Cotunnite, caracolite, sideronatrite
and other rare secondary minerals in the Ferruginosa mine - Cabo de Palos, Cartagena, Murcia, Spain -

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SEM photos and photomicrography: Christian Rewitzer

Introduction

Although in the surroundings of Cabo de Palos, in Cartagena, there are ancient workings, probably from Roman times, the documented mining history of this area begins in 1849 and 1850, when the Serpiente and Diana claims were registered on Atalayón hill by Juan Rubio, and the Segura, Gorriona, and Santa Rosalía claims by the company El Lirio de Murcia (Lasala, 1852). The workings, as in almost all the mines of Cartagena at this time, pursued argentiferous galena, which supposedly was in among the iron oxides that formed ferruginous outcrops in the quartzites and schists. Although there was some silver in these deposits, it was disseminated in the secondary minerals, so that miners were unable to recover it with the usual concentration systems. Consequently, the mines were abandoned. Later they were registered again under the names Cándida, Ferruginosa, Primitiva, 2ª Vulcano, and Cuba Española, among others.

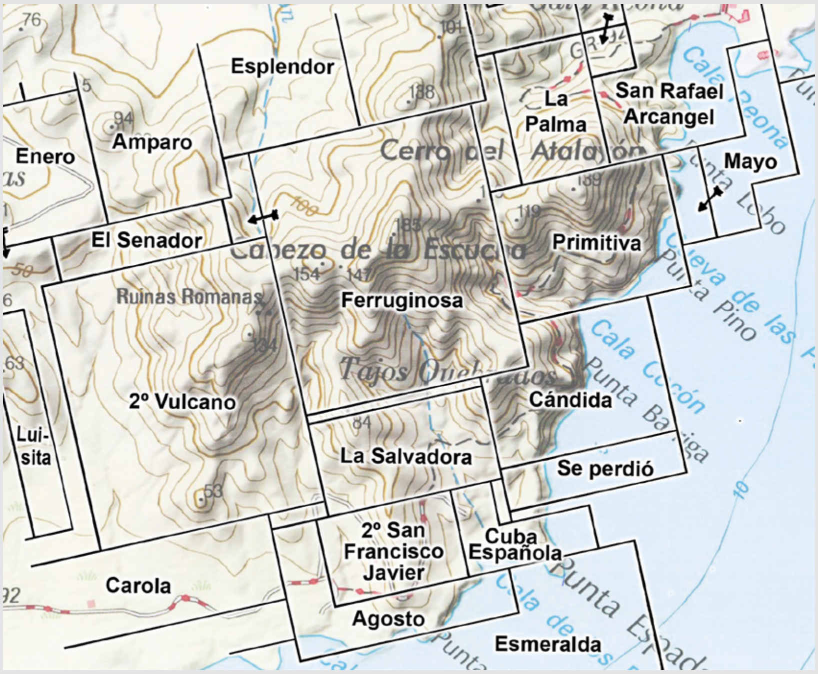
In 1907 the Société des Mines de Cabo de Palos was founded in Paris, which had 203 hectares of concessions in the area that gave it its name, contributed by Charles Bourgeois, a mining engineer. The company had a nominal share capital of 1,000,000 francs, divided into 10,000 shares, of which 6,500 would be subscribed in cash, each for 75% of its nominal value, while the remaining 3,500 would be delivered to Bourgeois in exchange for his contribution, in addition to 150,000 francs in cash and 4,000 beneficiary parties. The results must have been very bad, since not a single coupon of the shares was cut, and the company was dissolved in 1910.

In his detailed study of the mines of the Cartagena district, Guardiola (1927) indicates that in the mines Cándida, Ferruginosa, Primitiva, 2ª Vulcano, and Cuba Española, in the area of Cabo de Palos, galena nodules were found inside the masses of iron oxides.

Along with them appeared “lead chloride” (cotunnite) and “lead chlorocarbonate” (phosgenite).

The Ferruginosa mine, one of those cited by Guardiola (1927), has its workings located around the so-called Cabezo de la Escucha, the hill with the highest altitude (185 meters) of all those that make up El Atalayón.

