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- 1.- Cacozenite sphaerules on quartz. R. Muñoz collection. Honorio Cócera photomicrography.
- 2.- Natrodufrenite-dufrenite. Christian Rewitzer collection and photomicrography.
- 3.- Strengite crystals. Miguel Calvo collection. Joaquim Callén photomicrography.



Secondary phosphates of La Paloma mine, Zarza la Mayor, Cáceres, Spain

Joan Viñals and Miguel Calvo

INTRODUCTION

The phosphorite mineralizations worked in the Zarza la Mayor-Ceclavín area are located within a granitic mass whose dominant facies, and where the veins are, is a two-mica granite of medium grain size. These ore deposits also contain small amounts of sulfides (Palero *et al.*, 1985). In this area twelve major veins and six smaller outcrops have been identified and worked. The mineralization formed in a high-temperature stage of the hydrothermal process, with fluorine as concentrating agent for the phosphorus, which does not appear in elevated concentrations in the granite host rock (Rambaud *et al.*, 1983).

The La Paloma mine is located 4 kilometers SSE of Zarza la Mayor, to the left of the Alcantara road, at Km 14. It is located at the edge of the pluton, and also in a small zone at the contact with the slates. The biotite is largely muscovitized and exhibits megacrystals of quartz and mica (Palero *et al.*, 1985). In La Paloma mine there are two main veins and other smaller veins with a NE-SW direction, vertical or subvertical, 1.8 km long and ranging from centimeters to four meters in thickness, consisting of alternating quartz and apatite.

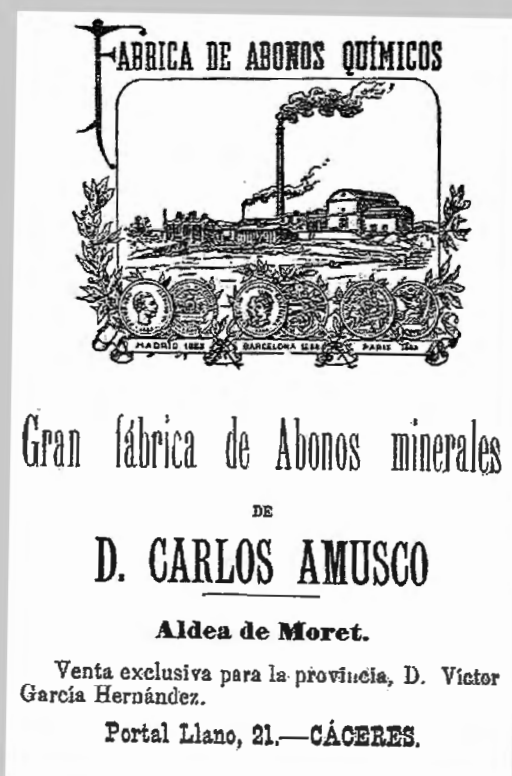
Sulphides appear at a later, lower temperature stage of the formation of the quartz-apatite mineralization, and appear in the brecciated areas (Palero *et al.*, 1985). The vein formation that is part of La Paloma mine extends to the northeast, having been exploited in two other mines too,

the La Blanca and La Esperanza. Another vein system that appears in the La Paloma mine was also worked in the La Maravilla, La Estrella and some other mines (Egozcue and Mallada, 1876).

The Zarza la Mayor mines began to be exploited in 1870 as an alternative to those in Logrosán, which were paralyzed by disputes between landowners and mining concessionaires. The La Paloma mine was initially exploited by open cuts, with trenches up to 10 meters deep. Also four shafts were dug, mostly just exploratory, up to 36 meters deep. At the bottom of the shafts, mineralization in veins was only about 30 cm thick at most, and even at 27 meters deep, where the first floor of the underground works was, the mineralization was clearly poorer than at the surface (Egozcue and Mallada, 1876).

The ore was hand cut and selected by groups of women, without the help of any mechanical system, and material of sufficient quality was carried out on the backs of donkeys or mules. Ore with better quality was transported by carts of 2 or 2 ½ tons capacity, drawn by oxen, to Alcántara. There it was transported along the Tajo river by boat to Lisboa and from there exported to England.

In general, the operators were not the owners of the deposits, but worked on a lease, paying a variable fee depending on the mineral quality, between 12 and 25 reales per ton, to the concession owners (who usually had obtained them in exchange for a small fee to the initial discoverers, laborers from the local area).



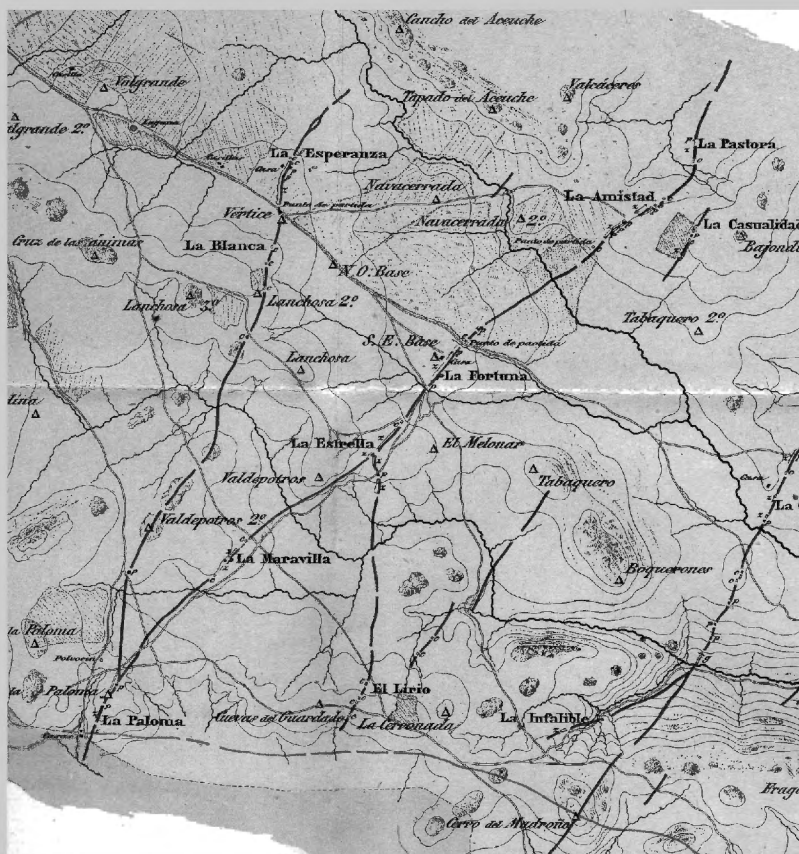
Advertising of Carlos Amusco's fertilizer factory, published in Revista de Extremadura, in 1904.

Extraction costs were about 20 reales per ton, river transport 135 per ton, and onward transport to England 60 reales per ton (Dalençon, 1872). Adding to these costs another 30 reales for the transport by land to Alcantara, the total cost reached 270 reales per ton. Given that ore between 55% and 60% richness was valued in England at the equivalent of 250 reales per ton (Dalençon, 1872), it is clear that they could sell only the higher quality ore. The high transport costs and the demands of the buyers entailed that only the purest phosphate minerals could be sold, leaving a lot of lower quality material in the tailings. Also in those years there was a major drought, which hindered navigation on the Tajo, which also resulted in more accumulation of mineral at the mines. In the summer of 1872 there were 20 drillers in the mine, between 14 and 16 laborers and 12

women selecting the ore, and another 5 people in complementary monitoring work, blacksmithing and carpentry. Production declined rapidly when the veins started to have less ore, and between November 1873 and February 1875 they extracted only 244 tonnes of marketable ore. (Egozcue and Mallada, 1876). The operator, The Estremadura Phosphate Co. Ltd. retained ownership of the mine, despite remaining inactive. In the late nineteenth century, the La Paloma and La Consecuente mines were acquired by Carlos Amusco, who also had interests in mines in El Calerizo area in Aldea Moret, Cáceres, and also in a fertilizer plant, which produced superphosphates with local phosphates and sulfuric acid obtained by roasting pyrite in Huelva, in their own facilities. This person, an historic political leader of La Rioja (he chaired the committee of the Provincial Council which proclaimed the First Republic in Logroño on June 22, 1873), and “regeneracionista” like Joaquín Costa,

also chaired the Chamber of Agriculture and the Chamber of Commerce, and wrote a book entitled “Memoria Agrícola” (Amusco, 1898), where he proposed measures for improvement of Rioja agriculture, including the use of chemical fertilizers. In 1889 he installed a superphosphate

factory in Logroño, subsidiary of their Cáceres factory. The Logroño factory also processed glauconite from the Alcantara mines. In 1891 he associated with Felix Azpilicueta, forming “Amusco y Compañía” for the exploitation of mines and the production of chemical fertilizers. At this time, some ore was extracted from the La Paloma mine, but it came from processed tailings. Later, the mine was abandoned, although between 1945 and 1950 some work was carried out to provide ore to the Aldea Moret factory, but they



Map of the veins in the La Paloma mine area, in Zarza la Mayor, Cáceres. (Egozcue and Mallada, 1876).

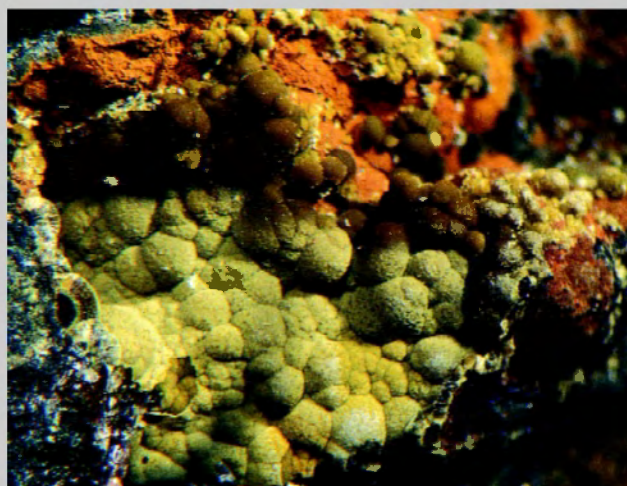
stopped because of the high transportation costs. In the early 1980s, Jose Manuel Jurado, who now is a well-known mineral dealer but at that time was a professor who, because of family relationships, was vacationing in the Zarza la Mayor, and examined the tailings. The presence of sulphides and minerals of unusual aspect drew his attention. Analyses and subsequent field studies made over the years have uncovered a remarkable assemblage of phosphates. In addition to their great scientific interest, many of them appear as microcrystals, outstanding because of their excellent aesthetic, crystalline forms and color contrast between species. This makes La Paloma mine, from the collector's point of view, one of the most interesting Spanish localities for micromounts. Currently there are visible gaps produced by emptying of the vein by open pit work, and there are some entrances to underground workings. However, interesting material is being recovered from the tailings.



