneite-(Ce) to deloneite. The mineral was named by KHOMEYAKOV, LISITIN, KULIKOVA and RASTSVETAeva in 1996 according to Russian mathematical crystallographer BORIS NIKOLAEVICH DELONE. The mineral usually occurs as anhedral to subhedral² crystals in the matrix. The locality and the structure of the mineral are shown in Fig. 22 and Fig. 23, respectively.



1) Koashva quarry, Koashva Mt, Khibiny Massif, Kola Peninsula, Murmanskaja Oblast', Northern Region, Russia

Fig. 22 The locality of deloneite.

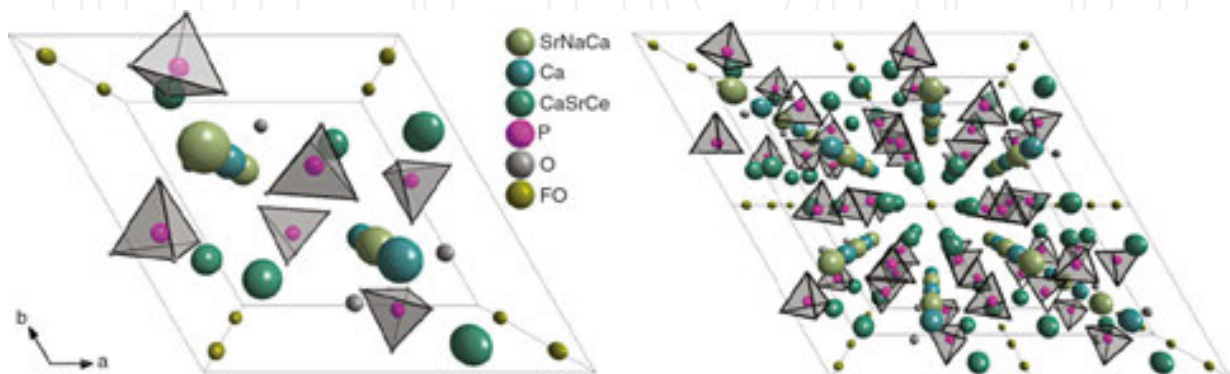


Fig. 23 The structure of the mineral deloneite (perspective view according to the *c*-axis).

Deloneite is a bright yellow mineral which crystallizes in trigonal systems with the unit cell crystallographic parameters $a = 9.51$, $c = 7.01$ Å, $a:c = 1:0.737$, $V = 549.05$ Å³ and $Z = 2$. The mineral is brittle, with a vitreous luster, white streak, an average density of 3.93 g·cm⁻³ and a hardness on the Mohs scale that is equal to 5.

2.2.5. Fluorcaphite

Fluorcaphite ($\text{SrCaCa}_3(\text{PO}_4)_3\text{F}$ [1],[77],[78]): the name of this mineral is an acronym for its elemental composition, i.e. fluorine, calcium and phosphorus. Fluorcaphite is a common accessory mineral in albitite,¹⁴ which developed at the contact between quartzite and peralkaline nepheline syenites¹⁵ of the Lovozero complex, in northwestern Russia. The rock consists predominantly of albite, aegirine, sodic amphibole (arfvedsonite ($\text{NaNa}_2(\text{Fe}^{2+}_4\text{Fe}^{3+})\text{Si}_8\text{O}_{22}(\text{OH})_2$) [79] – magnesio-arfvedsonite ($\text{NaNa}_2(\text{Mg}_4\text{Fe}^{3+})\text{Si}_8\text{O}_{22}(\text{OH})_2$) [80],[81] and narsarsukite ($\text{Na}_2(\text{Ti,Fe,Zr})\text{Si}_4(\text{O,F})_{11}$) [82].

Fluorcaphite forms euhedral prismatic crystals up to 0.3 mm in length. Most of the crystals are homogeneous, but a few contain resorbed core relatively depleted in Sr, Na and light rare-earth elements (LREE). This pattern of zoning arose from two overprinting episodes of metasomatism¹⁶ [83],[84]. In terms of composition, both the core and the rim are intermediate members of a solid solution between fluorapatite and belovite-(Ce). The structure and the crystal habit of the mineral fluorcaphite is shown in Fig. 24.

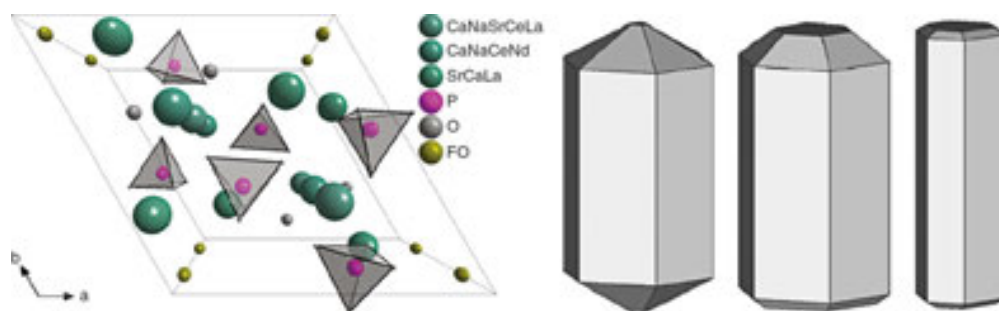


Fig. 24 The structure (view along c -axis) and the crystal habit of the mineral fluorcaphite.

Fluorcaphite is light or bright yellow hexagonal mineral which crystallizes in the space group $P6_3$ with the crystallographic parameters $a = 9.485$, $c = 7.000$ Å, $a:c = 1:0.738$, $V = 545.39$ Å³ and $Z = 2$. It has white streaks, vitreous luster and the hardness on the Mohs scale is 5. Calculated and measured densities are 4.09 and 3.6 g·cm⁻³, respectively. Fluorcaphite does not show any cleavage, the mineral is brittle with the formation of subconchoidal fractures.

¹⁴ Granular rock essential consisting of the mineral albite.

¹⁵ Coarse-grained intrusive rock crystallized slowly under conditions similar to granite, but is deficient of quartz.

¹⁶ The term was introduced by NEUMANN [83]. Metasomatism is a metamorphic process by which the chemical composition of a rock or rock portion is altered in a pervasive manner and which involves the introduction and/or removal of chemical components as the results of the interaction of the rock with aqueous fluids (solutions). During the metasomatism, the rock remains in a solid state.

2.2.6. Fluorstrophite

Fluorstrophite ($\text{SrCaSr}_3(\text{PO}_4)_3\text{F}$ [1],[85],[86]) formerly “strontium-apatite” [87] and later changed to apatite-(SrOH) [1]. It possesses massive, coarse granular to compact morphology. The crystal forms include short to long hexagonal prisms, they can also be thick and tabular. Similar to fluorcaphite, the name of the mineral reflects its chemical composition (fluorine, strontium and phosphorus). The localities of the mineral fluorstrophite are shown in Fig. 25.

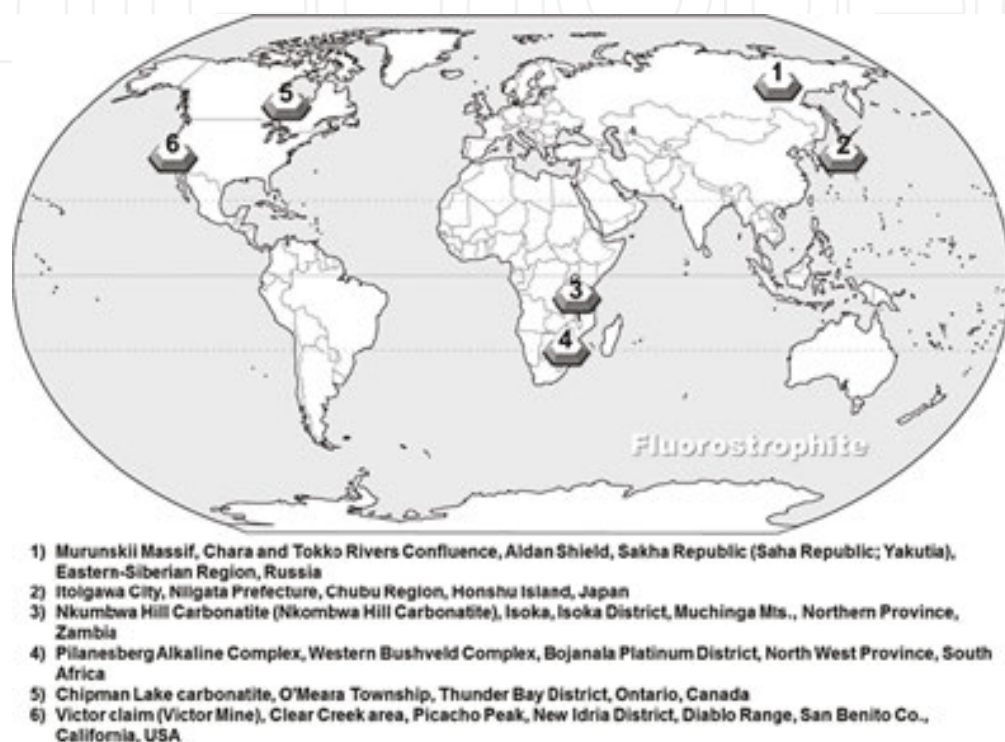


Fig. 25 Localities for the mineral fluorstrophite.

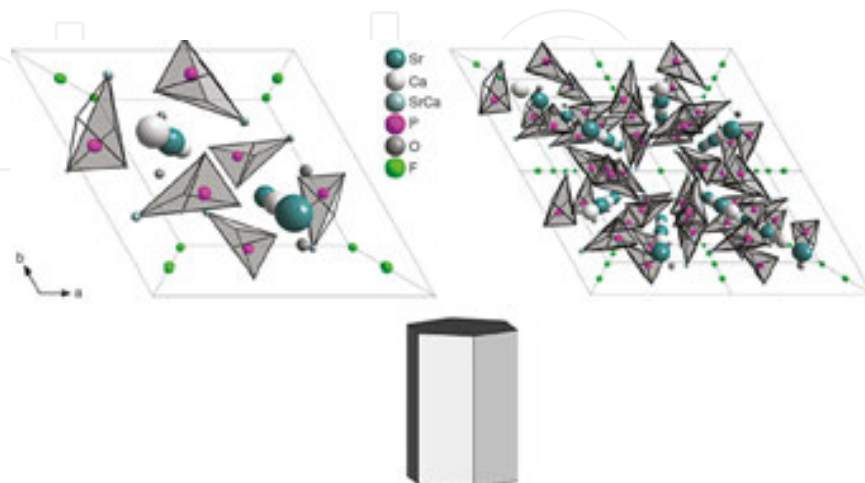


Fig. 26 The structure and the crystal habit of the mineral fluorstrophite.