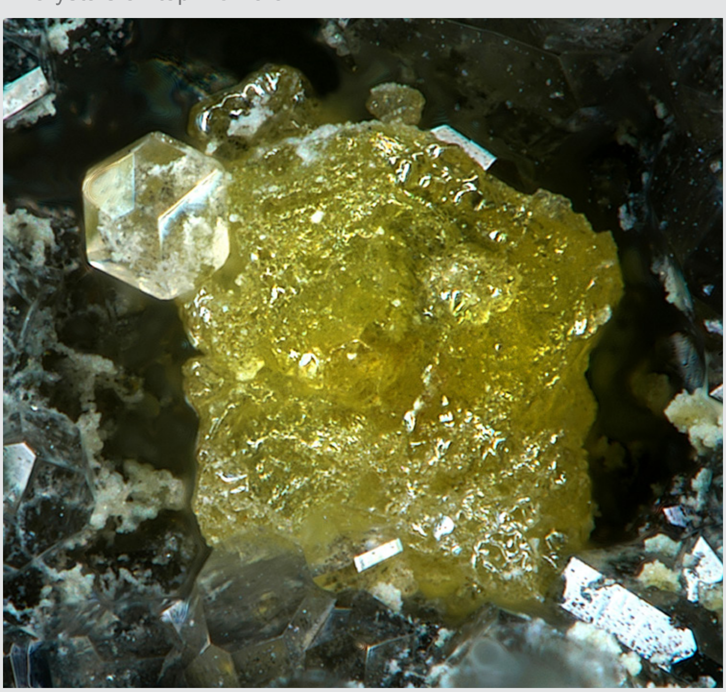
The workings in which the minerals described here were found is about 150 meters NW of the top of Cabezo de la Escucha, while the one considered the main pit of the mine, large and brick-lined, is located about 250 meters to the SSE from the top. In this mine, we could not find any phosgenite, so the mineral designated as such by Guardiola (1927) may have come from another pit, or have been confused with the caracolite.



Distribution of mining claims in the Cabo de Palos area. The arrows indicate the extensions of each concession.

Share of the French company “Mines de Cabo de Palos”

Crystalline aggregate of **chlorargirite** with **caracolite** crystals on top. FOV 0.6 mm.



Mineralogy

The primary mineralization was formed by siderite, which was transformed into iron oxides, in which galena nodules and probably small amounts of pyrite and chalcopyrite were disseminated. This ore is embedded in quartzite and black mica schists with garnet, staurolite and chloritoid belonging to the Lower Alpujárride Mantle. The secondary minerals, which are scattered among the iron oxides, are especially interesting.
These are halides and sulfates, mainly formed by the alteration of the galena and to a lesser extent of the other sulphides present, in an environment rich in chloride, probably derived from sea water, in an arid climate, so that the paragenesis is reminiscent of some Chilean mines.
Several of the minerals studied in this work (penfieldite, lesukite, and caracolite) had not been found before in Spain.

Sulfur   S

Native sulfur has been found in the Ferruginosa mine as a product of the oxidation of pyrite.
It appears as very bright, translucent and well developed microcrystals up to 0.4 mm, white or pale yellow in color, in fissures of limonite, together with scattered relict pyrite.

Galena   PbS

As already indicated, the galena appears in nodules that can reach a size of several centimeters inside the oxidized siderite. They have a coarse crystalline structure, and are surrounded by a crust of alteration minerals, which have not been studied in detail. Microcrystals of the secondary lead minerals, mainly caracolite, are found in the vicinity of these nodules.

Chlorargirite   AgCl

Small irregular aggregates have been found with the typical waxy or horn-like aspect of this mineral, creamy or yellowish-green in colour. It also appears as crystallized masses and occasionally as monocrystals with the cube or octahedron as the main forms, modified by other forms. These crystals reach a maximum size of 0.4 mm and are associated with caracolite and cotunnite. Chlorargyrite in this locality has a significant bromine content.

Halite NaCl
Halite appears as groups of colourless and transparent or white microcrystals in the fractures of siderite and limonite. Halite is always very young and seems to be the youngest formed mineral of the NaCl-rich solutions and always forms where there is no lead available.