Cacoxenite in radial aggregates of acicular crystals on quartz. J. Viñals collection.



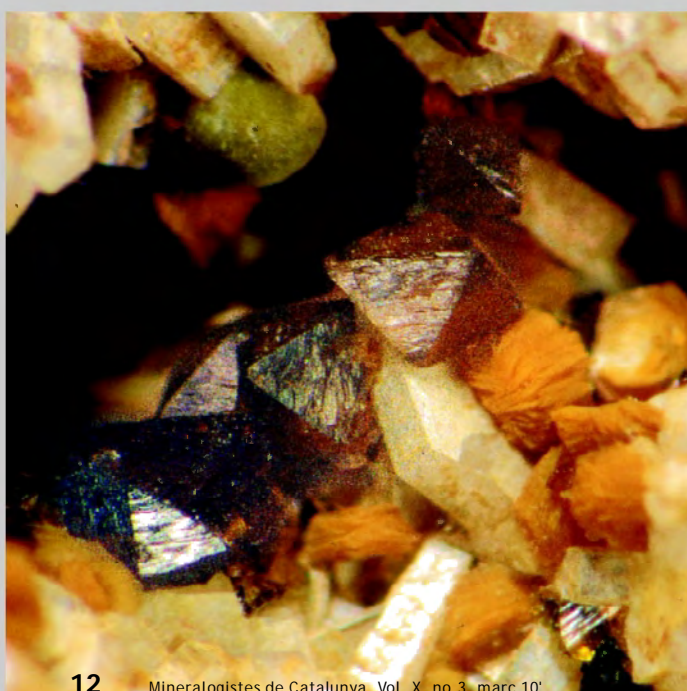
Group of strengite crystals with green spherules of chalcociderite on a carpet of small hexagonal prismatic crystals of apatite. Joan Viñals collection.



Kidwellite in botryoidal aggregates. www.prominersl.com collection.



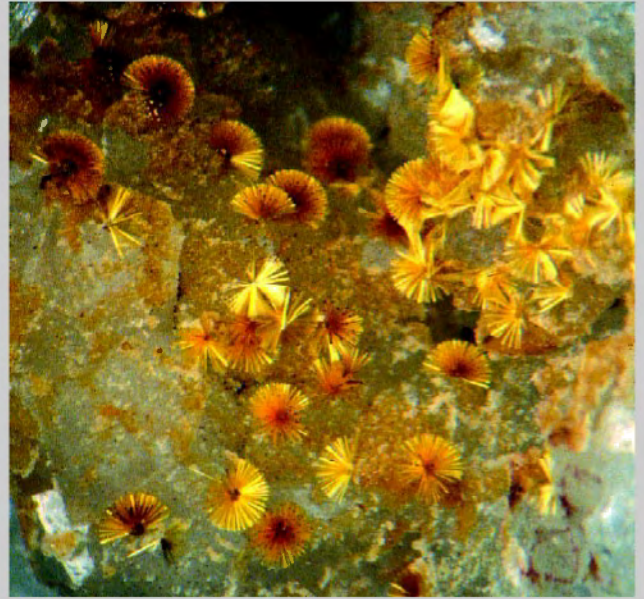
Strengite. 1.5 mm crystal. R. Muñoz collection. Photomicrography by Honorio Cócera.



Cyrilovite in pseudo-octahedral crystals with tabular white fluorapatite crystals, goyazite in micaceous rosettes and kidwellite (green spherule). www.prominersl.com collection. Photomicrography by Joaquim Callén.



Cacoxenite in divergent capillary sheaves with globular strengite. www.prominersl.com collection. Photomicrography by Joaquim Callén.



Cacoxenite on a druse of quartz crystals. www.prominersl.com collection.

Radial sheaves of cacoxenite. Christian Rewitzer collection and photomicrography.



MINERALOGY

The primary mineralization of the vein exploited in La Paloma mine is very simple: fluorapatite, quartz and small amounts of sulphides, especially pyrite, galena, sphalerite and chalcopyrite. From the mineralogical point of view, this mine is particularly interesting for the presence of a late hydrothermal paragenesis of low temperature, with jarosite and rare series of phosphates of secondary origin, especially of iron, formed by alteration of the sulphides. This mineralization has been developed in massive vuggy quartz, with phosphates sometimes filling gaps between grains, although they mostly grow over the quartz crystals inside cavities or in the voids formed by dissolution of other minerals, usually pyrite, which appears sometimes as relicts. The paragenesis of La Paloma is very similar to that of the Mine des Montmins (Échassières, Auvergne, France) (Cuchet *et al.*, 2000), from which it is distinguished by the absence of arsenic minerals present at the French site.

Native sulfur S

Occasionally found, produced by alteration of sulphides, as rounded and cavernous, bright microcrystals, on iron oxide crust. It may be also associated with jarosite.

Galena PbS

Galena seems to have been relatively abundant as leafy crystalline masses in the mineralization of La Paloma mine, or at least so indicate Egozcue and Mallada (1876). However, in the current tailings this mineral is found only occasionally, mainly as small patches, but also in cubic crystals up to 1.5 cm. The only secondary mineral associated with galena is cerussite. Pyromorphite has not been found until now in this locality.

Given the scarcity of lead secondary minerals in the assemblages studied, it is possible that galena was only abundant in a particular area of mineralization, rather than generalized, and that area was not reached by the low-temperature hydrothermal mineralization that led to the assemblage of rare phosphates.

Pyrite FeS₂

According to Palero *et al.* (1985), pyrite is the first sulfide that appears during the formation of the vein mineralization exploited in this mine. It is also the most abundant and the origin of the iron in the iron phosphates. It appears as cubic crystals which can reach an individual size of several millimeters, forming

groups that are trapped within the quartz or, smaller, growing freely inside vugs. The pyrite is often wholly or partially limonitized.

Sphalerite ZnS

Palero *et al.* (1985) indicate the presence of small amounts of sphalerite in the La Paloma mine. At present it is relatively scarce although it appears very disseminated, as millimetric sized crystals included in saccaroidal quartz and associated with pyrite. Occasionally it has been found as small orange crystals, in free growth, with rounded faces. The Zn detected in some secondary phosphates,

such as beraunite and plimerite, probably comes from the alteration of this mineral.

Other sulfides

Egozcue and Mallada (1876) indicate the presence of small amounts of chalcopyrite in the La Paloma mine, and occasionally large crystals of this mineral have been found. Chalcocite is rare, but occurs as small masses within the massive quartz. Traces of covellite, produced by alteration of chalcopyrite have also been found (Palero *et al.*, 1985).



Entrance to the La Paloma mine.



Construction in the upper part of the mine.

Quartz SiO_2

Quartz is an extremely common mineral in the La Paloma mine as part of the veins, and appears in three stages.

The first stage is formed by cryptocrystalline quartz, which appears associated with apatite, which is also in cryptocrystalline form. In a second stage there is recrystallized quartz, with apatite crystals, and thirdly it appears in vugs.

The crystals are colorless or milky. In the small pockets where phosphates are found, the quartz crystals are bright and hyaline, but they rarely reach a size of one centimeter. Generally, quartz crystals were formed before the deposit of phosphates, but there are exceptions. In some cases, small quartz crystals have growth phantoms, or inclusions of different minerals such as goethite.



Detail of part of the dumps.



Mine dump.

Cryptomelane $\text{K}(\text{Mn}^{4+}, \text{Mn}^{2+})_8\text{O}_{16}$

Egozcue and Mallada (1876) suggest the existence of “pyrolusite” in this mine, identified visually. The only manganese oxide reliably identified is cryptomelane, rarely in the form of microcrystals, of capillary habit, forming radial rows of about 1 mm on quartz crystals.

The crystals, because of their color and metallic luster, are similar to boulangierite, but they differ in their disposition, and are very similar to those found in the Esperanza mine, Laurion, Greece. Cryptomelane crystals are considered very rare, even globally, since this species, which otherwise is common, almost always occurs in concretionary masses.



Entrance to one of the galleries.

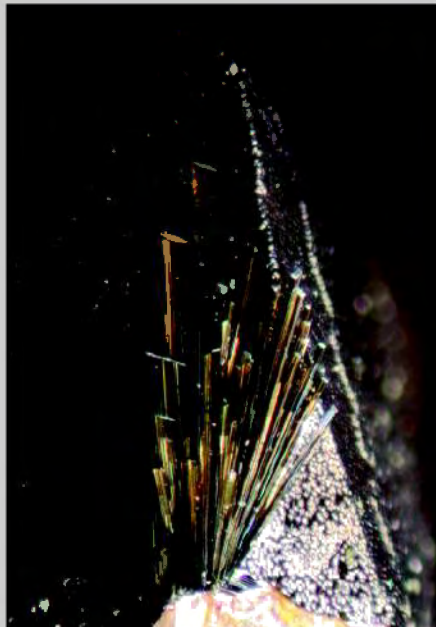


Remains of one of the surface cuts.

All photographs were taken in the La Paloma mine by Luis Francisco Martínez.



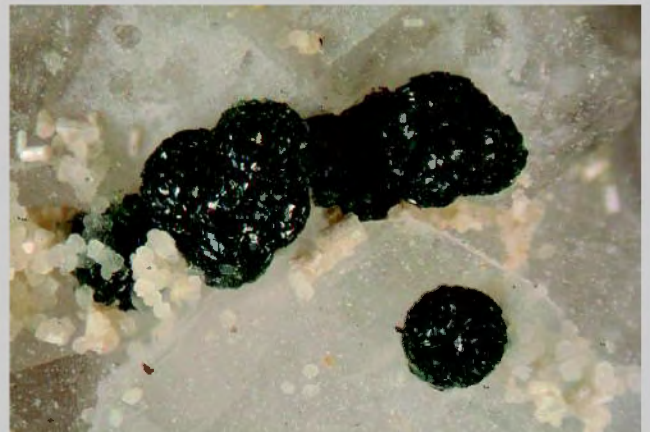
Strengite crystal.
Christian Rewitzer
specimen and
photomicrography.



Group of prismatic beraunite crystals (zinc-bearing) on a
quartz crystal covered with goethite. Joan Viñals collection.



Strengite in plumose aggregates. www.prominersl.com
collection. Photomicrography by Joaquim Callén.