The structure and the crystal habit of the mineral fluorstrophite are shown in **Fig. 26**. It is a green, yellow-green or colorless mineral with vitreous-greasy luster that crystallizes in hexagonal system with the space group $P6_3/M$ or $P6_3$. The crystallographic parameters of the unit cell are $a = 9.565$ and $c = 7.115$ Å, the ratio $a:c = 1:0.744$, $V = 563.74$ Å³ and $Z = 2$. The hardness of the mineral on the Mohs scale is 5. Calculated and measured densities are 3.74 and 3.84 g·cm⁻³, respectively. It has imperfect cleavage to {1010}.

2.2.7. Kuannersuite-(Ce)

The mineral kuannersuite-(Ce) ($\text{Na}_2\text{Ce}_2\text{Ba}_6(\text{PO}_4)_6\text{FCl}$ [88]) was found and named according to the locality (Kuannersuit plateau) in the Ilímaussaq alkaline complex, South Greenland (**Fig. 27**). It occurs associated with the minerals including aegirine, analcime, beryllite ($\text{Be}_3\text{SiO}_4(\text{OH})_2 \cdot \text{H}_2\text{O}$ [89]), chkalovite, galena, gmelinite¹⁷ [90],[91],[92],[93], gonnardite ($(\text{Na,Ca})_2(\text{Si,Al})_5\text{O}_{10} \cdot 3\text{H}_2\text{O}$ [94]), lovdarite ($\text{K}_2\text{Na}_6\text{Be}_4\text{Si}_{14}\text{O}_{36} \cdot 9\text{H}_2\text{O}$ [95],[96]), nabesite ($\text{Na}_2\text{BeSi}_4\text{O}_{10} \cdot 4\text{H}_2\text{O}$ [97],[98]), neptunite, pectolite, polyolithionite ($\text{KLi}_2\text{AlSi}_4\text{O}_{10}\text{F}_2$ [99]), pyrochlore¹⁸ [100], sphalerite (ZnS [101]) and tugtupite.

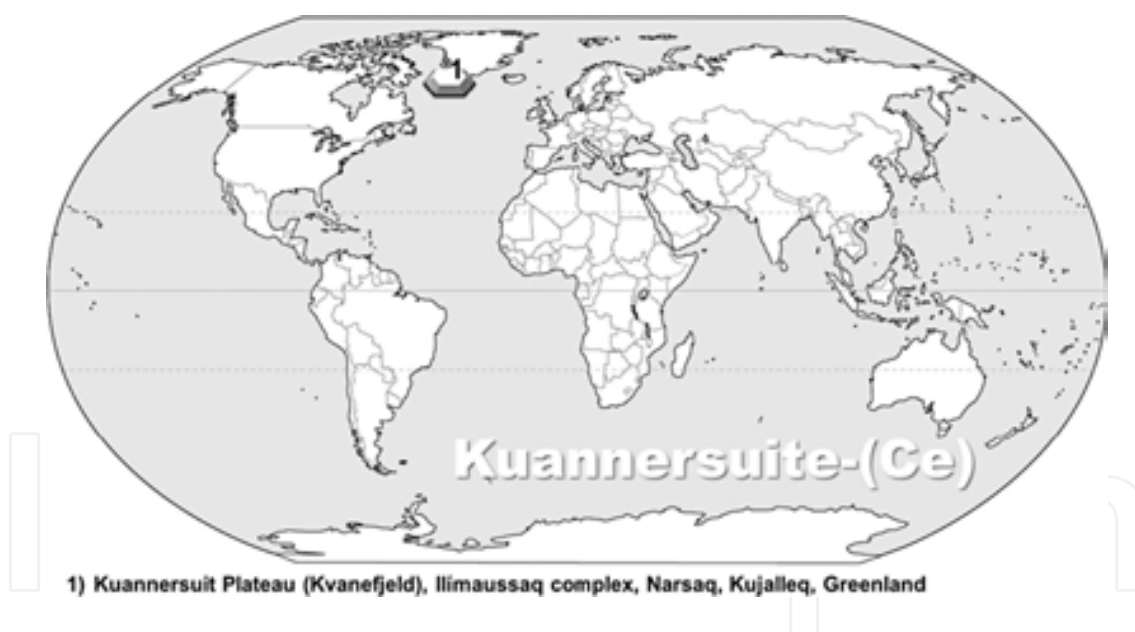


Fig. 27 The locality for the mineral kuannersuite-(Ce).

¹⁷ There are three minerals: gmelinite-(Ca), gmelinite-(K), and gmelinite-(Na) with the composition of $\text{Ca}_2(\text{Si}_8\text{Al}_4)\text{O}_{24} \cdot 11\text{H}_2\text{O}$ [90],[91], $\text{K}_4(\text{Si}_8\text{Al}_4)\text{O}_{24} \cdot 11\text{H}_2\text{O}$ [93], and $\text{Na}_4(\text{Si}_8\text{Al}_4)\text{O}_{24} \cdot 11\text{H}_2\text{O}$ [91],[93], respectively.

¹⁸ The member of the pyrochlore group ($(\text{Na,Ca})_2\text{Nb}_2\text{O}_6(\text{OH,F})$). A new scheme of nomenclature for the pyrochlore supergroup, approved by the CNMNC-IMA, is based on the ions at the A, B, and Y sites. The subgroups should be changed to the groups: pyrochlore (1), microlite (2), roméite (3), betafite (4), and elsmoreite (5). The new names are composed of two prefixes and one root name (identical to the name of the group). The first prefix refers to the dominant anion (or cation) of the dominant valence [either H_2O or \square] at the Y site. The second prefix refers to the dominant cation of the dominant valence [either H_2O or \square] at the A site. The prefix “keno-” represents “vacancy.” Where the first and the second prefix are equal, only one prefix is applied [100].

It occurs as light rose-colored hexagonal prismatic crystals, up to 1.5 mm long, with a white streak and a vitreous luster. It is a barium analogue of belovite-(Ce) (**Section 2.2.1**) and NaCeBa_3 analogue of fluorapatite (**Section 1.5.1**). The mineral is brittle and shows poor cleavage along $\{001\}$ and $\{100\}$. The structure and the crystal habit of the mineral kuannersuite-(Ce) are shown in **Fig. 28**.

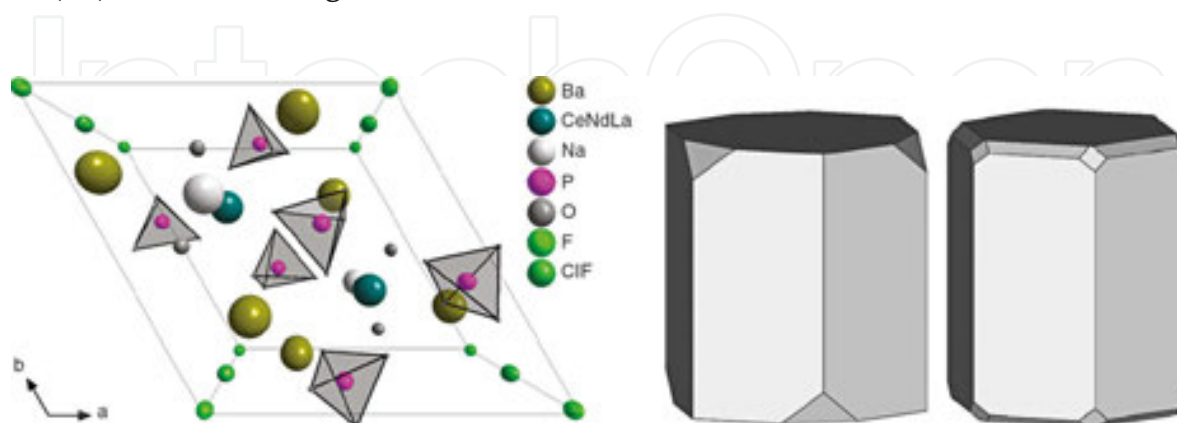


Fig. 28 The structure and the crystal habit of the mineral kuannersuite-(Ce).

Kuannersuite-(Ce) crystallizes in trigonal systems with the space group $P\bar{3}$. The parameters of unit cell are: $a = 9.9097$ and $c = 7.4026$ Å, $V = 629.558$ Å³ and $Z = 2$. There is no fluorescence under ultraviolet light (long or short wave). The Mohs hardness of kuannersuite is between $4\frac{1}{2}$ and $5\frac{1}{2}$, and calculated density is $4.5 \text{ g}\cdot\text{cm}^{-3}$.

2.3. The group of britholite

Britholites are typically phosphorus-bearing silicates with apatite structure and general formula: $(\text{REE},\text{Ca})_5[(\text{Si},\text{P})\text{O}_4]_3\text{Z}$, where REE is usually yttrium and $\text{Z} = \text{OH}^-$, F^- or Cl^- . The minerals from the group of britholite usually contain significant impurities of thorium and sometimes also uranium. These minerals are widespread in alkaline rocks such as pegmatites and metasomites¹⁹ related to syenite¹⁵ and nepheline–syenite complexes [102]. The name of this group is derived from the Greek word *brithos* for weight in order to refer to the high density of the mineral. The following minerals are described below.

The structure and the crystallographic data of some of the minerals from the group of britholite were introduced in **Fig. 29** and **Table 1**, respectively. The structural, thermodynamic and electronic properties of britholites were investigated by NJEMA et al [103].

¹⁹ The series of metamorphic processes whereby chemical changes occur in minerals or rocks as the result of the introduction of material, often in hot aqueous solutions, from external sources.