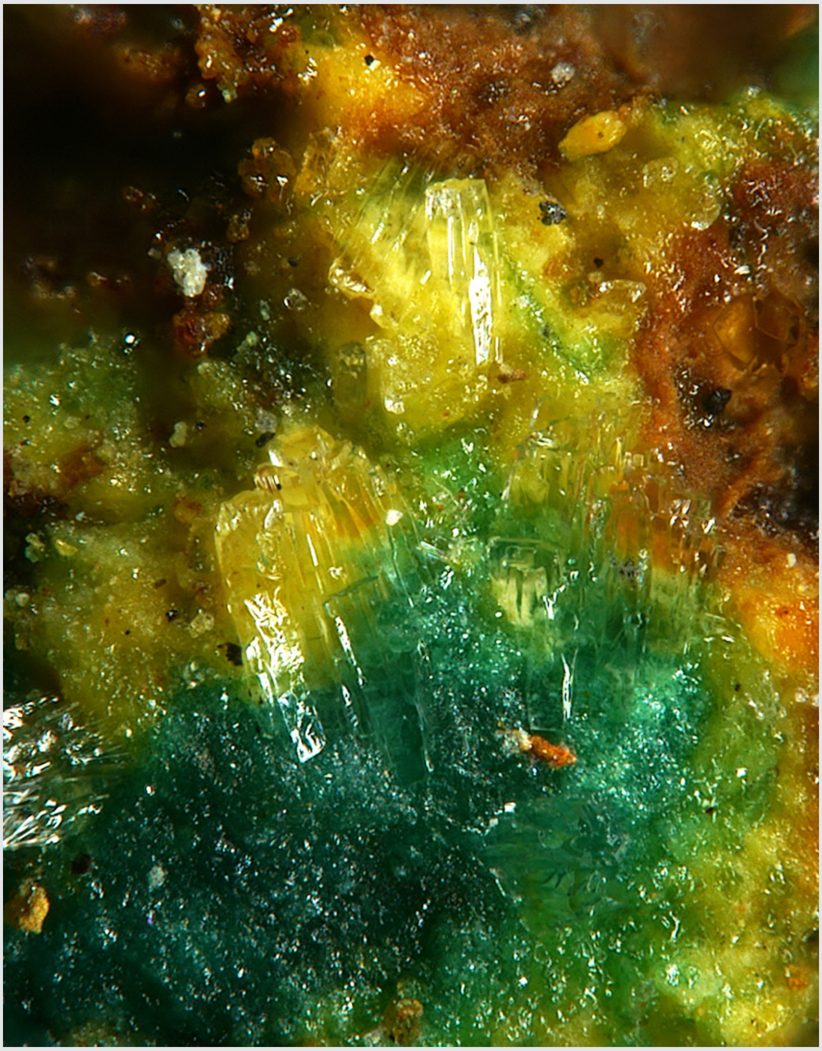
Lesukite $Al_2Cl(OH)_5 \cdot 2H_2O$
Lesukite is a very rare mineral, first described by Vergasova *et al*. (1997) from material obtained in a fumarole on Tolbachik volcano in the Kamchatka peninsula
Its formation occurred at a relatively low temperature of less than 50 ° C (Filatov *et al*., 2012). It has also been found in saline deposits (Chaikovsky and Korotchenkova, 2016).
In the Ferruginosa mine, lesukite forms small yellow crystalline masses with vitreous luster in the limonite matrix, associated with atacamite. Apparently it is a very scarce mineral at this locality, since until now it has been found only in two specimens.
The lesukite of the Ferruginosa mine is the first recorded in Spain for this species.

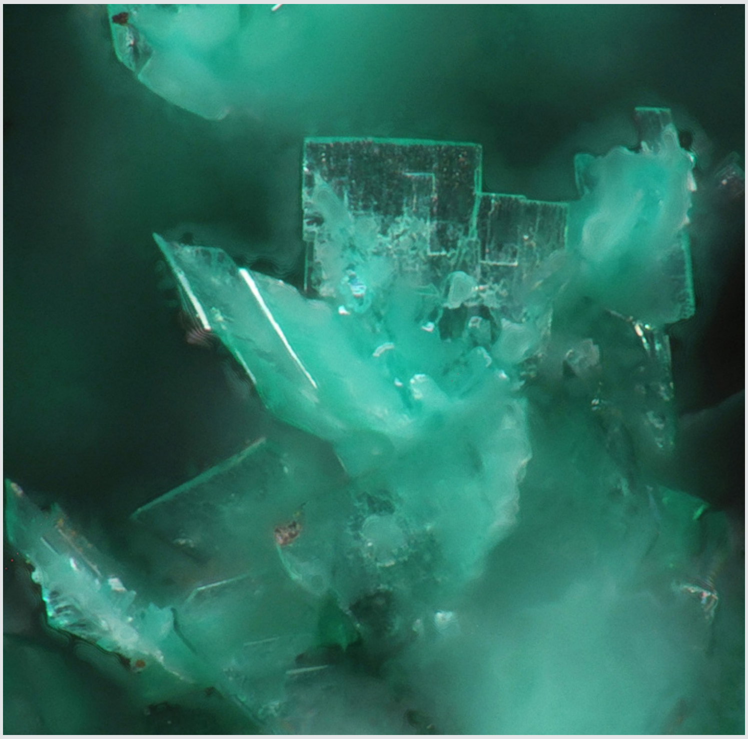
Atacamite $Cu_2(OH)_3Cl$
Atacamite is very rare in the Ferruginosa mine. It occurs as very small green tabular crystals or as crystalline aggregates, as a product of alteration of chalcopyrite.