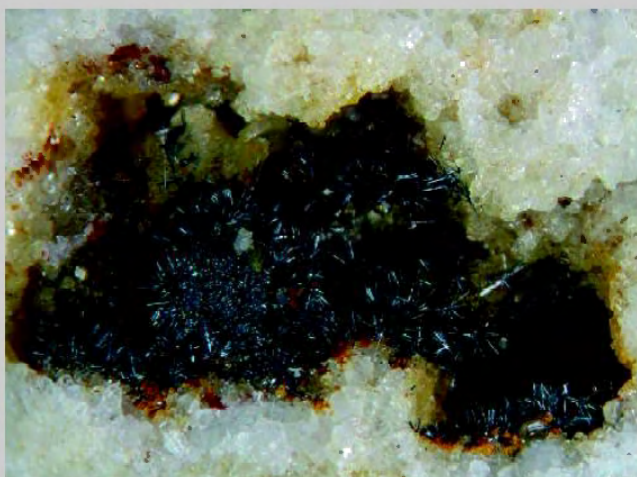
Chalcosiderite in spherules on quartz. Joan Viñals collection.
Photomicrography by Joaquim Callén.



Group of cacoxenite spherules. César Menor Salvan
collection and photomicrography.



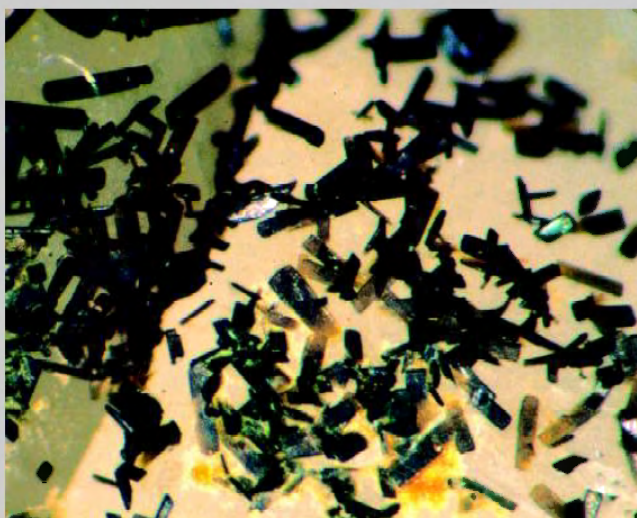
Group of strengite crystals. www.prominersl.com
collection. Photomicrography by Joaquim Callén.



Acicular crystals cryptomelane. Joan Viñals collection.

Goethite $\text{Fe}^{3+} \text{O} (\text{OH})$

Goethite appears with some frequency coating quartz crystals as small botryoidal formations, black outer surface and brown, or even orange fibrous radiated section. Over it, various phosphates can be found. Occasionally it yields some well-defined crystals, although very small ones, less than a tenth of a millimetre. They have been found in small isolated groups. In some cases, one sees acicular crystals of goethite as inclusions in quartz crystals.



Crystals of goethite on quartz. www.prominersl.com collection.

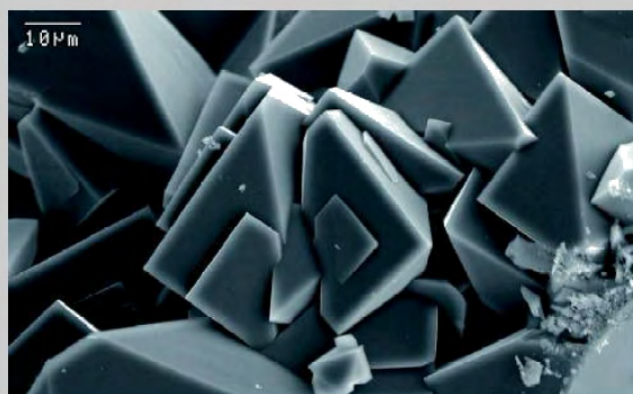
Gypsum $\text{Ca} (\text{SO}_4) \cdot 2 \text{H}_2\text{O}$

Gypsum appears coating the quartz vugs and the phosphates present there, forming a millimeter thick continuous layer, from which arise small and round crystals, apparently partially redissolved. Coatings formed by parallel aggregates of gypsum microcrystals are also found.

It is therefore of very late formation, which in some cases has acted as a protective varnish in some phosphate vugs exposed to the weather. By dissolving this gypsum coating some good specimens have been recovered, for example strengite.

Jarosite $\text{KFe}_3^{+3} [(\text{OH})_3 | \text{SO}_4]_2$

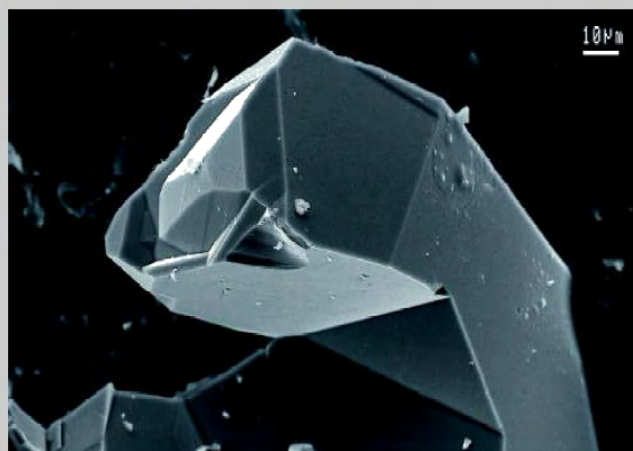
Jarosite is quite abundant in the La Paloma mine inside quartz cavities but is not generally associated with secondary phosphates. It appears as centimetric crusts formed of microcrystals and also as isolated crystals. The crystals have a size usually smaller than a millimeter, the dominant figures being a combination of two rhombohedra $\{10\bar{1}1\}$ and $\{01\bar{1}2\}$, with nearly right angles, truncated by a large c -face $\{0001\}$.



Jarosite as typical crystals (SEM). J. Viñals collection and photo.

Libethenite $\text{Cu}_2(\text{PO}_4)(\text{OH})$

Libethenite has been found occasionally as tiny transparent prismatic crystals, olive green in colour, associated with pseudomalachite in small quartz vugs, always in the vicinity of more or less altered small masses of copper sulphides, chalcopyrite or chalcocite.



Twinned libethenite crystals (SEM). M. Calvo collection, Joan Viñals photo.

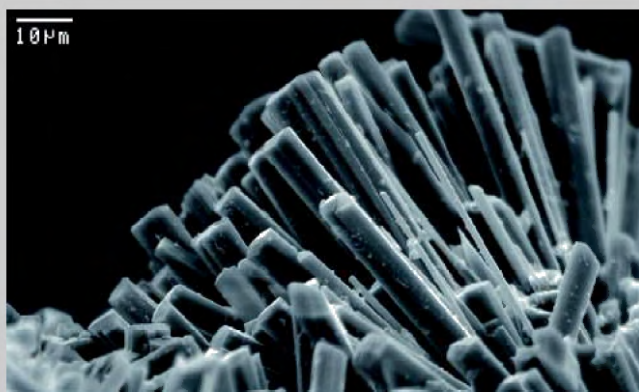
Plimerite $\text{ZnFe}^{3+}_4(\text{PO}_4)_3(\text{OH})_5$

Plimerite, the zinc analogue of rockbridgeite and frondelite, is a very rare mineral, described so far from only two locations in the world: Broken Hill, New South Wales, Australia, which is the type locality, and Reaphook Hill, Flinders Range, South Australia, Australia (Elliot *et al.*, 2009). Probably it's not a too rare mineral in the phosphate deposits of altered pegmatites or other phosphate deposits containing zinc, but it has gone unnoticed so far in many of them, having been confused with rockbridgeite. For example, the presence of zinciferous rockbridgeite was mentioned in various localities such as the Huber Shaft complex, Krasner, Czech Republic, and with compositions of up to 19% ZnO (Sejkora *et al.*, 2006), that most likely correspond to plimerite.

About six years ago, an iron phosphate, similar in appearance to natrodufrenite but with a higher content of zinc, was recognized by us in La Paloma mine. Analysis by electron microprobe showed a composition similar to the ideal formula $\text{ZnFe}_4(\text{PO}_4)_3(\text{OH})_5$, which did not correspond to any mineral described in the literature. The scarcity of sample as well as its mediocre quality (intergrown with polycrystalline quartz) made it less

interesting to destroy the few specimens to do X-ray diffraction study. After the publication of Elliot *et al.* (2009), the re-characterization was resumed, and about 30 samples of doubtful “natrodufrenite” were examined. Fortunately, among them there were more plimerite specimens, which allowed confirmation by microdiffraction.

The chemical composition of the La Paloma mine plimerite shows an almost negligible substitution of As in the TO_4 group, with small substitutions of Al on the M^{3+} site and Mn in the M^{2+} . X-ray diffraction showed a diffractogram similar to those of rockbridgeite and frondelite, noticing, as in the plimerite from the type locality, a slight displacement of peaks to smaller spaces,



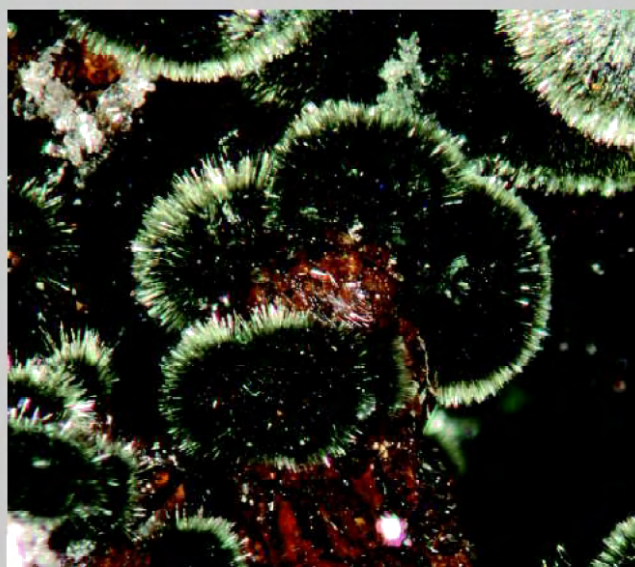
Close-up of plimerite crystals (SEM). Joan Viñals collection and photo.



Close-up of plimerite crystals (SEM). Joan Viñals collection and photo.



Plimerite as nodules with internal radial structure. Joan Viñals collection. Photomicrography by Joaquim Callén.



Plimerite as spherical aggregates of capillary crystals. Joan Viñals collection. Photomicrography by J. Callén.

which is consistent with the smaller size of the cation Zn^{2+} with respect to Fe^{2+} and Mn^{2+} .