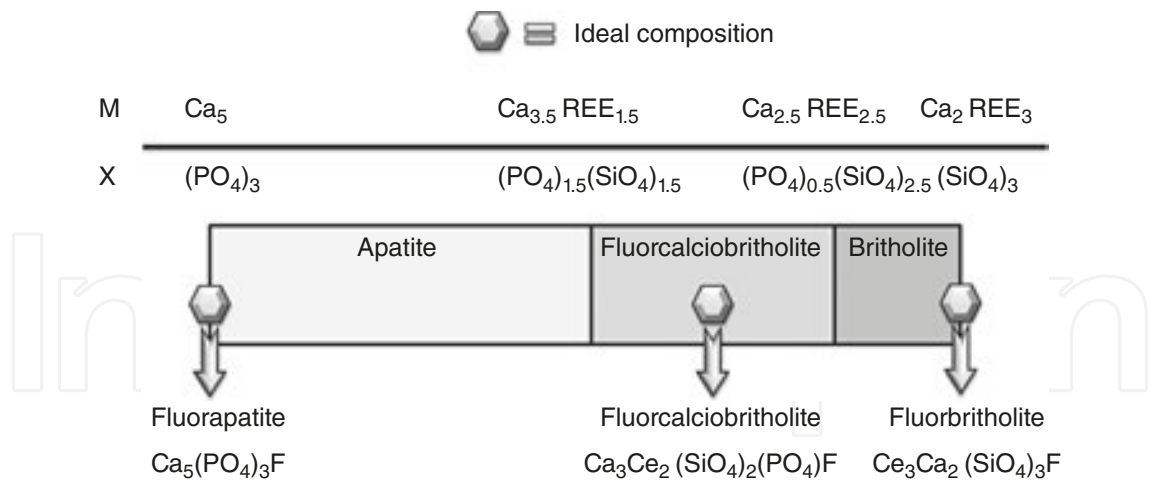


Fig. 29 The structure (the view according to axis *c*) of mineral: (a) britholite-(Ce), (b) britholite-(Y) and (c) fluorbritholite-(Ce). Coupled heterovalent substitution at M and T site in the series apatite–calciobriholite–britholite [1].

Mineral name	Crystallographic parameters							Hardness (Mohs)
	<i>a</i>	<i>c</i>	<i>a</i> : <i>c</i>	<i>Z</i>	<i>V</i>	SG	Density*	
	[Å]	—	—	—	[Å ³]	—	[g·cm ^{−3}]	
Britholite-(Ce)	9.63	7.03	1:0.730	2	564.60	P6 ₃ /M	4.45/4.49	5½
Britholite-(Y)	9.43	6.81	1:0.722		524.45		4.25/4.07	5.0
Fluorbritholite-(Ce)	9.52	6.98	1:0.734		547.74		4.66/4.67	
Fluorbritholite-(Y)	9.44	6.82	1:0.722		526.68		—/4.61	5½
Fluorcalciobriholite	9.58	6.99	1:0.729		555.17		4.20/4.25	5½
Tritomite-(Ce)	9.35	6.88	1:0.736		520.89		4.20/5.02	5.5
Tritomite-(Y)	9.32	6.84	1:0.734		514.54		3.22/4.48	3.5-6.5

Measured/calculated

Table 1 The crystallographic data of minerals from the group of britholite

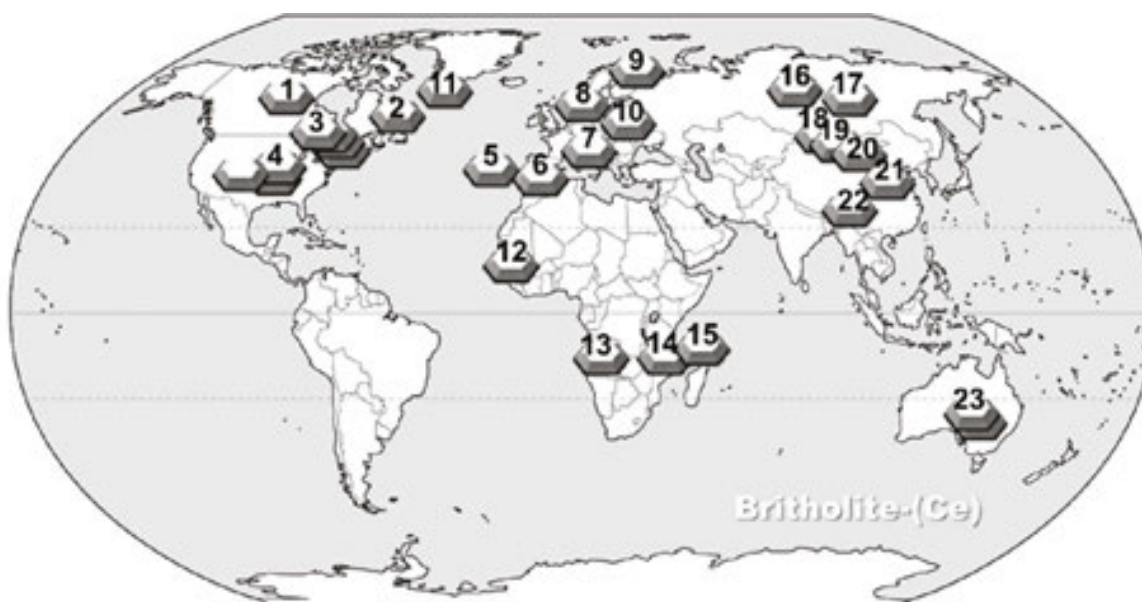
2.3.1. Britholite-(Ce)

The britholite-(Ce) (Lessignite-(Ce), (Ce,Ca)₅(SiO₄)₃OH) [104],[105],[106]) mineral (**Fig. 30**) was first recognized as the new mineral by G. FLINK (1897) in the pegmatite form of the nepheline–syenite at Naujakasik, Ilímaussaq complex, Greenland. Known localities for the mineral britholite are shown in **Fig. 31**.

The specimen was named and described by CHR. WINTHER [104] as opaque, brown crystals of the composition of 3[4SiO₂,2(Ce,La,Di,Fe)₂O₃,3(Ca,Mg)O,H₂O,NaF],2[P₂O₅,Ce₂O₃], which are apparently hexagonal prisms with pyramids, but it actually consists of biaxial orthorhombic individuals twined together as in aragonite. The Th-rich britholite-(Ce) was also known as fenghuangshite [107]. Britholite-(Ce) (first described as britholite) is the forefather of the



Fig. 30 The crystal (13 mm) of britholite-(Ce) from Ostkogen, Tvedalen, Norway.



- 1) Thor Lake syenite complex, Blachford Lake alkaline complex, Mackenzie District, Northwest Territories, Canada
- 2) Red Wine Alkaline Complex, Labrador, Newfoundland and Labrador, Canada
- 3) Coldwell complex, Thunder Bay District, Ontario, Canada (a), Kipawa alkaline complex, Les Lacs-du-Témiscamingue, Témiscamingue RCM, Abitibi-Témiscamingue, Québec, Canada (b), Manly zone (Dufresne property), Oka complex, Oka, Deux-Montagnes RCM, Laurentides, Québec, Canada (c) and Fallon Brothers Quarry (Quincy Quarry; Ballou Quarry; Old Colony Crushed Stone Company Quarry), Quincy, Norfolk Co., Massachusetts, USA (d).
- 4) Pea Ridge Mine, Sullivan, Washington Co., Missouri, USA (a), Magnet Cove, Hot Spring Co., Arkansas, USA (b) and Iron Hill (Iron Hill carbonatite complex), White Earth District (Powderhorn District), Gunnison Co., Colorado, USA (c).
- 5) Água de Pau volcano (Fogo volcano), San Miguel Island, Azores District, Portugal
- 6) Jebel Bou-Agrao, Tamazeght Mountain Range, Khénifra Province, Meknès-Tafilalet Region, Morocco (a) and Sierra de las Cabras, Cancarix, Hellín, Albacete, Castile-La Mancha, Spain (b)
- 7) San Vito quarry, San Vito, Ercolano, Monte Somma, Somma-Vesuvius Complex, Naples Province, Campania, Italy
- 8) Norra Kärr, Gränna, Jönköping, Småland, Sweden (a) and Middjället Quarry (Mellomjället Quarry), Malersd, Larvik, Vestfold, Norway (b).
- 9) Afrikanda Massif, Afrikanda, Kola Peninsula, Murmanskaja Oblast', Northern Region, Russia
- 10) Yastrebet Massif (Yastrebet'skiy; Yastrubetskiy), Ukrainian Shield, Dnipropetrovsk's Oblast' (Dnepropetrovsk Oblast'), Ukraine
- 11) Tuperssuatlat Bay, Tunulliarfik Fjord (Tunugdliarfik), Ilimaussaq complex, Narsaq, Kujalleq, Greenland
- 12) Los Archipelago (Los Islands), Guinea
- 13) Vinukunda, Tombwa City Council, Namibe Province, Angola
- 14) Junguni Hill, Balaka District, Malawi
- 15) Ampasibitika, Ampasindava Peninsula, Ambanja District, Diana Region (Northern Region), Antsiranana Province, Madagascar
- 16) Kizik alkaline massif (Kiziskoe), Enisei Range (Yenisei Ridge; Enisei Ridge), Krasnoyarsk Territory (Krasnoyarsk Krai; Krasnoyarsk Krai), Eastern-Siberian Region, Russia
- 17) Burpala alkaline Massif, Maigunda River, Mama River Basin, Buriatia (Buryatia), Prebalkatia (Pribalka'e), Eastern-Siberian Region, Russia
- 18) Khaldzan Buragtag massif, Altai Mts, Hovd Aimag (Khovd Aimag), Mongolia
- 19) Mushgai Khudag carbonatite complex (Mushgai Hudag; Mushgai Khuduk; Mushgai Khuduk), Shara Hulasa Hild, Ömnögovi Aimag, Mongolia
- 20) Bayan Obo deposit (Bayun-Obo deposit; Baiyunebo deposit), Bayan Obo, Bayan Obo Mining District, Baotou League (Baotou Prefecture), Inner Mongolia Autonomous Region, China
- 21) Weishan Mine (Chisan Mine; Xishan Mine; Deposit No. 101), Weishan Co., Jining Prefecture, Shandong Province, China
- 22) Maoniping Mine, Mianping Co., Llangshan Autonomous Prefecture, Sichuan Province, China
- 23) Olympic Dam Mine, Roxby Downs, Stuart Shelf, South Australia, Australia (a) and Paratoo copper mine, Yunta, Olary Province, South Australia, Australia (b).

Fig. 31 The localities for the mineral britholite-(Ce).