Paratacamite
$Cu_3(Cu,Zn)(OH)_6Cl_2$
Paratacamite has been found as rhombohedral crystals of green or blue-green color, or crystalline aggregates, sometimes forming clusters up to 3 mm size, perimorphic after another mineral. It is associated with malachite and atacamite, and is very rare in this locality.

Halite. Cubic microcrystals on oxidized siderite. FOV 1.6 mm.

Lesukite (yellow) associated with atacamite or paratacamite. FOV 1.2 mm.



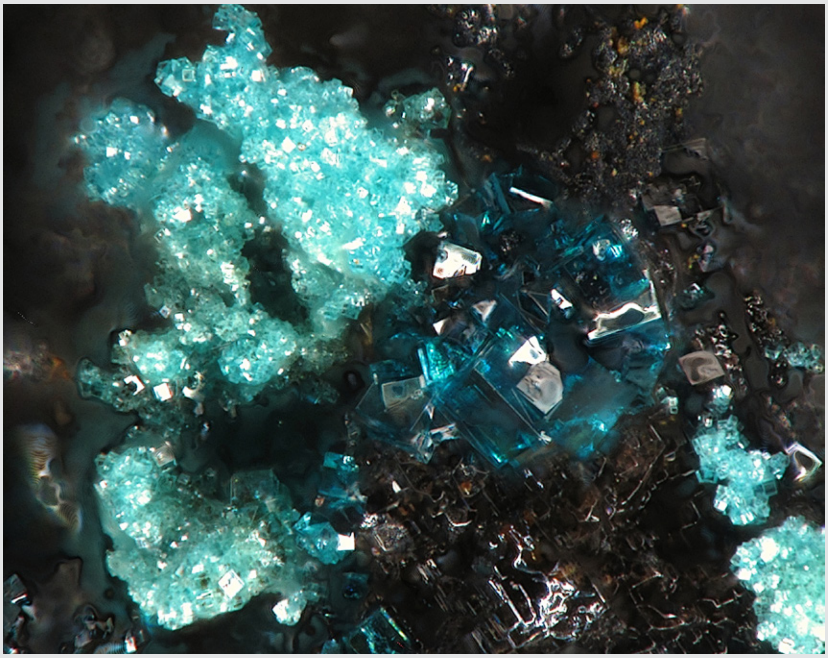


Atacamite. SEM photo.

Atacamite. Tabular crystals. FOV 0.3 mm.

Paratacamite. Arborescent aggregate of mycrocrystals. FOV 5 mm.

Boleite
$KPb_{26}Ag_9Cu_{24}(OH)_{48}Cl_{62}$
Boleite is not very common in this locality. It appears as tiny crystals of around 0.1 mm, with the usual cubic shape of this mineral, rarely modified by {111} and {011}, with its typical blue color, and intense vitreous luster. It is usually associated with caracolite.

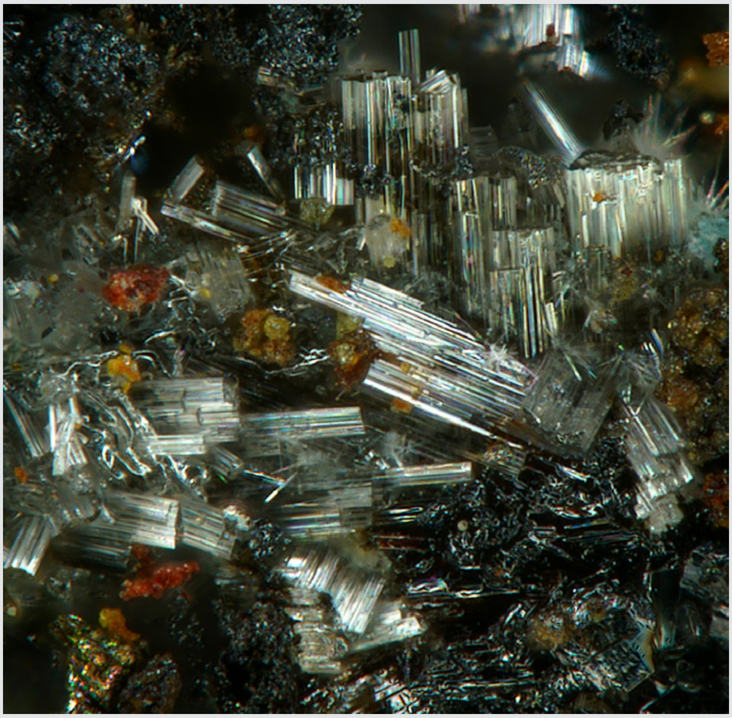


Boleite. Cubic mycrocrystals. FOV 0.2 mm.