Plimerite appears in the La Paloma mine usually in the form of globules of up to 5 mm, with fibrous-radial internal structure, of quite thick fibers. Unlike natrodufrenite globules, which are usually very dark green, almost black, these are of a less dark green and with a quite characteristic olive touch. Furthermore, the rupture of the plimerite fibers show a cleavage parallel to $\{100\}$, much more perfect than the one observed in the natrodufrenite nodules, whose fracture is usually more indefinite, even earthy. Another feature is that the mineral, which appears with goethite in vugs inside quartz blocks, is not associated with the common phosphate minerals apatite, strengite, cacoxenite and natrodufrenite, but sometimes with the variety of zinciferous beraunite already described. In this latter association, the plimerite also appears in nodular form but with the surface formed by the ends of needle-like crystals, giving it a quite attractive velvety look. The morphology of these crystals is simple, rectangular rhombic prisms elongated along the direction $[001]$ with the dominant $\{100\}$ and a small development of $\{010\}$ and $\{001\}$.

Pseudomalachite $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$

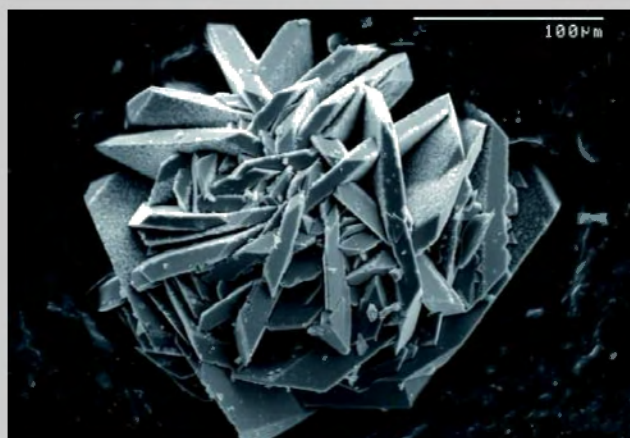
Pseudomalachite appears very occasionally, only in areas where copper sulphides are locally abundant, as tiny spherules, slightly bluish green, with the surface formed by aggregates of extremely small crystals, visible only by SEM. Pseudomalachite is associated only with libethenite and not with any other of the phosphates found in this locality.

Corkite $\text{PbFe}_3[(\text{OH})_6/\text{SO}_4/\text{PO}_4]$ **Kintoreite** $\text{PbFe}_3[(\text{OH}, \text{H}_2\text{O})_6/\text{PO}_4]$

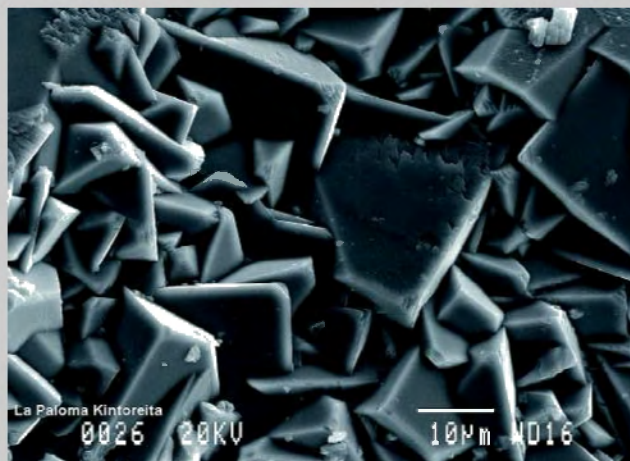
These two minerals form a series within the alunite supergroup, differing mainly by the different proportions of ions of SO_4^{2-} and PO_4^{3-} in structure, and the partial protonation of -OH groups to H_2O , which takes place to offset the different valences of PO_4^{3-} and SO_4^{2-} .



Detail of a pseudomalachite spherule (SEM). M. Calvo collection, Joan Viñals photo.



Corkite-kintoreite in tabular crystals (SEM). M. Calvo collection, Joan Viñals photo.



Corkite-kintoreite in rhombohedral (pseudocubic) crystals (SEM). Joan Viñals collection and photo.

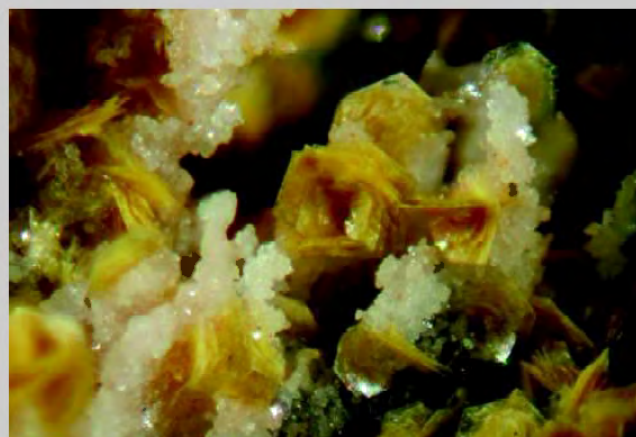


Corkite-kintoreite in rhombohedral (pseudocubic) crystals. www.prominersl.com collection.

The analyses made so far in the material obtained from the La Paloma mine show atomic ratios P/S from 1.5 (predominance of the term corkite) to over 13 (predominantly kintoreite), being indistinguishable without individual analysis. Thus, it seemed reasonable to classify them as kintoreite-corkite series, which is what is usually done in similar situations. In this site, they appear as aggregates of microcrystals with honey color, very bright due to its relatively high refractive index. They occur in the form of isolated crystals, usually of submillimetric size, and also forming clusters of rough looking prisms, in the latter case being most likely pseudomorphs after apatite or pyromorphite. The isolated crystals show several morphologies, typical of the alunite supergroup. Thus, crystals have been observed both in the form of rhombohedra {10T2} (with nearly right angles giving them a pseudocubic aspect) and as a combination of rhombohedra {10T1} and {01T2} (and pseudo-octahedral appearance), but flattened hexagonal crystals, with well developed {0001}, have also been observed. These minerals have been mainly found associated with strengite and less frequently with natrodufrenite, but they are really rare in the La Paloma mine, and also difficult to distinguish from jarosite, which is much more common, and the cyrilovite. With respect to jarosite, the main difference is that it does not appear associated with phosphates. Regarding cyrilovite, the principal difference is the brightness, adamantine in the case of corkite-kintoreite and vitreous in the cyrilovite.



*Micaceous goyazite crystals. Joan Viñals collection.
Photomicrography by Joaquim Callén.*



Micaceous goyazite crystals. Joan Viñals collection.

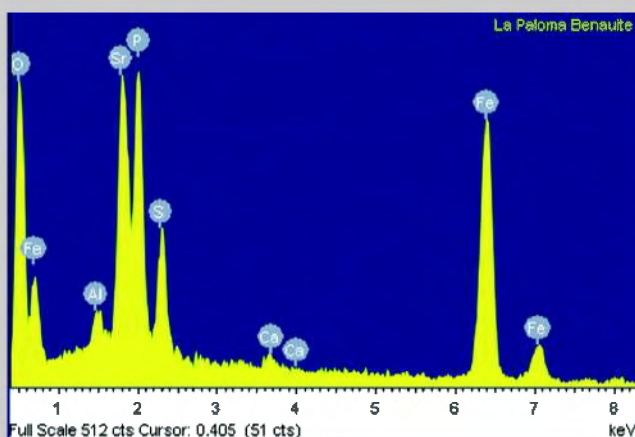
Goyazite $\text{SrAl}_3[(\text{OH})_5 | (\text{PO}_4)_2] \cdot \text{H}_2\text{O}$

Goyazite is another mineral of the alunite supergroup, relatively common in many phosphate deposits of various origins, such as granitic pegmatites, hydrothermal deposits, carbonatites, etc. And even in alluvial deposits. Hundreds of localities are known, such as the Yukon phosphates (Canada), many pegmatites in Brazil, U.S. and Germany, Lengenbach dolomites (Binn, Switzerland), etc. It is not a common mineral in the La Paloma mine, but neither can it be considered especially rare. It appears on the quartz vugs in aggregates of tabular crystals of hexagonal shape up to 1 mm, extremely flat, looking almost micaceous due to the great development of the form {0001}. The color ranges from white to cream, or to ochre, in the latter case being due to a thin layer of iron oxides that coats the crystals. The pearly luster and micaceous appearance are very characteristic in La Paloma, but possibly this fact has made this mineral go unnoticed in some cases, having been confused with mica. It can also be confused with some particularly flat fluorapatite crystals, but they are not like goyazite.

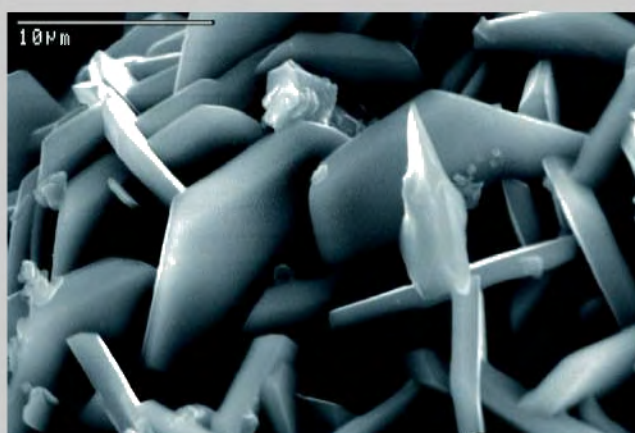
In La Paloma, goyazite is associated with strengite and natrodufrenite. Its chemical composition is very close to the ideal composition, and only evidence of Ca replacing Sr was found. The name of the series endmember with Ca as the dominant element is crandallite, a much more common mineral, but it has not been observed at this site, which is not surprising if we consider the absence of calcium in phosphates formed after the apatite. However, its presence should not be dismissed, since it may be present in the earthy masses of poorly defined phosphates that have not been characterized.

Benauite $\text{SrFe}^{3+}_3[(\text{OH})_6 | (\text{HPO}_4, \text{PO}_4) | (\text{PO}_4, \text{SO}_4)]$

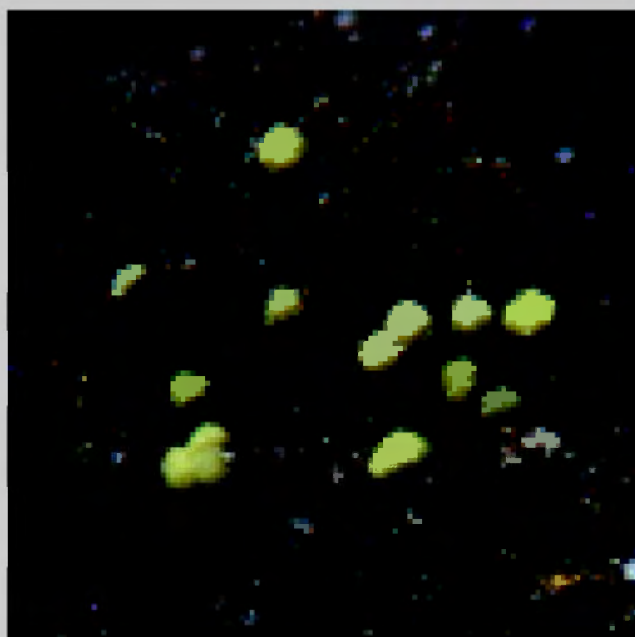
Benauite is the ferric equivalent of goyazite. The type locality is the famous Clara mine, Wolfach, Baden-Württemberg, Germany, where it is very rare, unlike many other minerals of this extensive supergroup (Walenta *et al.*, 1996).