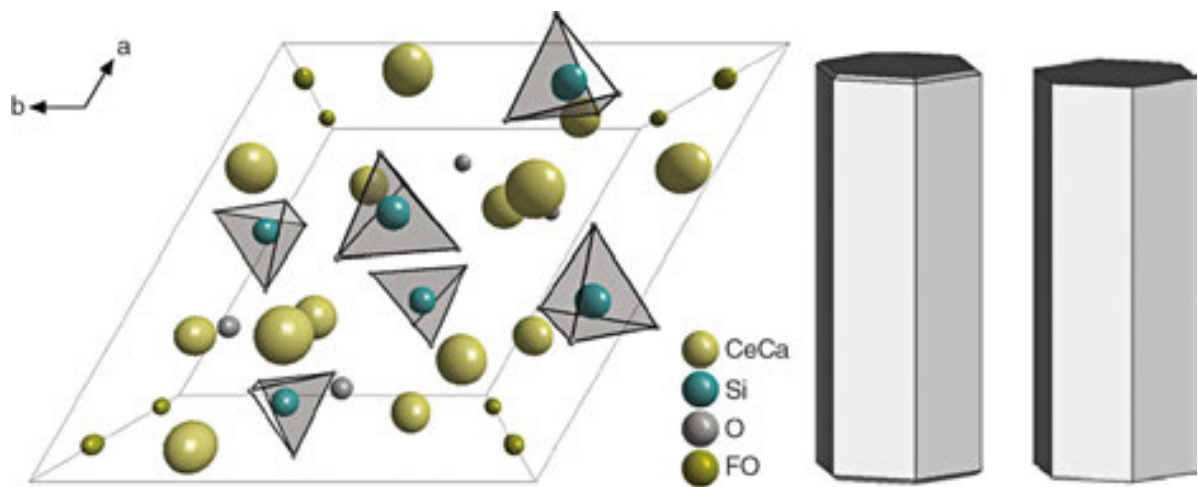


Fig. 32 The crystal structure (perspective view according to *c*-axis) of britholite-(Ce) and some common crystal shapes.

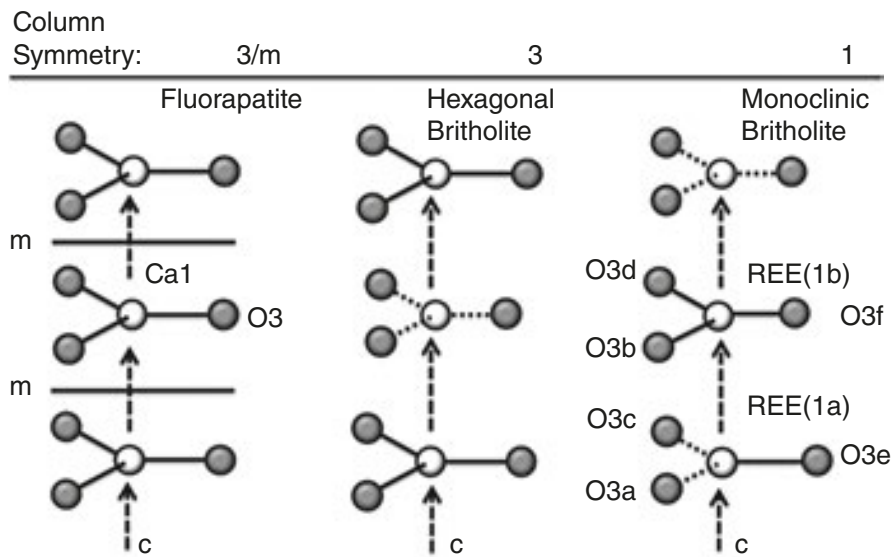


Fig. 33 Depiction of Ca(1)-O(3) triangles in apatite (a) and REE(1)-O(3) triangles in hexagonal (b) and monoclinic britholite (c). The dashed and solid lines in the structure of britholite indicate short and long REE-O bonds, respectively [106].

britholite group [108]. The structure of monoclinic britholite-(Ce) is shown in Fig. 32 and the crystallographic data are listed in Table 1.

The crystal structure of monoclinic dimorphs Fig. 33 of the mineral britholite-(Ce) (and also of britholite-(Y)described below) was solved in $P2_1$ space group by NOE et al [106]. The monoclinic britholite dimorph differs from its hexagonal counterpart principally in the ligation of the REE equivalent of the apatite Ca(1) site. Whereas in $P6_3$ britholite each Ca(1) equivalent has either three short or three long REE-O(3) bonds; in the $P2_1$ dimorph, the Ca(1) equivalents have either one long and two short REE-O(3) bonds or one short and two long REE-O(3) bonds. Arrangement of short and long bonds leads to $P6_3$ symmetry in hexagonal britholite due to removal of m from symmetry elements of apatite, and $P2_1$ symmetry in monoclinic

britholite due to removal of symmetry elements **3** and **m**. The reduction in symmetry explains the common observation of biaxial optical characteristics of britholite samples [106].

2.3.2. Britholite-(Y)

The mineral britholite-(Y) $((Y,Ca)_5(SiO_4)_3OH)$, abukumalite, [105], [109]) occurs similarly to britholite-(Ce) in granite, alkaline rocks, skarns and hydrothermal veins [107]. The structure of monoclinic ($P2_1$, refer the discussion to Fig. 33) britholite-(Y) and known localities are shown in Fig. 35 and Fig. 34, respectively.

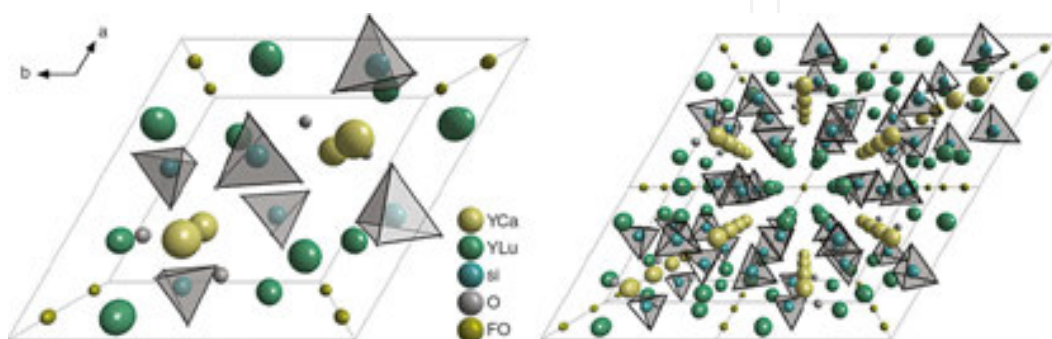


Fig. 34 The structure (perspective view along the *c*-axis) of britholite-(Y).



Fig. 35 The localities for the mineral britholite-(Y).

Britholite-(Y) is very brittle mineral with reddish brown or black color, pale brown streak and resinous luster that crystallizes as hexagonal in the space group $P6_3/m$ with the unit cell parameters $a = 9.43$ and $c = 6.81 \text{ \AA}$, $a:c = 1:0.722$, $V = 524.45 \text{ \AA}^3$ and $Z = 2$. Calculated and measured densities of the mineral are 4.07 and $4.25 \text{ g}\cdot\text{cm}^{-3}$, respectively.

2.3.3. Fluorbritholite-(Ce)

The mineral fluorbritholite-(Ce) $((\text{Ce,Ca})_5(\text{SiO}_4)_3\text{F})$ [1],[110]) is the fluorine-rich analogue of britholite-(Ce). The structure and known localities of the mineral fluorbritholite-(Ce) are shown in Fig. 36 and Fig. 37, respectively. The mineral has a yellow, reddish-brown color, or

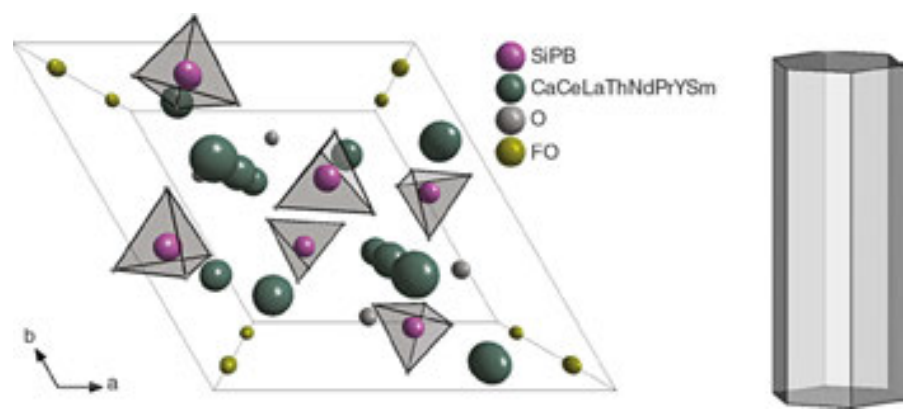


Fig. 36 The structure (perspective view along the c -axis) and the crystal habit of fluorbritholite-(Ce).



Fig. 37 The localities for the mineral fluorbritholite-(Ce).

it may be colorless. Its hardness on the Mohs scale is 5. Measured and calculated densities of fluorbritholite-(Ce) are 6.67 and 4.66 g·cm⁻³, respectively.

Fluorbritholite-(Ce) is a very brittle mineral that crystallizes as hexagonal in the space group P6₃/M. The unit cell shows following crystallographic parameters: $a = 9.517$ and $c = 6.983$ Å, $a:c = 1:0.734$, $V = 547.74$ Å³ and $Z = 2$.

2.3.4. Fluorbritholite-(Y)

The mineral fluorbritholite-(Y) ((Y,Ca)₅(SiO₄)₃F) [108]) was named as the fluorine-dominant analogue of britholite-(Y), where the Levinson-type suffix modifier, -(Y), indicates the dominance of yttrium among rare-earth elements. It forms irregular grains, hexagonal to tabular crystals and short-prismatic to thick-tabular crystals. The known localities and structures of the mineral fluorbritholite-(Y) are shown in **Fig. 38** and **Fig. 39**, respectively.

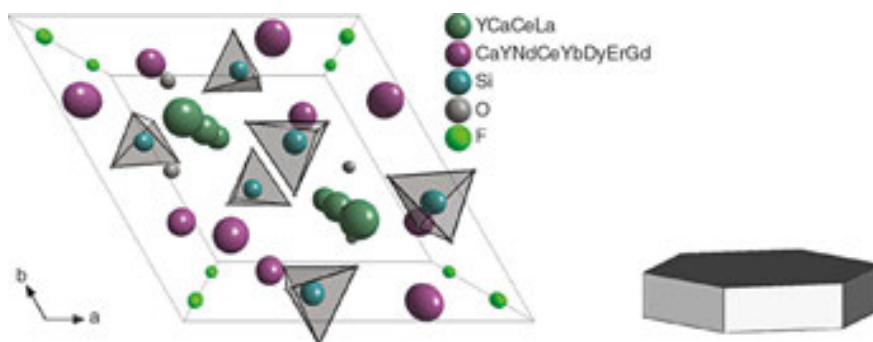


Fig. 38 The structure (perspective view along the c -axis) and the crystal habit of fluorbritholite-(Y).