Penfieldite **$Pb_2Cl_3(OH)$**
Penfieldite generally appears as tiny hexagonal prismatic crystals, somewhat irregular, colorless and with adamantine luster, with a maximum size of 0.3 mm, in parallel growth. Penfieldite is rare at this mine, and in the few specimens in which it has been found it is always associated with boleite and often with caracolite. Penfieldite was described as a new species from the ancient slags of the Laurium mine in Greece (Genth, 1892), and the vast majority of the finds of this mineral have been in slag or in old lead objects extracted from the sea.

Until now, it has only been found in natural form in Sierra Gorda, Chile (Merlino *et al.*, 1995). This is the first time that the presence of this mineral is reported from a Spanish deposit, and is also natural.

Penfieldite. Prismatic crystals in parallel growth. FOV 1.4 mm.



Cotunnite. Parallel group of prismatic microcrystals. FOV 1.8 mm.

Cotunnite. Crystals with skeletal growth associated with caracolite microcrystals. FOV 0.9 mm.

Cotunnite $PbCl_2$

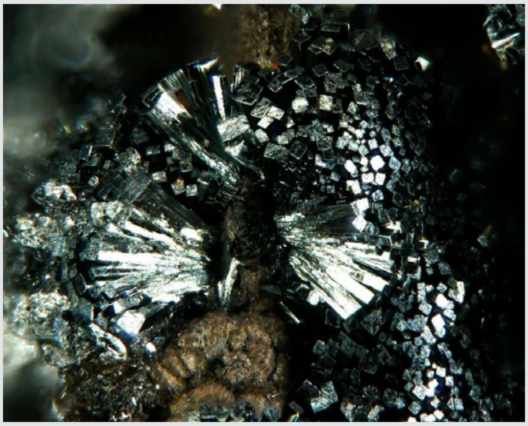
Cotunnite is common at Ferruginosa. It occurs as shapeless crusts, and as white opaque prismatic crystals, elongated on [001] and flattened on {010}, up to 1 mm in size. Skeletal crystals with large cavities and with the equivalent faces developed unequally are frequent. Many of the cotunnite crystals are partially or totally covered by transparent and colorless caracolite microcrystals. The cotunnite crystals of the Ferruginosa mine are among the best in the world for this mineral.

Pyrolusite $Mn^{4+}O_2$

Pyrolusite forms short prismatic crystals of black to very dark gray color with an intense metallic luster, in sizes up to 1 mm. Also common are the globular aggregates of prismatic crystals, or botryoidal formations of centimetric size.

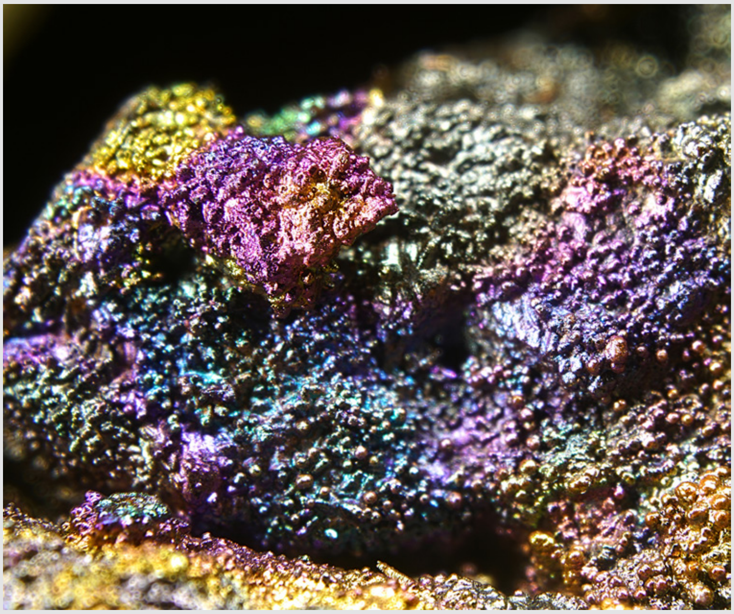
Cotunnite. Crystals with skeletal growth associated with caracolite microcrystals. FOV 2.1 mm.

Pyrolusite. Group of divergent prismatic crystals. FOV 1 mm.



Coronadite $Pb(Mn^{4+}_6Mn^{3+}_2)O_{16}$
Coronadite has been found in the form of deep black to dark grey thick fibrous masses and hedgehogs of tiny needles. This mineral is very common in the Ferruginosa mine, frequently associated with caracolite.