EDS spectrum of benauite.



Close-up of crystals of benauite (SEM). Joan Viñals collection and photo.



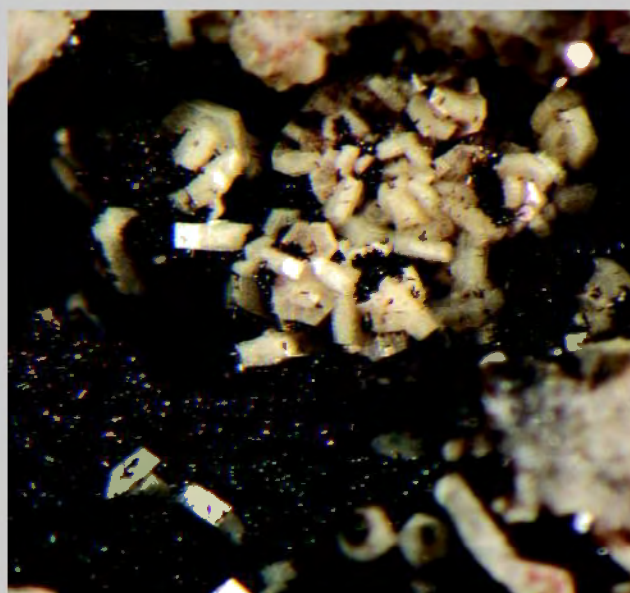
Spherules of benauite. Joan Viñals collection. Photomicrography by Joaquim Callén.

On a global level it also appears to be very scarce, although recently (Mills *et al.*, 2010) its presence was described in the Kobokobo pegmatite in the Congo. The La Paloma mine would be then, at the date of publication, only the third world locality.

In the La Paloma mine, only one specimen of benauite has been found, forming isolated bright yellow spherules, with a size of about 0.25 mm, on a layer of goethite, which covers the quartz crystals in a vug, without other associated phosphates. The spherules consist of groups of very small crystals, between 10 and 15 microns. Their habit is identical to the one observed in the crystals from the Clara mine, characterized by a great development of the form {0001}, which gives them a tabular hexagonal appearance. The chemical composition of the benauite from La Paloma was determined by semiquantitative EDS analysis. We detected small amounts of Al substituting for Fe (Al / Fe approx. 0.1) and even less Sr replacing Ca (Ca / Sr approx. 0.05). Ba and Pb substitutions as described for the benauite type locality were not detected (Walenta *et al.*, 1996)

Fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$

According to Egozcue and Mallada (1876), the apatite that formed the veins that were exploited was generally cryptocrystalline or colloform, massive, and also forming concentric structures composed of diverging prismatic white, creamy-white or pink crystals, and also areas with macrocrystalline apatite with gray, purple or green colors.



Fluorapatite as hexagonal tabular crystals. www.prominersl.com collection. Photomicrography by Joaquim Callén.



Tabular crystals of cream-colored fluorapatite, associated with rosettes of pseudo-octahedral yellow goyazite and crystals of cyrilovite.

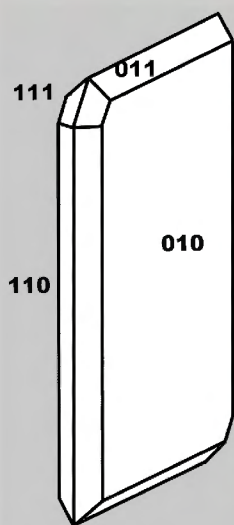
www.prominersl.com collection.

Photomicrography by Joaquim Callén.

In the quartz vugs on the tailings, fluorapatite is quite abundant as equidimensional tabular or prismatic crystals, hexagonal, opaque white or cream, with a size on the order of a millimeter. This apatite is probably one of the first phosphates that crystallizes in these vugs, as other secondary phosphates are often over them. In the La Paloma mine, modern specimens of this mineral were not found, in contrast to other mines in the area

Phosphosiderite $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$

This mineral, a strengite polymorph, also known by the obsolete name “metastrengite”, is rarely found in tabular



Morphology of crystals of phosphosiderite from the La Paloma mine.

*Group of phosphosiderite crystals.
Joan Viñals collection.
Photomicrography by Joaquim Callén.*



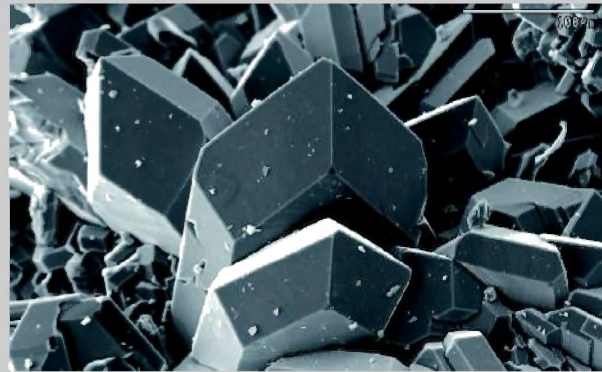
crystals with a size of up to 2 mm, transparent and pink. It can be visually distinguished with precision from the strengite by its crystal morphology.

The most important faces are the pinacoid {010}, which are combined with {011} and {110} to form a square or rectangular “tablet”, in which small changes can be distinguished in the two vertices due to the presence of {111} faces. In the few specimens found, the phosphosiderite does not appear associated with any other phosphate.

However, as in many other localities, it is possible that phosphosiderite appears intergrown with strengite in pink microcrystalline crusts that are generically considered to be “strengite”, but this has not been proven.

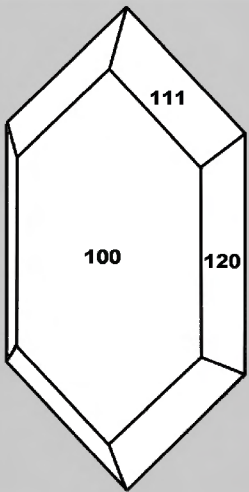
Strengite $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$

Strengite is an abundant mineral among the secondary phosphates in the La Paloma mine and is one of the most spectacular specimens, when its pink color, which is



*Close-up of strengite crystals (SEM).
Joan Viñals collection and photo.*

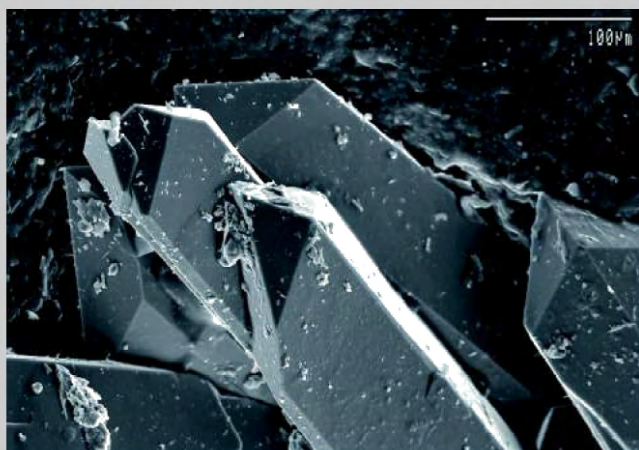
enhanced over the white quartz, is combined with the morphological perfection. It usually appears in spherules formed by crystals with a tabular or lamellar development, whose ends give rise to an irregular surface.



*Morphology of
strengite crystals
from the La
Paloma mine.*



*Group of strengite
crystals. Miguel
Calvo collection.
Photomicrography
by Joaquim Callén.*

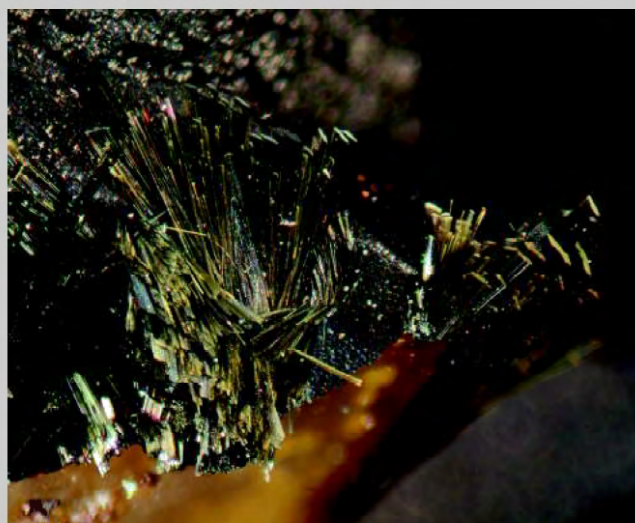


*Detail of arsenical strengite crystals (SEM).
Joan Viñals collection and photo.*

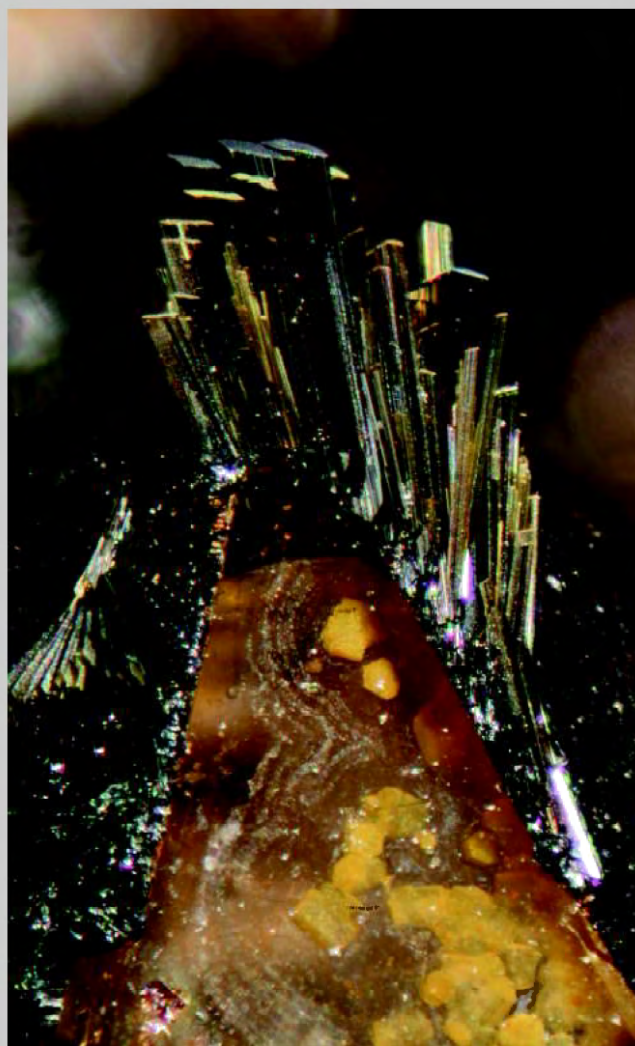
Although normally these spherules have millimetric sizes, they have been found exceptionally up to a centimeter in diameter. They usually show the deep pink color typical of this mineral, although very pale specimens, very light gray and light pink have been found, and generally bright. Very well formed strengite crystals are frequent, transparent and sometimes very bright. Exceptionally they can have a size of several millimeters. These large crystals form groups of a few individuals. The morphology is very simple, and the forms are easily distinguishable. The two larger faces correspond to pinacoids {100}, which is accompanied by the prism {120}, with four faces, and bipyramid {111} with eight faces. Very occasionally, a variety of arsenical strengite has also been found, with yellow color, as aggregates of longer crystals of micro prismatic habit, different from that described above. Strengite appears associated with all the phosphates of this locality except plimerite and beraunite. The most frequent association is with apatite, kidwellite and natrodufrenite. It appears less frequently associated with cacoxenite, although sometimes there are divergent glass spherules of strengite coated by acicular crystals of cacoxenite also divergent, forming a spherical crown over the strengite.