Fig. 39 The localities for the mineral fluorbritholite-(Y).

The mineral fluorbritholite crystallizes in hexagonal systems of the space group $P6_3/m$ with the crystallographic parameters of unit cell $a = 9.444$ and $c = 6.819$ Å, $a:c = 1:0.722$, $V = 526.68$ Å³ and $Z = 2$. It is a brittle mineral of light-pink or brown color and calculated density of 4.61 g·cm⁻³. It has a pale brownish or white streak and its hardness on the Mohs scale is 5.

2.3.5. Fluorcalciobritholite

The mineral fluorcalciobritholite $((Ca,REE)_5(SiO_4,PO_4)_3F; [1],[102])$ was found at Mount Kukisvumchorr, Khibiny alkaline complex, Kola Peninsula, Russia and differs from fluorbritholite and fluorapatite in the content of calcium ($Ca > \Sigma REE$) and phosphorus ($Si > P$), respectively. The main crystal form is a hexagonal prism. The mineral is transparent, with a pale pinkish to brown color and a white streak. The structure and the locality of fluorcalciobritholite is shown in **Fig. 40** and **Fig. 41**, respectively.

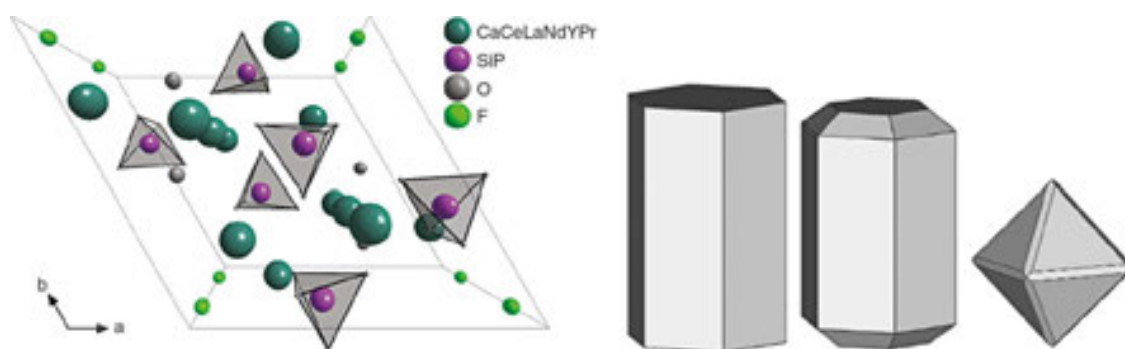


Fig. 40 The structure (perspective view along the c -axis) and the crystal habit of the mineral fluorcalciobritholite.

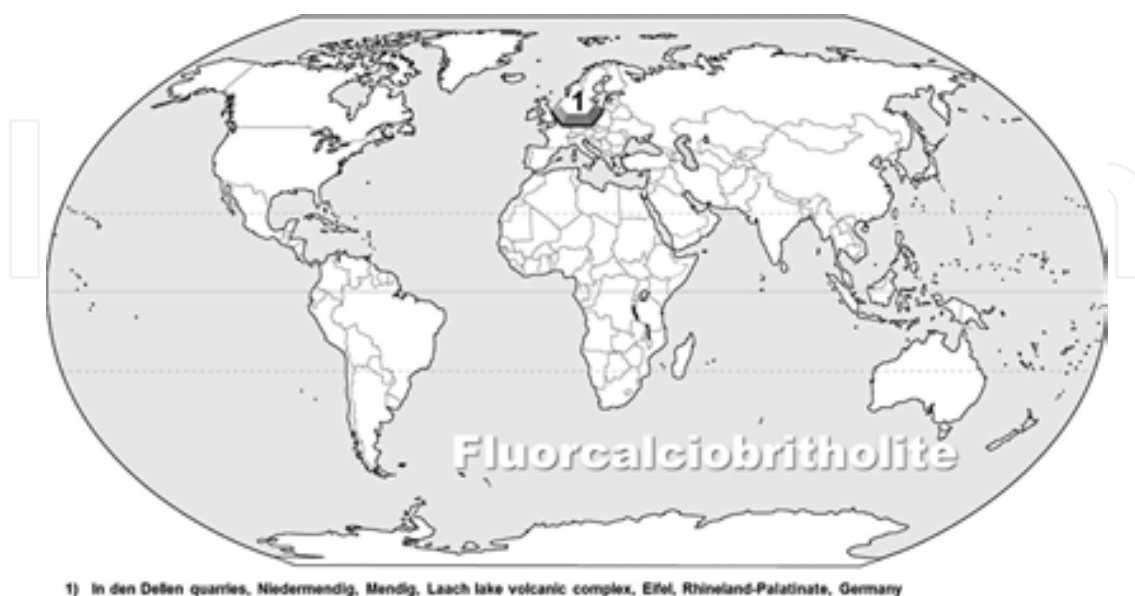


Fig. 41 The localities for the mineral fluorcalciobritholite.

The ideal chemical formula for fluorcalciobriitholite may be written as $(\text{Ca}_3\text{REE}_2)[(\text{SiO}_4)_2(\text{PO}_4)]\text{F}$. In the view of coupled heterovalent substitutions occurring at the M and T sites in the series apatite–calciobriitholite–briitholite, it is more practical in this case for nomenclature purposes to consider the total abundance of M cations as a single, composite site [1].

Pale pinkish brown or brown mineral fluorcalciobriitholite crystallizes as hexagonal in the space group $\text{P6}_3/\text{M}$ with the crystallographic parameters $a = 9.58$ and $c = 6.985 \text{ \AA}$, $a:c = 1:0.729$, $V = 555.17 \text{ \AA}^3$ and $Z = 2$. Calculated and measured densities of the mineral are 4.25 and $4.2 \text{ g}\cdot\text{cm}^{-3}$, respectively. It has white streak and vitreous luster. The mineral is brittle and its hardness on the Mohs scale is equal to $5\frac{1}{2}$.

2.3.6. Tritomite-(Ce)

Tritomite-(Ce) $(\text{Ce}_5(\text{SiO}_4)_3\text{BO}_4)(\text{OH},\text{O})$ [105],[111]) was first found by WEIBYE in 1849 at the island of Låven in Langesundsford as dark tetrahedral crystals in leucophanite $(\text{Na,Ca})_2\text{BeSi}_2(\text{O},\text{OH},\text{F})_7$ [112] or analcime. Chemically and structurally, it is very similar to melanocerite (melanocerite-(Ce),²⁰ $\text{Ce}_5(\text{SiO}_4)_3\text{BO}_4(\text{OH},\text{O})$ [1],[105],[111]) and caryocerite [111]. The pyramidal crystal of mineral tritomite-(Ce) is shown in Fig. 42.

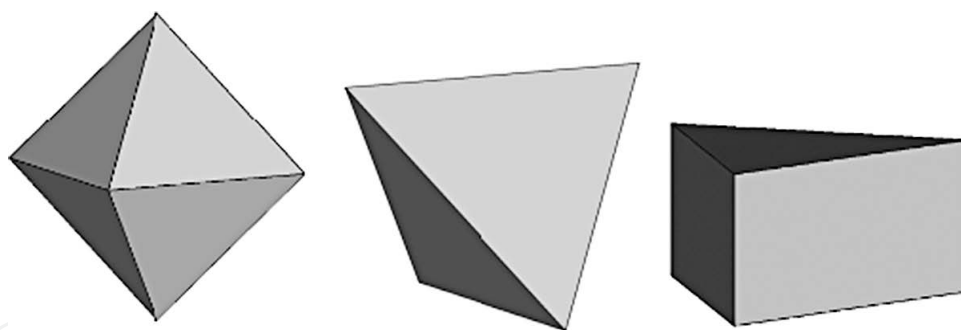


Fig. 42 The crystal habit of the mineral tritomite-(Ce) and tritomite-(Y).

The mineral was named from the Greek *tpitwos* meaning “cut in three parts” in allusion to the triangular and pseudo-tetrahedral crystal habit [113],[114]. Known localities for the mineral tritomite-(Ce) are shown in Fig. 43.

Tritomite-(Ce) crystallizes as hexagonal mineral in the space group $\text{P6}_3/\text{M}$ with crystallographic parameters $a = 9.35$ and $c = 6.88 \text{ \AA}$, $a:c = 1:0.736$, $V = 520.89 \text{ \AA}^3$ and $Z = 2$. It is a very brittle mineral of dark brown color with a hardness (on the Mohs scale) of $5\frac{1}{2}$.

²⁰ Since the mineral is equal to tritomite-(Ce), the name of melanocerite-(Ce) is discredited [1].



Fig. 43 Known localities for the mineral tritomite-(Ce).

2.3.7. Tritomite-(Y)

The mineral tritomite-(Y) ($(Y_5(SiO_4,BO_4)_3(OH,O,F), [Y^{3+}(Cr, Pr, Th)^{4+}Ca](Si_2B)O_{12}O$ [111],[113], [115]) was first described by FRONDEL. It is also known as the hexagonal mineral spencite (named after Canadian geologist H.S. SPENCE) [116]. The mineral tritomite-(Y) is formed in the nepheline syenite pegmatites of the area, which carries rare earths predominantly from the yttrium group. Known localities of mineral tritomite-(Y) are introduced in Fig. 44.



Fig. 44 Known localities for the mineral tritomite-(Y).

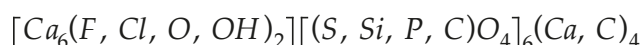
When heated in air to temperatures ranging from 600°C to 1000°C, tritomite-(Y) recrystallizes to the structure of apatite and amorphous phase, presumably to a calcium borosilicate glass [60]. The pyramidal crystals of the mineral tritomite-(Y) are similar to tritomite-(Ce) ones, which are shown in **Fig. 42**.

Tritomite-(Y) crystallizes as hexagonal in the space group $P6_3/M$ with unit cell parameters $a = 9.32$ and $c = 6.84$ Å, $a:c = 1:0.734$, $V = 514.54$ Å³ and $Z = 2$. It is dark green-black, red-brown, nearly black mineral with vitreous or resinous luster and average density of $3.22 \text{ g}\cdot\text{cm}^{-3}$. It is a brittle mineral forming small fragments with conchoidal fracture. The hardness of tritomite-(Y) on the Mohs scale ranges from 3.5 to 6.5 [111],[113],[115].