Goethite $\alpha\text{-}Fe^{3+}O(OH)$
Goethite is very abundant in the Ferruginosa mine, as earthy masses or pseudomorphing large siderite crystals. It is also found as botryoidal or globular masses, sometimes with beautiful iridescence. Hematite appears along with goethite.



Iridescent **goethite** on limonite. FOV 8 mm.

Coronadite as coatings of acicular microcrystals. FOV 12 mm.

Chalcophanite. Aggregate in the form of a flower of very thin lamellar crystals with internal reddish reflections. FOV 2.8 mm.

Chalcophanite (Zn,Fe,Mn) $Mn_3O_7 \cdot 3H_2O$

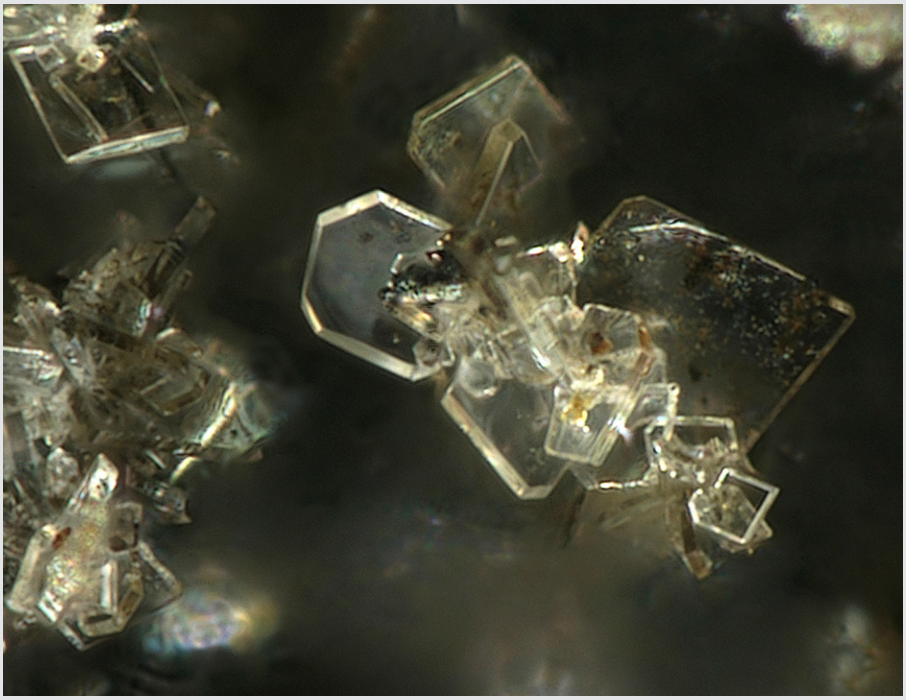
In this mine, rosette aggregates composed of rounded and very thin plates with deep red internal reflections are very abundant. The similarity to the same type of aggregates of hematite, and the internal reflections, lead to it being initially considered to be that mineral. However, the brown color of the rosettes is clearly different from that of hematite of a similar size. Analyses have shown that it is actually chalcophanite. The rosettes have an individual size up to 1 mm. Chalcophanite also appears as botryoidal and stalactitic aggregates.

Siderite $FeCO_3$

Siderite was the main component of the outcrops in the El Atalayón area, although mostly completely transformed into more or less compact or earthy iron oxides.
In the Ferruginosa mine, large "siderite" crystals of up to 5 cm in beautiful clusters have been found, totally pseudomorphed to iron oxides, sometimes with iridescent coatings of goethite. A white to greyish nodular mass of about 4 cm diameter embedded in oxidized siderite was identified by x-ray diffraction as a mixture of alunite and rectorite.

Malachite $Cu_2(CO_3)(OH)_2$

Malachite has occasionally been found in the Ferruginosa mine as small short prismatic crystals, associated with atacamite and paratacamite.