Beraunite $\text{Fe}^{2+}\text{Fe}^{3+}_5[(\text{OH})_5/(\text{PO}_4)_4]\cdot 4\text{H}_2\text{O}$

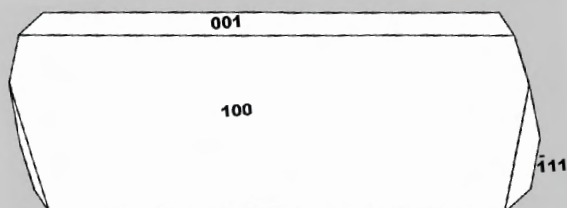
In the La Paloma mine excellent specimens of this mineral have been found, but unfortunately only in small quantity. It appears as radiated or irregular bundles of prismatic crystals up to 1 mm, with a dark olive green color over goethite that covers quartz vugs. It is not associated with other phosphates, with the exception of plimerite. The habit of the beraunite crystals is the typical prismatic one, with dominant very long pinacoid {100} and little development of {001}, and small oblique truncations due to the $\{111\}$ faces.



*Crystals of beraunite. Joan Viñals collection.
Photomicrography by Joaquim Callén.*



Group of zinc-bearing beraunite crystals on quartz. Joan Viñals collection. Photomicrography by Joaquim Callén.



Morphology of beraunite crystals from the La Paloma mine.

Both the crystal habit and the color of the specimens from La Paloma mine are very similar to those of the Blaton phosphate deposit in Belgium (Peacor *et al*, 1987), and the site of Les Montmins (Échassières, Auvergne, France) (Cuchet *et al.*, 2000).

However, the green color of the La Paloma beraunite, which ought to be the “true” color for this mineral, is not very common. This species has a reddish color in most other localities. This is because the Fe^{2+} is transformed, totally or just partially, into Fe^{3+} , an alteration that produces “oxiberaunite”, with a different structure than the one of beraunite, and therefore perhaps susceptible to further consideration as a different mineral species. The green color seems indicative of fresh, unaltered beraunite. Another chemical characteristic of the La Paloma beraunite is the presence of Zn^{2+} , which partially replaces Fe^{2+} in the structure. This substitution had not been previously reported for this species, as has been the substitution by Mn^{2+} , for example in Mangualde beraunite (Marzoni *et al.*, 1989). Therefore, crystals from La Paloma” were studied by EPMA and XRD in order to determine whether it could be a new species, with Zn^{2+} as dominant divalent cation. Diffraction confirmed the beraunite structure type, but the composition observed ($\text{ZnO } 2.78 \pm 1.77\%$) indicates too low an occupancy, less than 50%, of Zn in the M2 + site. Therefore, the beraunite of La Paloma can be classified just as zinc-bearing beraunite.

Cacoxenite $\text{Fe}^{3+}_{24}\text{Al}[(\text{OH})_{12}|\text{O}_6|(\text{PO}_4)_{17}]\cdot 17\text{H}_2\text{O}$

Cacoxenite is a very abundant mineral in the La Paloma mine and some of the most spectacular specimen material.

Especially when presented as urchin-like spherules formed by the association of bacillary or acicular crystals, which, for this species, are relatively thick and generally as good individuals, without merging into each other. Individual crystals usually do not have well defined terminations, although occasionally a terminal face can be more or less flat. The size of individual spherules is small, of the order of a millimeter, but they have a very good contrast against the white background quartz, contrary to what happens in most localities, where the matrix is often a ferruginous material.

Cacoxenite spherules also appear as compact tapestries of disordered aggregates of thin acicular crystals.



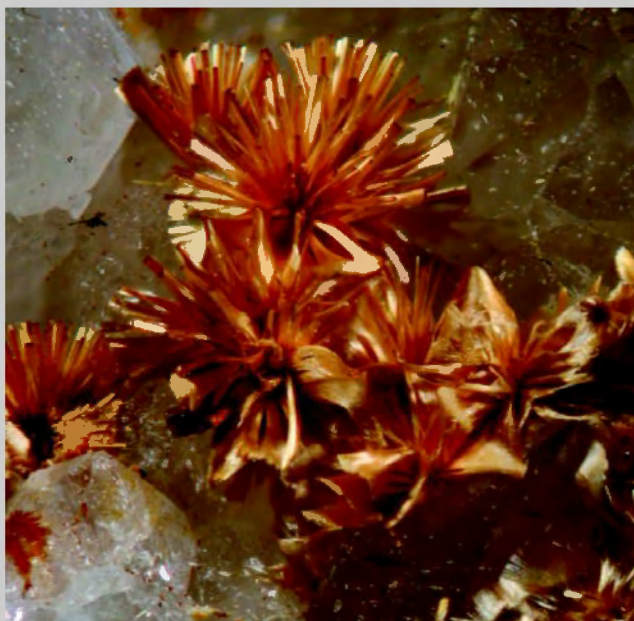
*Cacoxenite in spherules on quartz.
Honorio Cócera collection and photo.*



*Cacoxenite in spherules on quartz.
www.prominersl.com collection*



*Detail of spherules of cacoxenite. Joan Viñals collection.
Photomicrography by Joaquim Callén.*



*Cacozenite as fibrous aggregates. Joan Viñals collection.
Photomicrography by Joaquim Callén.*

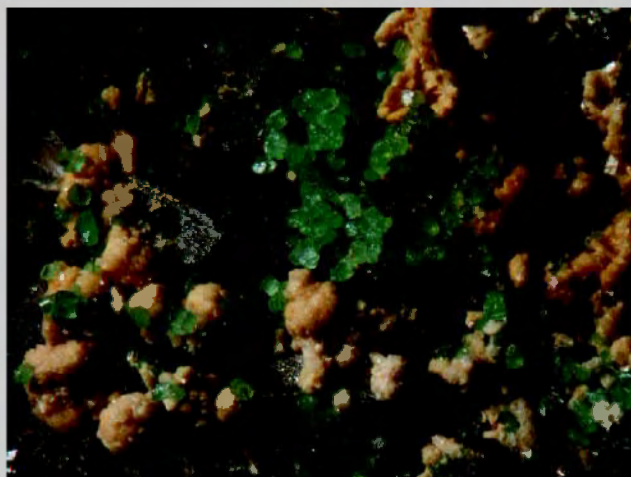


*Spherules of cacozenite. Joan Viñals collection.
Photomicrography by Joaquim Callén.*

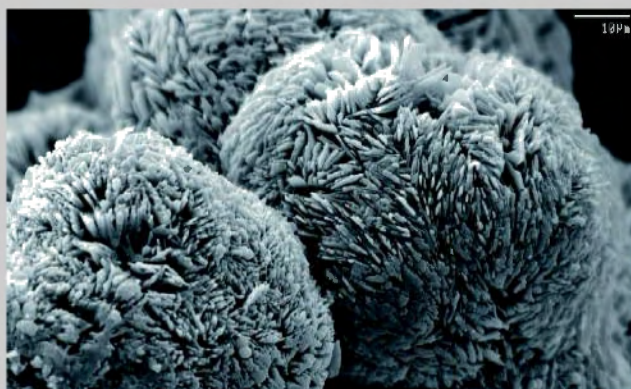
Cacozenite appears in the La Paloma mine often as the only phosphate on the specimens. However it is also associated, although rarely, with apatite and strengite, and especially with chalcosiderite. Association with natrodufrenite, even though that is quite abundant in La Paloma, is practically unknown, indicating different conditions of formation.

Turquoise $\text{Cu}(\text{Al}, \text{Fe}^{3+})_6[(\text{OH})_4 | (\text{PO}_4)_2]_2 \cdot 4\text{H}_2\text{O}$

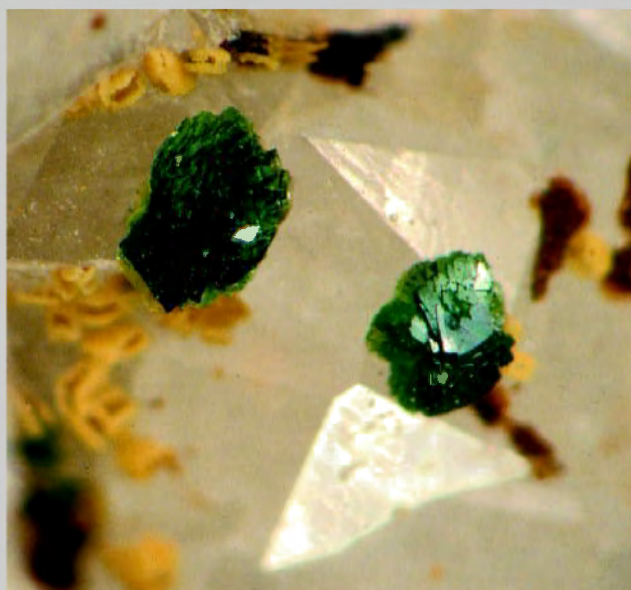
In the La Paloma mine turquoise appears very occasionally, as typical tiny blue spherules, usually less than one tenth of a millimeter in diameter and formed of divergent lamellar microcrystals. In the few specimens found, turquoise is associated with cacozenite.