2.4. The group of ellestadite

Ellestadites *sensu lato* are sulfato-silicates. For stoichiometric reasons, the incorporation of the sulfate anion $(\text{SO}_4)^{2-}$ in the structure of apatite in the place of $(\text{PO}_4)^{3-}$ or $(\text{AsO}_4)^{3-}$ must be coupled with a concurrent substitution by silicate anions $(\text{SiO}_4)^{4-}$. This holds in all cases in which the M sites are occupied by divalent cations. Pure sulfates with an apatite structure may occur only by reducing overall positive charge associated with the M cations, as is the case in cesanite and caracolite from the group of hedyphane (**Section 2.1**) [1].

The structural formula of ellestadite and (with slight modification) of wilkeite can be expressed as follows [117]:

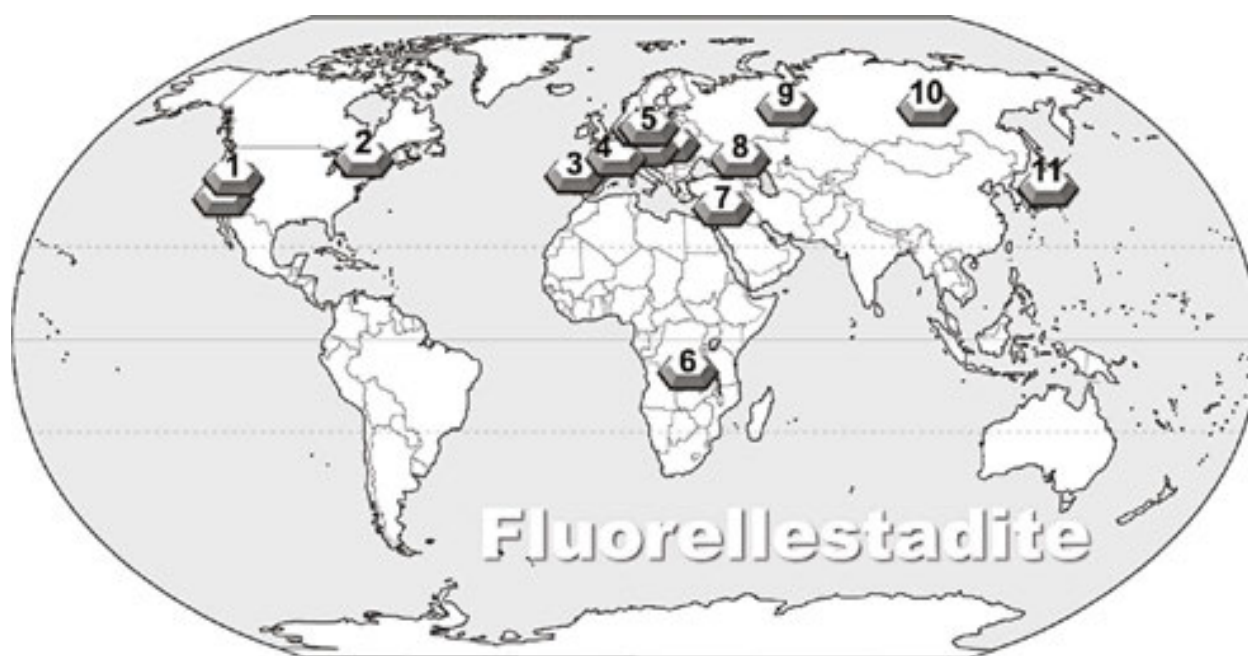


This formula indicates that two-fifths of the Ca^{2+} ions are located on threefold axes and can be replaced by carbon. Three-fifths of the Ca^{2+} ions are tied to F^- , Cl^- and O^- anions or OH^- groups and cannot be replaced by carbon. All Ca^{2+} ions are tied to O-ions, which are arranged in tetrahedral coordination with S-, Si-, P- or C-ions at the centers.

2.4.1. Fluorellestadite

The mineral fluorellestadite (formerly called ellestadite-(F) [85],[118],[119] $\text{Ca}_5(\text{SiO}_4)_{1.5}(\text{SO}_4)_{1.5}\text{F}$ [1],[120]) is a rare mineral found in nature in skarns or metamorphosed limestones²¹ [121]. It was named according to American analytical chemist R.B. ELLESTAD and fluorine in the chemical composition. The mineral occurs as needles, as hexagonal prismatic, poorly terminated crystals up to 3 mm long, and as fine-grained aggregates. Thin needles are colorless, crystals are transparent and aggregates are translucent. Known localities of fluorellestadite are introduced in **Fig. 45**. The structure of mineral ellestadite is shown on **Fig. 46**.

²¹ Limestone is a name used for sedimentary rock composed mainly of calcium carbonate, usually in the form of calcite (trigonal CaCO_3) or aragonite (orthorhombic CaCO_3), but there could also be considerable amounts of magnesium carbonate (MgCO_3 , trigonal mineral magnesite) or dolomite (trigonal $\text{CaMg}(\text{CO}_3)_2$) [121].



- 1) Crestmore quarries, Crestmore, Riverside Co., California, USA (a) and Champion Mine (White Mountain Mine; Jeffrey Mine; Diaspore; Vulcanus; Black Eagle; Champion Silimanite Mine; Champion Andalusite Mine; Vulcanite Mine; Vulcanite & Vulcanus No. 156; Black Eagle & Vulcanus Nos. 8 and 9 No. 157), White Mountain Peak, White Mts, Mono Co., California, USA (b)
- 2) Oka complex, Oka, Deux-Montagnes RCM, Laurentides, Québec, Canada
- 3) Bendada Mines, Bendada, Sabugal, Guarda District, Portugal
- 4) Lapanouse-de-Séverac slag locality, Aveyron, Midi-Pyrénées, France
- 5) Caspar quarry, Bellerberg volcano, Ettringen, Mayen, Eifel, Rhineland-Palatinate, Germany (a), Zeilberg Quarry, Maroldsweisach, Franconia, Bavaria, Germany (b), Basalt quarry, Klösch, Bad Radkersburg, Styria, Austria (c) and Zlatno, Vysoká, Banská Štiavnica Co., Banská Bystrica Region, Slovakia (d)
- 6) Kampijimpanga, Solwezi District, North-Western Province, Zambia
- 7) Hatrurim (Hatrurim Basin), Negev, Israel (a) and Har Ye'elim, Southern District (HaDarom District), Israel (b)
- 8) Upper Chegem volcanic caldera, Baksan Valley, Kabardino-Balkarian Republic, Northern Caucasus Region, Russia
- 9) Kopeisk, Chelyabinsk coal basin, Chelyabinsk Oblast', Southern Urals, Urals Region, Russia (a) and Chelyabinsk coal basin, Chelyabinsk Oblast', Southern Urals, Urals Region, Russia (b)
- 10) Yoko-Dovyrensky Massif, Dovyren Highlands, Buriatia Republic (Buryatia), Transbaikalia (Zabaykalye), Eastern-Siberian Region, Russia
- 11) Chichibu mining district (Chichibu mine), Nakatsugawa, Ohtaki-mura, Chichibu City, Saitama Prefecture, Kanto Region, Honshu Island, Japan

Fig. 45 Known localities for the mineral fluorellestadite.

Fluorellestadite is colorless, blue or pale bluish green hexagonal mineral belonging to the space group $P6_3/M$. The unit cell parameters are $a = 9.485$, $c = 6.916$ Å, $Z = 2$ and $V = 538.84$ Å³. Calculated density is 3.10 g·cm⁻³. The hardness of the mineral on the Mohs scale is $4\frac{1}{2}$.

The mineral is also known from burned coal dumps, where its formation is possible in the presence of carbonaceous and carbonate rocks such as the rests of pyrometamorphism²² [9] of sedimentary rocks. The generalized formula of this mineral can be expressed as $\text{Ca}_{10}(\text{SiO}_4)_{3-x}(\text{SO}_4)_{3-x}(\text{PO}_4)_{2x}(\text{OH},\text{F},\text{Cl})_2$, where the parameter x varies from 0 (ellestadite) to 3 (apatite).

²² The term pyrometamorphism, which is derived from the Greek word *pyr/pyro* (fire), *meta* (change), and *morph* (shape or form) was first used by BRAUNS to describe high-temperature changes which take place at immediate contact of magma and country rock with or without interchanges of material. Tyrrell defined pyrometamorphism as pertaining to the "effect of the highest degree of heat possible without actual fusion." There are a number of rock terms commonly used in association with the phenomenon of pyrometamorphism including hornfels,³ buchite, porcellanite, sanidinite, emery, paralava, clinker, fulgurite, or with other general terms such as fused or burnt rock [121].

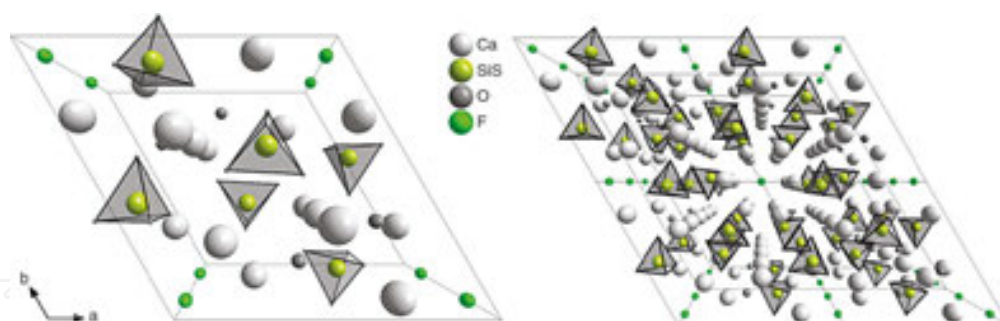


Fig. 46 The structure of the mineral fluorellestadite (perspective view along the *c*-axis).

2.4.2. Hydroxylellestadite

Hydroxylellestadite (formerly called ellestadite-(OH) [85], $\text{Ca}_5(\text{SiO}_4)_{1.5}(\text{SO}_4)_{1.5}(\text{OH})$ [1],[117], [122],[123]) was first reported at cornet Hill by PASCAL et al [124] and MARINCEA et al [125]. Natural hydroxylellestadite²³ occurrences were reported from pegmatite veins, skarn and pyrometamorphic deposits and from mine dumps, but this mineral has never been reported from a cave. The mineral forms aggregates of xenomorphic crystals which have a maximum length of 0.5 mm and a maximum width of about 0.1 mm.