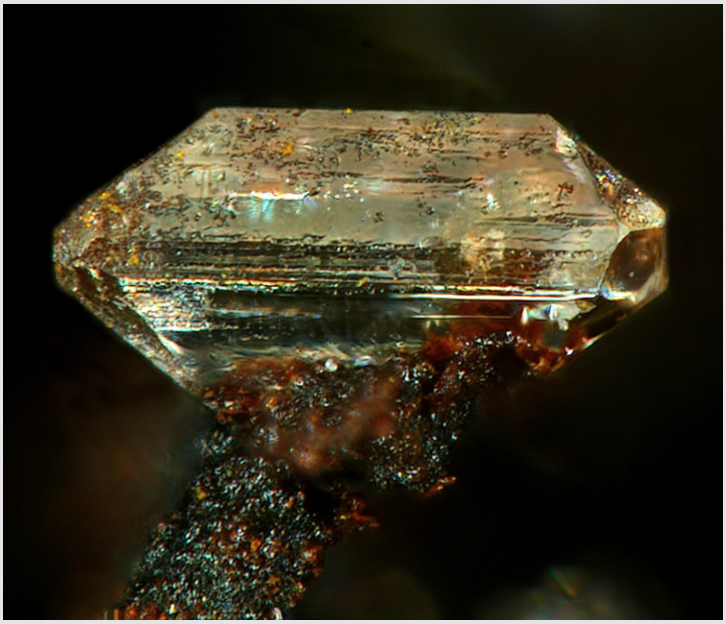
Glauberite as well defined microcrystals. FOV 0.8 mm.

Glauberite $Na_2Ca(SO_4)_2$

Glauberite has occasionally been found in the form of small, colourless or whitish tabular crystals on altered siderite. The mineral seems to be of neoformation.

Celestine $(Sr,Pb)SO_4$

Celestine is very rare in the Ferruginosa mine, appearing only occasionally as hedgehogs up to half a millimeter in size, formed by divergent acuminate crystals of greyish white color. However, it is of great interest, since it has a high lead content, apparently replacing strontium, of the order of one out of four atoms. The substitution of strontium for barium is common and well known, since there is a complete solid solution series between barite and celestine, although natural specimens usually have compositions close to the extremes (Hanor, 1968). However, although in synthetic materials there seems to be a complete solid solution series between celestine and anglesite (Alía *et al*., 2000), we did not find any data about the existence of natural specimens of lead-rich celestine, so this material deserves more detailed study.



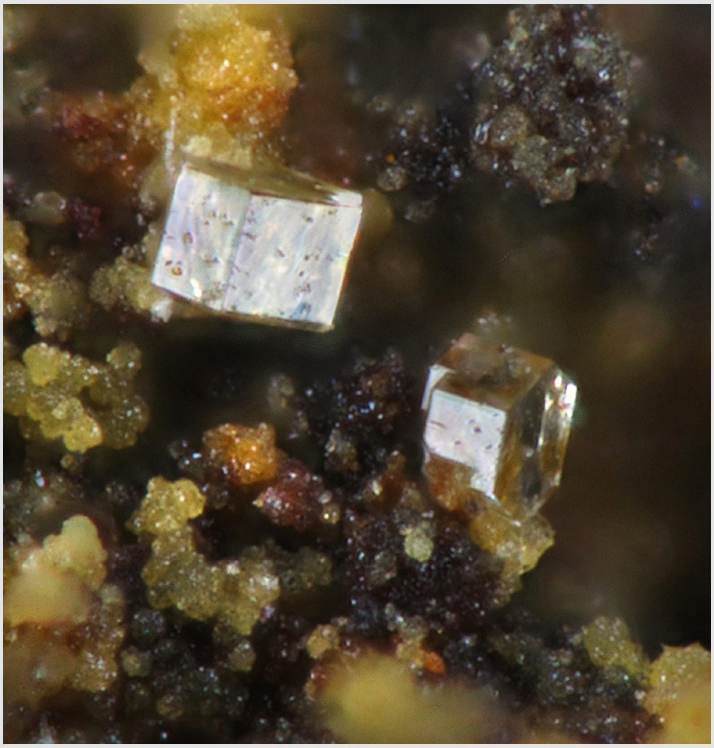
Anglesite. Sharp microcrystal. FOV 0.3 mm.

Anglesite $PbSO_4$

Anglesite is a very rare mineral in this mine, appearing as fine tabular crystals, vertically striated as is usual in this mineral, with a maximum size of 0.3 mm. It is associated with alterated galena.

Lead-rich **celestine** forming divergent associations of micro-crystals. FOV 1.6 mm.

Natrojarosite. Microcrystals in arborescent growth. FOV 1.7 mm.