*Globular turquoise. Joan Viñals collection.
Photomicrography by Joaquim Callén.*



*Close-up of turquoise globules (SEM).
Joan Viñals collection and photo.*

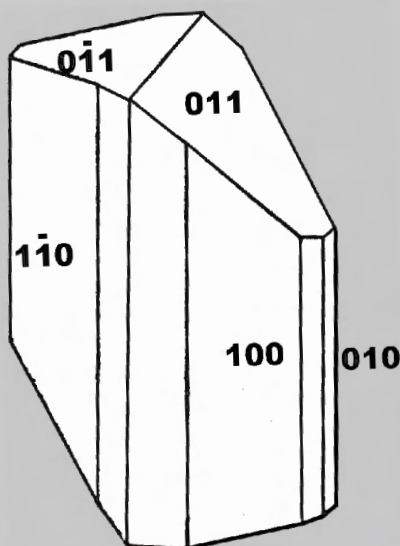


*Crystals of chalcosiderite. www.prominersl.com collection.
Photomicrography by Joaquim Callén.*



*Chalcosiderite as green spherules associated with pink strengite and cream fluorapatite. Joan Viñals collection.
Photomicrography by Joaquim Callén.*

*Morphology of
chalcosiderite
crystals from the
La Paloma mine.*



Chalcosiderite $\text{Cu}(\text{Fe}^{3+}, \text{Al})_6[(\text{OH})_4|(\text{PO}_4)_2]_2 \cdot 4\text{H}_2\text{O}$

Chalcosiderite appears commonly in this locality as grass green translucent spherules. Exceptionally, chalcosiderite crystals are relatively well formed and doubly terminated, with a grayish green color and blade-like habit. Some of the forms can be distinguished with relative ease, while others are too small to be identified. The most visible faces are those of the $\{011\}$ and $\{110\}$ pinacoid. Along with these there are the $\{100\}$ and $\{hk0\}$ faces, which sometimes give the appearance of vertically striated crystals. Chalcosiderite is primarily associated with cacoxenite, sometimes growing directly over it, and more rarely with strengite. In the La Paloma mine, very aesthetic specimens of this mineral have been found, where the green crystals are associated with golden needles of cacoxenite over a matrix of quartz crystals.

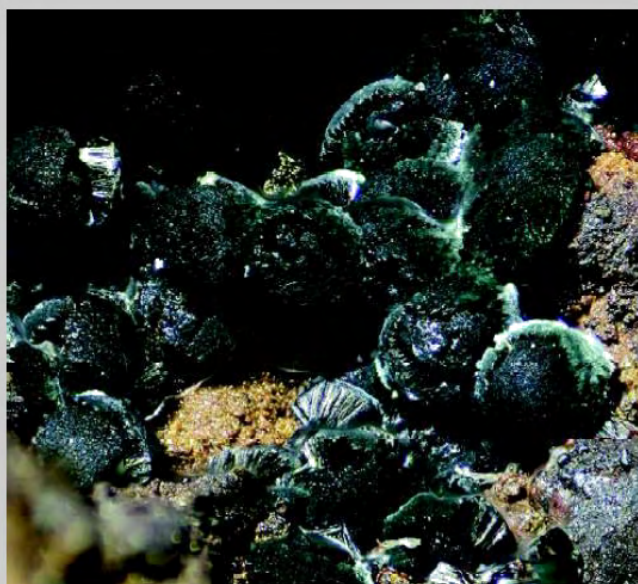
Natrodufrenite $\text{NaFe}^{2+}(\text{Fe}^{3+}, \text{Al})_5[(\text{OH})_3|(\text{PO}_4)_2]_2 \cdot 2\text{H}_2\text{O}$

Natrodufrenite is a very abundant mineral in the La Paloma mine, which yields specimens of good quality for the species. The best are those in which the natrodufrenite appears in well formed crystals, separated, glossy and dark green, almost black, over white apatite vugs. However, the natrodufrenite appears in the La Paloma in several other forms too. The most common is as spherules, isolated or aggregated, with a smooth outer surface, more or less glossy, dark green, sometimes almost black. The spherules may be more than 1 mm, although it commonly ranges between 0.1 and 1mm. They have radiated internal structure, consisting of very fine fibers, which makes some sections have a silky shine. The spherules sometimes have a concentric zoning, with bands of different shades of green. However, when the transition is too clear gray-green on the surface, the mineral that forms those layers is not natrodufrenite but kidwellite.

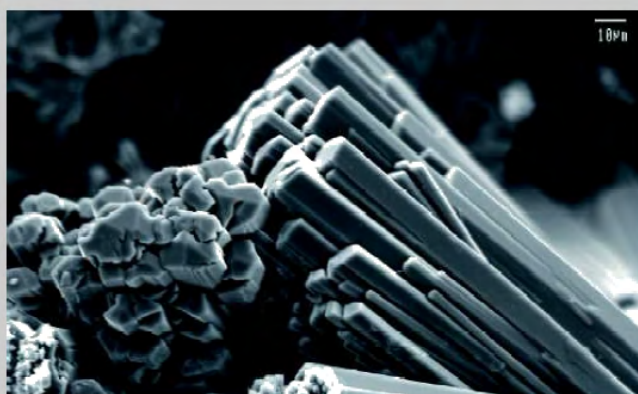
They also appear, although more rarely, as sheaf-like crystal aggregates, and only exceptionally as individual crystals with prismatic habit, bacillary or even capillary. These crystals, when they are relatively thick, are very dark, almost black, and bright, but sometimes with a silky reflection, probably caused by the existence of parallel fiber microgrowths



*Well formed crystals of natrodufrenite. J. Viñals collection.
Photomicrography by Joaquim Callén.*



*Spherules of natrodufrenite. Field of view 5 mm.
R. Muñoz collection. Photomicrography by Honorio Cócera.*



*Close-up of prismatic natrodufrenite crystals (SEM).
Joan Viñals collection and photo.*

The natrodufrenite is associated with almost all the other phosphates, iron oxides and very often with pyrite, even growing directly over the relicts that remain from the corrosion of this mineral. Also sometimes it grows as a layer of acicular microcrystals over goethite on botroidal formations. The most common associated phosphate, in addition to the above transition to kidwellite, is with apatite and strengite. Much less common is an association with cacoxenite, and it has never been seen or associated with plimerite or beraunite.

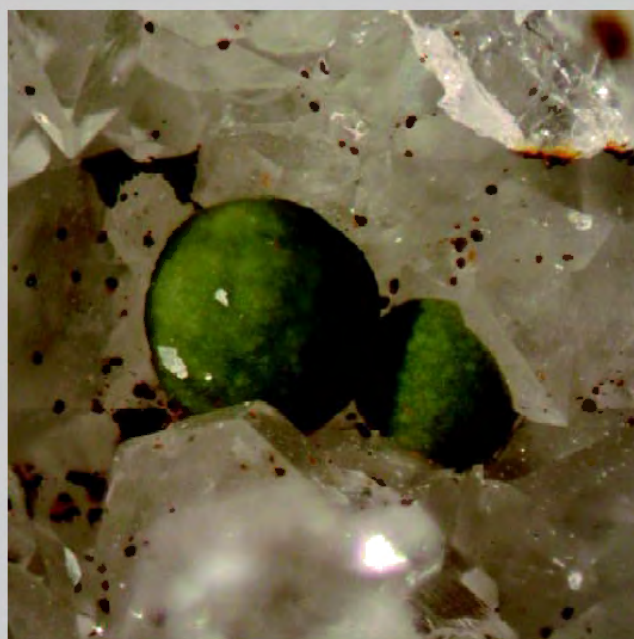
Although we have suspected the presence in the La Paloma mine of its calcium analogue, dufrenite, all specimens analyzed so far have a natrodufrenite composition, with clear predominance of sodium over calcium ($\text{Na} / \text{Ca} > 3$). Moreover, the content of Al in the “natroalunite” of La Paloma is almost negligible ($\text{Al} / \text{Fe} < 0.05$).

Kidwellite $\text{NaFe}^{3+}_9(\text{PO}_4)_6(\text{OH})_{11} \cdot 3\text{H}_2\text{O}$

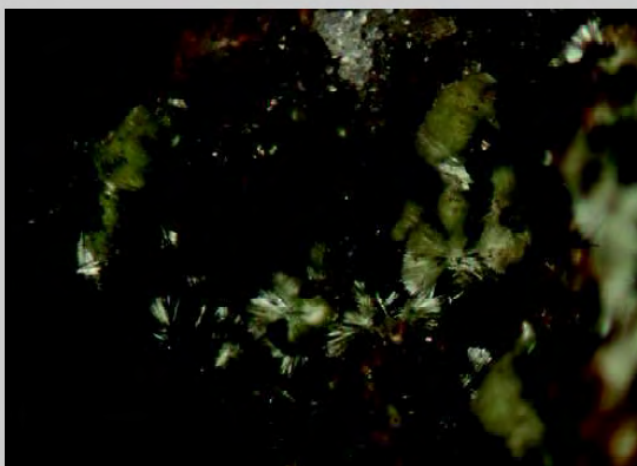
Kidwellite is a mineral related to natrodufrenite and dufrenite, but in which all the iron appears as Fe^{3+} . In the La Paloma mine, the most common form in which this mineral occurs is as millimeter-size light green spherules, somewhat gray, with silky luster. The spherules often have an irregular outer surface and are formed by the association of extremely thin divergent crystals.