Fig. 47 Known localities for the mineral hydroxylellestadite.

²³ Synthetic analogs are known as “technical products,” such as burnt industrial waste and cement [122].

Hydroxyllellestadite is associated with berlinite²⁴ (AlPO_4 [126]) , another high-temperature mineral. It is likely to have formed within highly phosphatized, silicate-rich, carbonate-mudstone sediments heavily compacted and thermally transformed due to *in situ* bat guano combustion. Known localities, where the mineral hydroxyllellestadite can be found, and its structure are shown in **Fig. 47** and **Fig. 48**, respectively.

Hydroxyllellestadite is a pink or purple-gray hexagonal mineral, which belongs to the space group $P6_3/m$. The unit cell parameters are $a = 9.491$, $c = 6.921$ Å, $Z = 2$ and $V = 539.91$ Å³. Calculated density is $3.11 \text{ g}\cdot\text{cm}^{-3}$. The hardness of the mineral on the Mohs scale is in the range of $3\frac{1}{2}$ to $4\frac{1}{2}$. Hydroxyllellestadite shows faded white-yellow fluorescence when irradiated with UV light, independently of the excitation frequency [122].

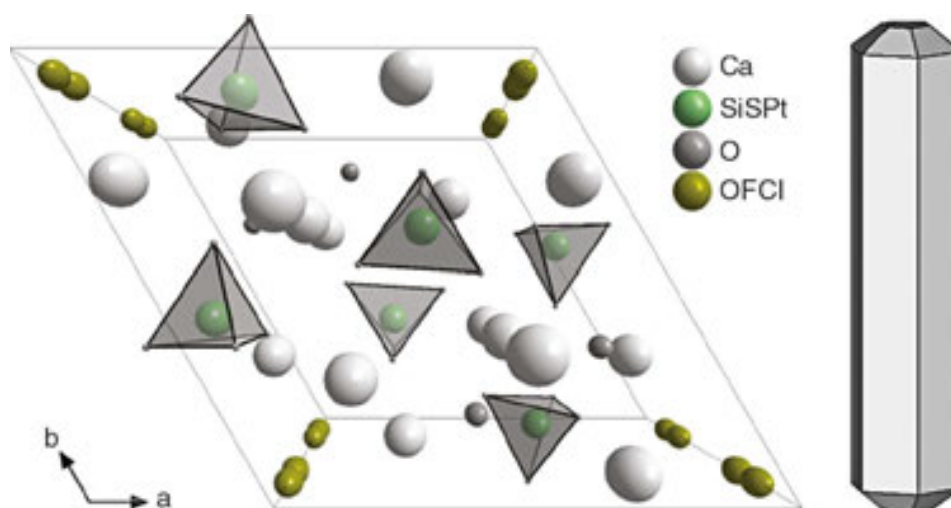


Fig. 48 The structure (perspective view along the c -axis) and the crystal habit of mineral hydroxyllellestadite.

2.4.3. Chlorellestadite

The mineral chlorellestadite²⁵ [127],[128] was named in 1892 according to American analytical chemist R.B. ELLESTAD (**Section 2.4.1**) and the content of chlorine in its chemical composition in veinlets cutting contact with metamorphosed limestone. The structure of the mineral ellestadite is shown in **Fig. 49**.

The mineral occurs as a compact mass. The mineral chlorellestadite is associated with diopside, wollastonite, vesuvianite ($\text{Ca}_{10}\text{Mg}_2\text{Al}_4(\text{SiO}_4)_5 (\text{Si}_2\text{O}_7)_2(\text{OH})_4$ [129]), monticellite (CaMgSiO_4 [130]) and calcite.

²⁴ The mineral was named after Swedish pharmacologist N.J. BERLIN. The mineral is Al-P analogue of quartz.

²⁵ The IMA status of the mineral was discredited in 2010.

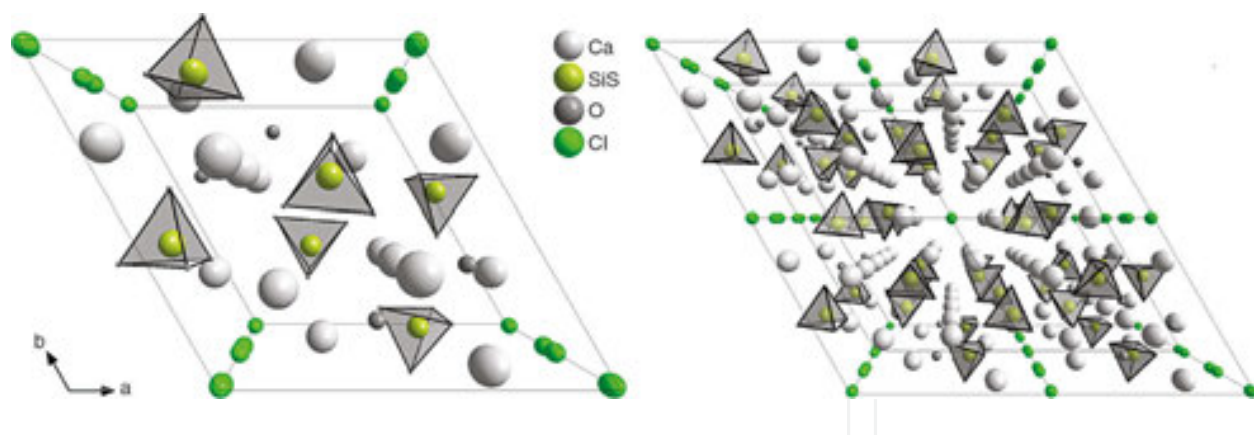


Fig. 49 The structure of the mineral chlorellestadite (perspective view along the c -axis).

Chlorellestadite is a hexagonal mineral that crystallizes in the space group $P6_3/M$ with crystallographic parameters $a = 9.53$ and $c = 6.91$ Å, $a:c = 1:0.725$, $V = 543,49$ Å³ and $Z = 2$. It has white streaks and a vitreous luster. The color of the mineral is pink, yellowish green, pale rose, orange, but it can also be colorless. The hardness on the Mohs scale is $4\frac{1}{2}$. Calculated and measured densities of the mineral are 3.068 and 3.113 g·cm⁻³, respectively.

2.4.4. Mattheddleite

Mattheddleite [131],[132],[133],[134] is a mineral with the composition $Pb_{10}(SiO_4)_3(SO_4)_3Cl_2$ (LIVINGSTONE et al [131]) or $Pb_5(Si_{1.5}S_{1.5})O_{12}(Cl_{0.57}OH_{0.43})$ (STELLE et al [134]) which is a lead member of apatite supergroup where phosphorus is totally replaced by sulfur and silicon: $Si^{4+} + S^{6+} \leftrightarrow 2P^{5+}$. Mattheddleite was first recognized in typical Pb mineral region at Leadhills, Scotland and named after Scottish mineralogist MATTHEW FORSTER HEDDLE (1828–1897). The $Z = OH^- + Cl^-$ anion position is zoned from an OH-rich interior to a Cl-rich exterior. Known localities, where the mineral hydroxyllestadite can be found, and its structures are shown in Fig. 50 and Fig. 51, respectively.

Mattheddleite is a colorless or white hexagonal mineral belonging to the space group $P6_3/M$. The unit cell parameters are $a = 9.963$ (10.0056 [134]) and $c = 7.464$ (7.4960 [134]) Å, $Z = \frac{1}{2}$ ($Z = 2$ [134]) and $V = 641.63$ (649.9 [134]) Å³. Calculated density is 6.96 (6.822 [134]) g·cm⁻³. The hardness of the mineral on the Mohs scale is $4\frac{1}{2}$.



Fig. 50 Known localities for the mineral mattheddleite.

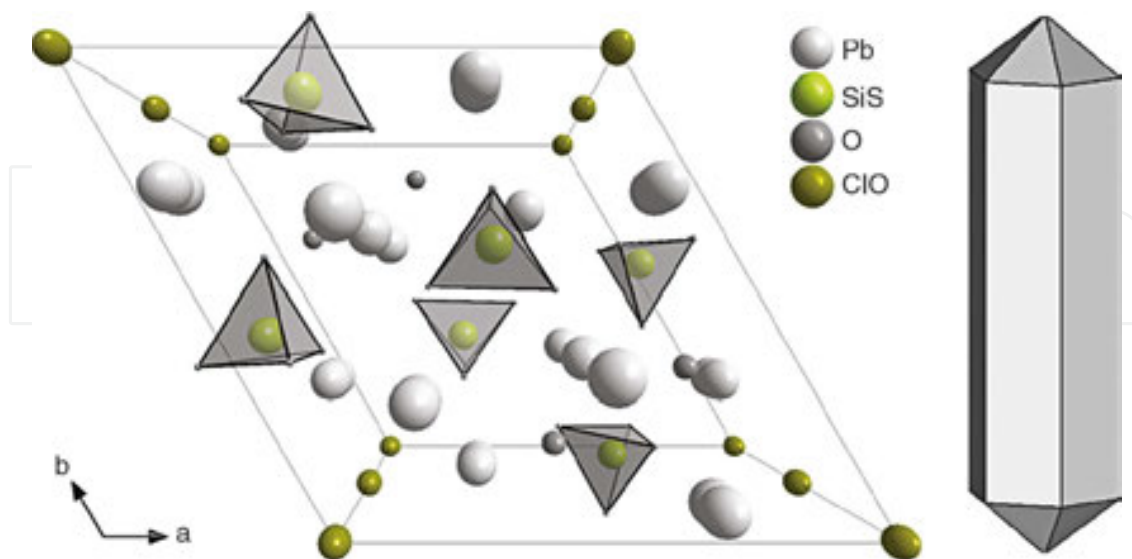


Fig. 51 The structure and the crystal habit of the mineral mattheddleite (perspective view along the *c*-axis).

2.5. Pieczkaite

The mineral pieczkaite ($\text{Mn}_5^{2+}(\text{PO}_4)_3\text{Cl}$ [135],[136]) was found in the Southeastern shoreline of a small, unnamed island in Cross Lake, Manitoba, Canada ($54^\circ 41' \text{N}$, $97^\circ 49' \text{W}$; **Fig. 52**) and classified as the member of the supergroup of apatite. It is isostructural with calcium fluorapatite (**Section 1.5.1**). The approximate composition of hydrothermally grown manganese chlorapatite is $\text{Mn}_5(\text{PO}_4)_3\text{Cl}_{0.9}(\text{OH})_{0.1}$ [136].



1) Pegmatite No. 22, (Gottcha Claim), North Group, Cross Lake, Manitoba, Canada

Fig. 52 Locality for the mineral pieczkaite.

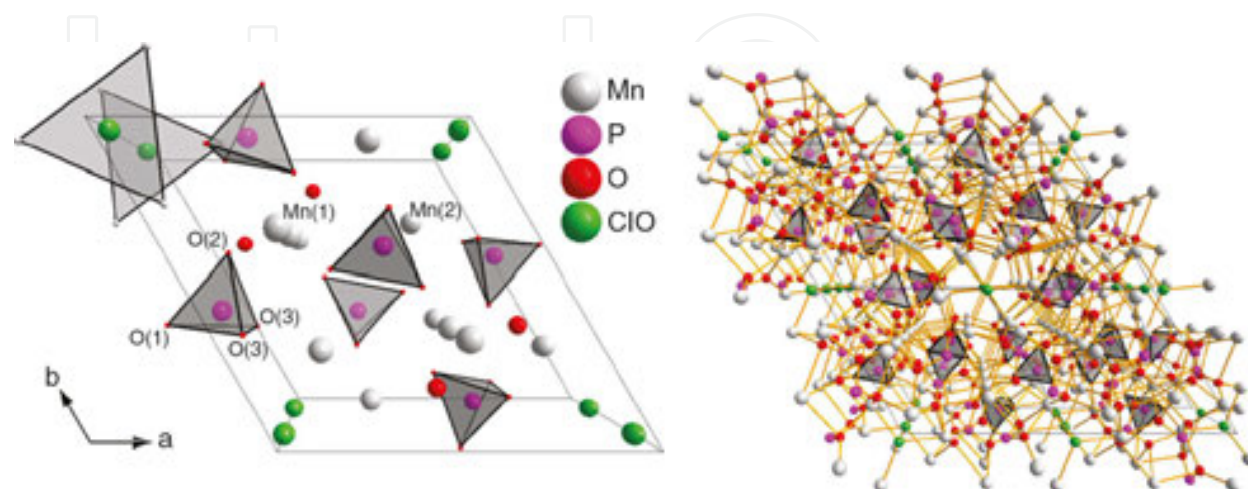


Fig. 53 The structure of the mineral pieczkaite (perspective view along the c-axis).

It is a hexagonal mineral that crystallizes in the space group $P6_3/M$ with the crystallographic parameters of unit cell $a = 9.532$ and $c = 6.199$ Å, $a:c = 1:0.6501$, $V = 587.78$ Å³ and $Z = 2$. Calculated density of pieczkaite is 3.783 g·cm⁻³. The hardness of the mineral on the Mohs scale varies in the range from 4 to 5. The structure of the mineral pieczkaite is shown in **Fig. 53**.

The coordination polyhedron around Mn(1) has the point-group symmetry 3 and is a trigonal prism in which the two triangles of oxygen atoms are slightly rotated relative to each other. The coordination polyhedron around Mn(2) is a severely distorted octahedron. The phosphate group is more distorted than in any of the other apatites. The chlorine atom is located in the center of an equilateral triangle formed by three Mn(2) atoms [136].

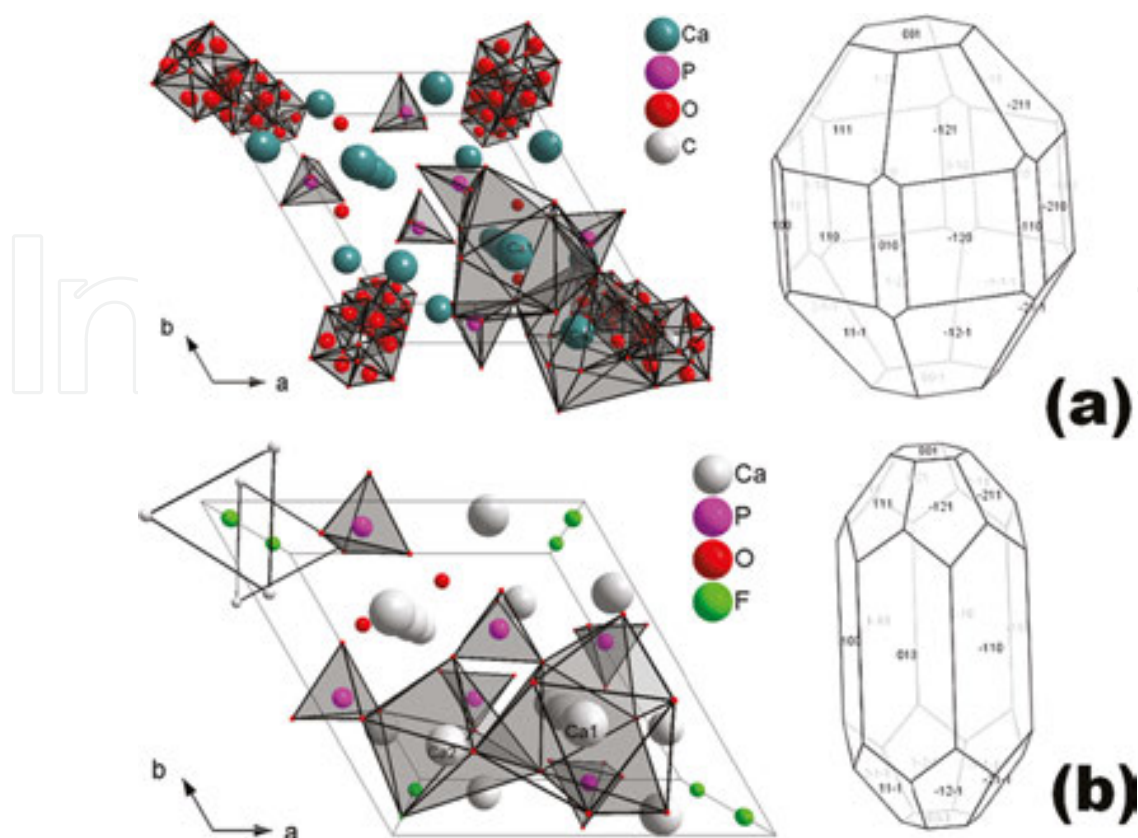
2.6. Carbonate-apatites

As mentioned previously (**Section 1.1**) the name of both most typical examples, i.e. carbonate-hydroxylapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) and carbonate-fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), was discredited from the IMA list of minerals [1]. The structure and the crystal shape of carbonate-apatite and carbonate-fluorapatite are shown in **Fig. 54**. The carbonate-apatites, the properties of which are listed in **Table 7 (Chapter 1)**, are intensively studied as the mineral constituents of bones and teeth as described in **Section 10.9**.

The carbonate-rich apatites are:

1. **Francolite** ($\text{Ca}_{10-x-y}\text{Na}_x\text{Mg}_y(\text{PO}_4)_{6-z}(\text{CO}_3)_z\text{F}_{0.4z}\text{F}_2$ or $\text{Ca}_5(\text{PO}_4)_3\text{F}$) [137] is the name used for massive, cryptocrystalline or amorphous varieties of carbonate-rich hydroxyl- and fluorapatite. Francolite and staffelite are the synonyms for carbonate-fluorapatite.

This complex carbonate-substituted apatite is found only in marine environments, and, to a much smaller extent, in weathered deposits, for instance above carbonatites [138]. The mineral was named according to its occurrence at Wheal Franco, Whitchurch, Tavistock District, Devon, England.



- i. **Type A:** carbonate ion of ideal geometry in upright open configuration (bisector of $[\text{CO}_3]^{2-}$ triangle parallel to c -axis); configuration with apical oxygen located at the position of OH^- (a)
- ii. **Type B:** closed (bisector normal to c -axis) configuration of type A1 carbonate ion in the space group $\text{P6}_3/\text{M}$ (b)
- iii. **Type AB:** open (and inverted) type A2 carbonate ion and the location of type B carbonate ion close to the sloping face of substituted $[\text{PO}_4]^{3-}$ tetrahedron (c).

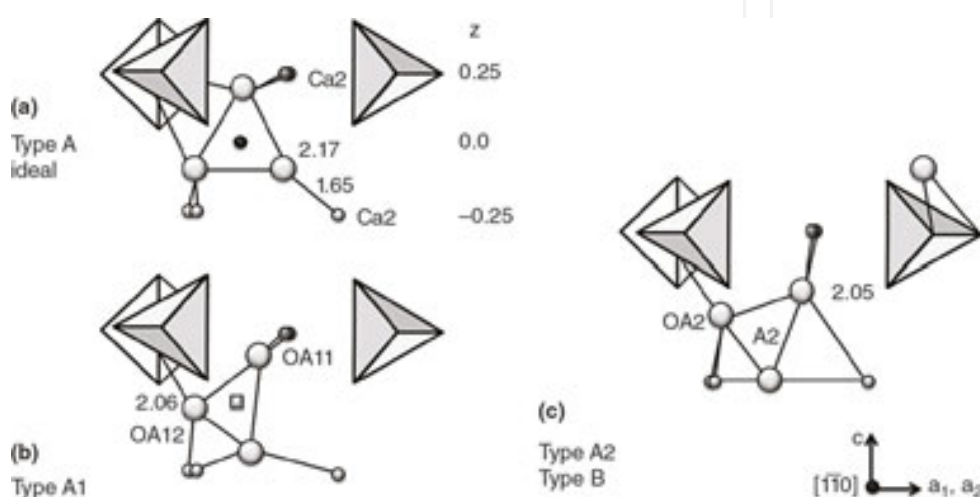


Fig. 55 Part of the c -axis channel showing the accommodation of carbonate ion in the structure of hydroxylapatite [144].

Individual types of carbonate apatite and their importance for bone and dental enamel are described in **Section 10.9.2**.

Carbonate apatites have distinctive X-ray patterns and rather small cell parameter a . An empirical relationship between the content of CO_2 in apatite and the separation (Δ [Å]) of the 211 and 112 X-ray diffraction lines has been given by O'BRIEN et al [145],[146]:

$$\text{CO}_2 \text{ [wt.\%]} = 17.335 - (615.524 \cdot \Delta) \quad (1)$$

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