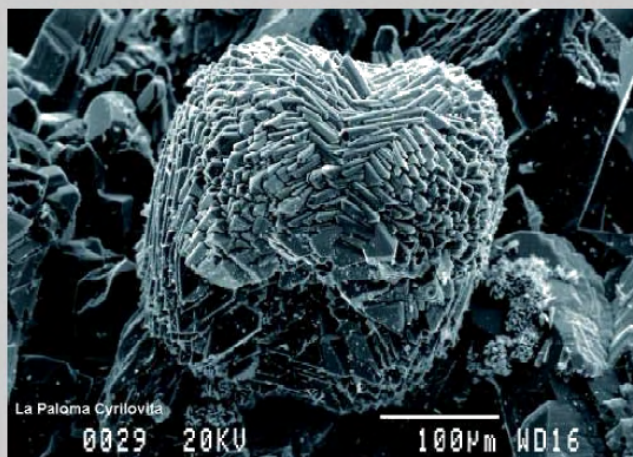
*Spherules of light green kidwellite showing a nucleus of
dark green natrodufrenite. Joan Viñals collection.
Photomicrography by Joaquim Callén.*



*Spherule of kidwellite on quartz. J. Viñals collection.
Photomicrography by Joaquim Callén.*



*Crystals of kidwellite on quartz. J. Viñals collection.
Photomicrography by Joaquim Callén.*



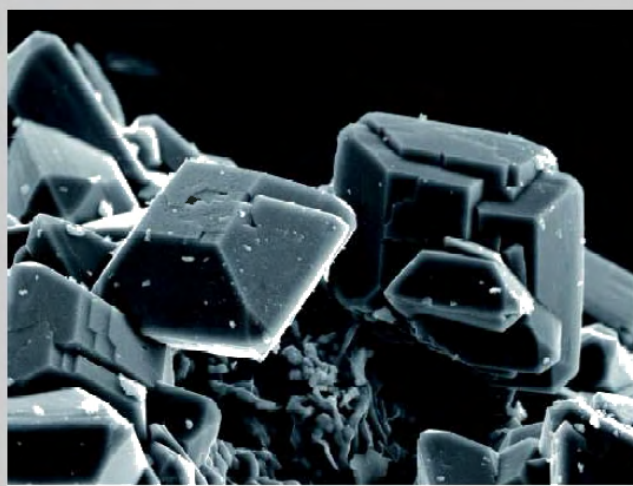
*Detail of aggregates of cyrilovite (SEM).
Joan Viñals collection and photo.*

They often have a dark green natrodufrenite core, indicating probable epitaxial growth. Note that b and c cell parameters of natrodufrenite (5.15 Å, 13.77 Å) are virtually identical to those of kidwellite (5.15 Å, 13.75 Å), so to distinguish them the a parameter must be used (25.83 Å for natrodufrenite and 20.61 Å for kidwellite). However, the natrodufrenite structure is not yet well enough known to draw a comparison with kidwellite, which is known in detail (Kolitsch, 2004). Moreover, the color change from the dark core of natrodufrenite to the light green, sometimes almost white, of kidwellite is surely due to the change of the oxidation state of Fe^{2+} a Fe^{3+} . Occasionally, kidwellite also appears in La Paloma as isolated capillary microcrystals or grouped in small bundles. Apart from the association with natrodufrenite, the kidwellite also appears associated with apatite, strengite and cacoenite.

Cyrilovite $\text{NaFe}^{3+}_3[(\text{OH})_2|\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}$

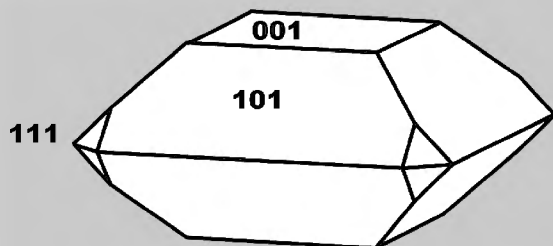
This rare species corresponds to the Fe^{3+} analogue of wardite. Well formed bipyramidal crystals were found in quartz vugs. The color is bright yellow, transparent and crystals can reach up to one milimeter on edge, an abnormally large size for this mineral. The only distinguishable faces in large crystals are those of the bipyramid, with a development similar to that of an octahedron, probably {011}, with all sides equally developed, very slightly horizontally striated, and with extremely small changes and not always present corresponding to pinacoid {001}.

*Cyrilovite as pseudo-octahedral crystals with cream-colored fluorapatite and yellow micaceous goyazite.
www.prominersl.com collection.
Photomicrography by Joaquim Callén.*



Crystals of cyrilovite (SEM). J. Viñals collection and photo.

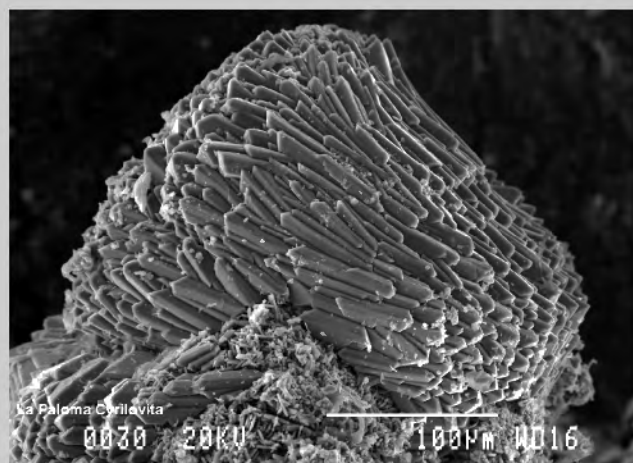




Morphology of cyrilovite crystals from the La Paloma mine.

Powder diffractogram of plimerite from La Paloma compared with that of Broken Hill (The La Paloma pattern was obtained by microdiffraction on a monocrystal of Si utilizing Bragg-Brentano geometry.)

La Paloma		Broken Hill (Elliot <i>et al.</i> , 2010)		
d obs (Å)	I obs	d obs (Å)	I...	hkl
8,419	5	8,599	5	0 0 2
6,950	41	6,992	30	0 2 0
6,448	2	6,391	5	0 2 1
4,652	7	4,638	50	1 1 1
4,365	11	4,343	5	0 2 3
4,254(quartz)	11			
4,206	38	4,194	100	0 0 4
3,665	7	3,651	35	1 1 3
3,599	81	3,579	28	0 2 4
3,404	85	3,433	35	0 4 0
3,373	17	3,369	55	1 3 1
3,343(quartz)	100			
3,192	55	3,198	10	0 4 2
3,173	20	3,168	100	1 3 2
3,029	49	3,017	10	0 2 5
2,956	10	2,936	5	0 4 3
2,805	46	2,794	10	0 0 6
2,763	29	2,753	60	1 1 5
2,680	17	2,667	5	0 4 4
2,582	15	2,575	90	2 0 0
2,457(quartz)	8			
2,427	47	2,414	75	2 2 0
2,409	31	2,400	50	2 2 1
2,310	1	2,317	5	2 2 2
2,272	49	2,263	15	0 6 1
2,223	3	2,213	5	2 2 3
2,177	11	2,166	10	2 0 4
2,154	20	2,143	25	1 1 7
2,128(quartz)	7			
2,116	12	2,104	10	1 5 4
2,102	11	2,092	10	2 2 4
2,058	7	2,049	20	2 4 1
2,031	20	2,014	10	0 2 8
1,979(quartz)	7			
1,965	19	1,957	40	2 2 5
1,947	3	1,938	5	2 4 3
1,901	6	1,893	20	2 0 6
1,856	8	1,842	5	1 7 0



Crystals of cyrilovite in subparallel aggregates (SEM).
J. Viñals collection and photo.

The smaller crystals have a complex morphology with {001} pinacoid highly developed and the presence of very small faces of another bipyramid, probably {111}. Cyrilovite has also been found as sheaf-like aggregates, consisting of flattened crystals in subparallel arrangement. Exceptionally, some specimens with a continuous crust of cyrilovite have been found, up to 3 cm, and whose appearance (color and the pseudocubical faces) is reminiscent of common jarosite. However, even in these crusts, the cyrilovite is associated with other phosphates, unlike what happens in the jarosite at this locality.

Composition (weight %) of plimerite from La Paloma compared with that of Broken Hill and Reaphook Hill.

	Theoretical ZnFe ₂ (PO ₄) ₂ (OH) ₂	La Paloma (mean of 20analyse)	Broken Hill (Elliot <i>et al.</i> , 2010)	Reaphook Hill (Elliot <i>et al.</i> , 2010)
P ₂ O ₅	32,32	34,20 (std 0,46)	32,37-33,98	30,92
As ₂ O ₅		0,18 (std 0,06)	0,05-0,23	0,04
SiO ₂		0,05 (std 0,02)	-	-
Al ₂ O ₃		0,78 (std 0,09)	0,93-4,48	1,48
Fe ₂ O ₃	48,49	42,35 (std 0,53)	29,82-36,42	33,51
FeO		-	2,98-4,47	3,73
MnO		1,89 (std 0,17)	0,02-0,36	0,56
MgO		0,03 (std 0,03)	0,00-0,11	0,84
CaO		0,05 (std 0,03)	0,14-0,80	1,41
CuO		-	0,00-0,24	0,00
ZnO	12,35	14,30 (std 0,37)	14,43-20,17	18,38
PbO		-	0,20-0,37	0,03
Na ₂ O		0,26 (std 0,04)	-	-
H ₂ O	6,84	5,91*	6,84**	6,84**

*: by difference

**: calculated by theoretical structure

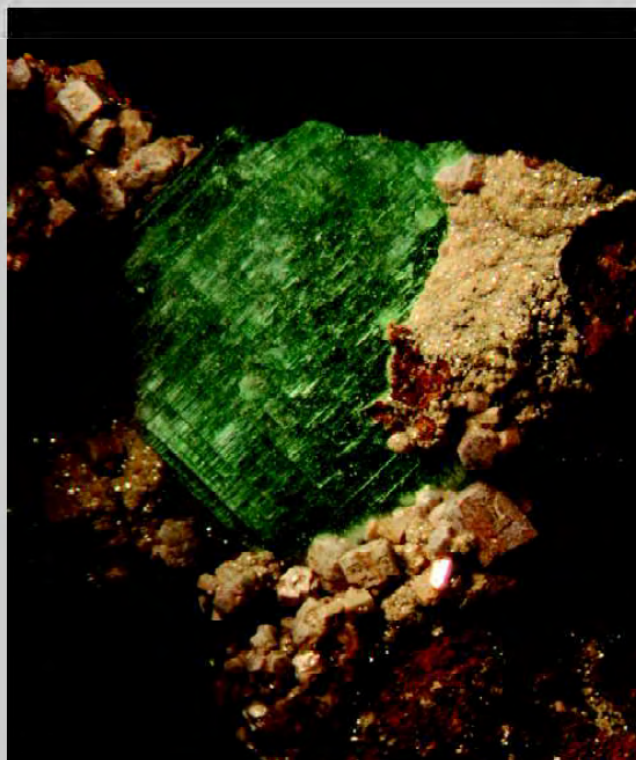
Usually cyrilovite appears associated with small tabular apatite crystals or with strengite. More unusual is the association with kidwellite and cacoxenite. It is much less common than other phosphates present in this locality.

Metatorbernite $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$

Metatorbernite is occasionally found associated with strengite as not too intense green crystals, opaque, tabular, very thin, almost lamellar, of square or rectangular shape and with a size of up to 4 mm. The crystals present a parallel growth in mosaic, typical of this mineral. The absolutely dominant faces of these crystals are those of the basal pinacoid {001}, but the sides of the tables can also be appreciated, probably belonging to the bipyramid {011}. More rarely, some small crystals (0.1 mm) have been found, very thin and transparent, of intense green color, which may correspond to the hydrated phase, torbernite.

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*Crystal of metatorbernite on fluorapatite. J. Viñals collection.
Photomicrography by Joaquim Callén.*

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