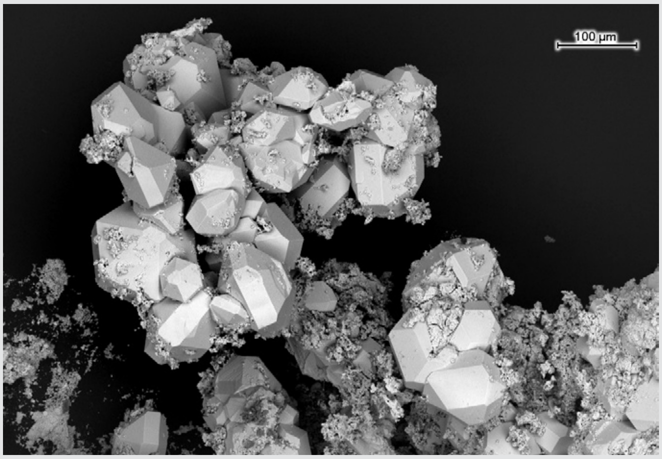
Natrojarosite $NaFe_3(SO_4)_3(OH)_6$

Natrojarosite has been found as small crystals of about 0.2 mm, typically pseudocubic, generally forming groups or coatings as earthy crusts or powdery masses, very rarely as small individual crystals.
The color varies from yellowish brown to deep honey yellow, with a bright vitreous luster. There is a solid solution between jarosite and natrojarosite, although the vast majority of the specimens analyzed were clearly on the natrojarosite side of the boundary.
The natrojarosite is usually associated with sideronatrite, and rarely with caracolite.

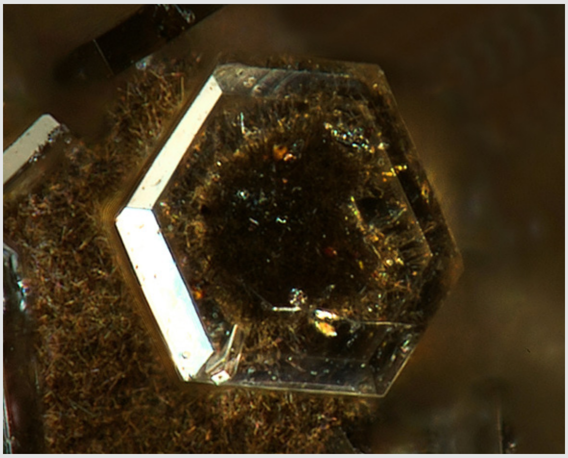
Caracolite. Twins with the appearance of hexagonal prisms. FOV 0.8 mm.

Caracolite $Na_3Pb_2(SO_4)_3Cl$

Caracolite is a very common mineral in this deposit, appearing as colorless, totally clear, gemmy and very bright micro-crystals, in sizes up to one millimetre. It has the appearance of a hexagonal prism with a tabular and equidimensional development, sometimes modified by proportionally large faces pertaining apparently to a dipyramid. However, in this case, the geometric shape does not correspond to the crystallographic one. Although caracolite belongs structurally to the hedyphane group, it is the only mineral in this group that crystallizes in the monoclinic system and not in the hexagonal system. From the first studies carried out on this mineral (Websky, 1886) it was observed that the optical properties of the crystals actually corresponded to complex, triple or polysynthetic twins, probably similar to those of aragonite. In some cases, the outline of the geometric prism is not hexagonal, but differences in growth between the sectors of the twin make the section look rather trapezoidal. The crystals (twins) are colorless and totally transparent, so that at large magnifications the details of the matrix under them can be observed. Caracolite is usually associated with cotunnite, boleite and coronadite, and less frequently with sideronatrite and natrojarosite. Caracolite reacts with water, forming anglesite and halite, and some crystals are in fact slightly altered on their surface. The Ferruginosa mine is the first locality in which it has been found in Spain, and the only one in the world in which it is relatively abundant, apart from those in Chile.

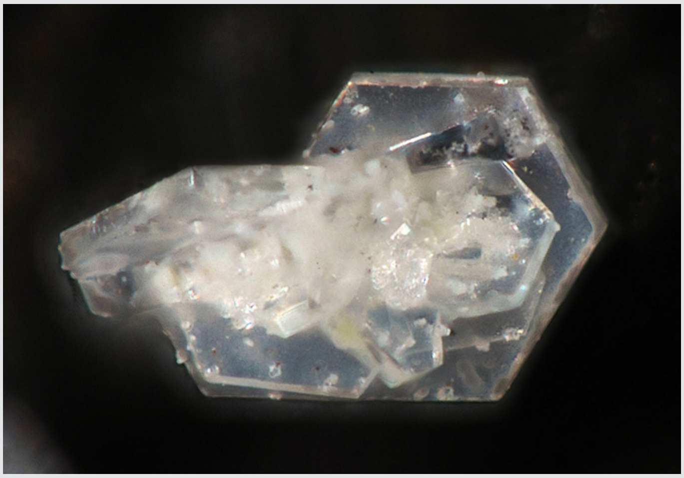


Caracolite. Twins with the appearance of a hexagonal prism modified by large dipyramid faces. SEM photo.



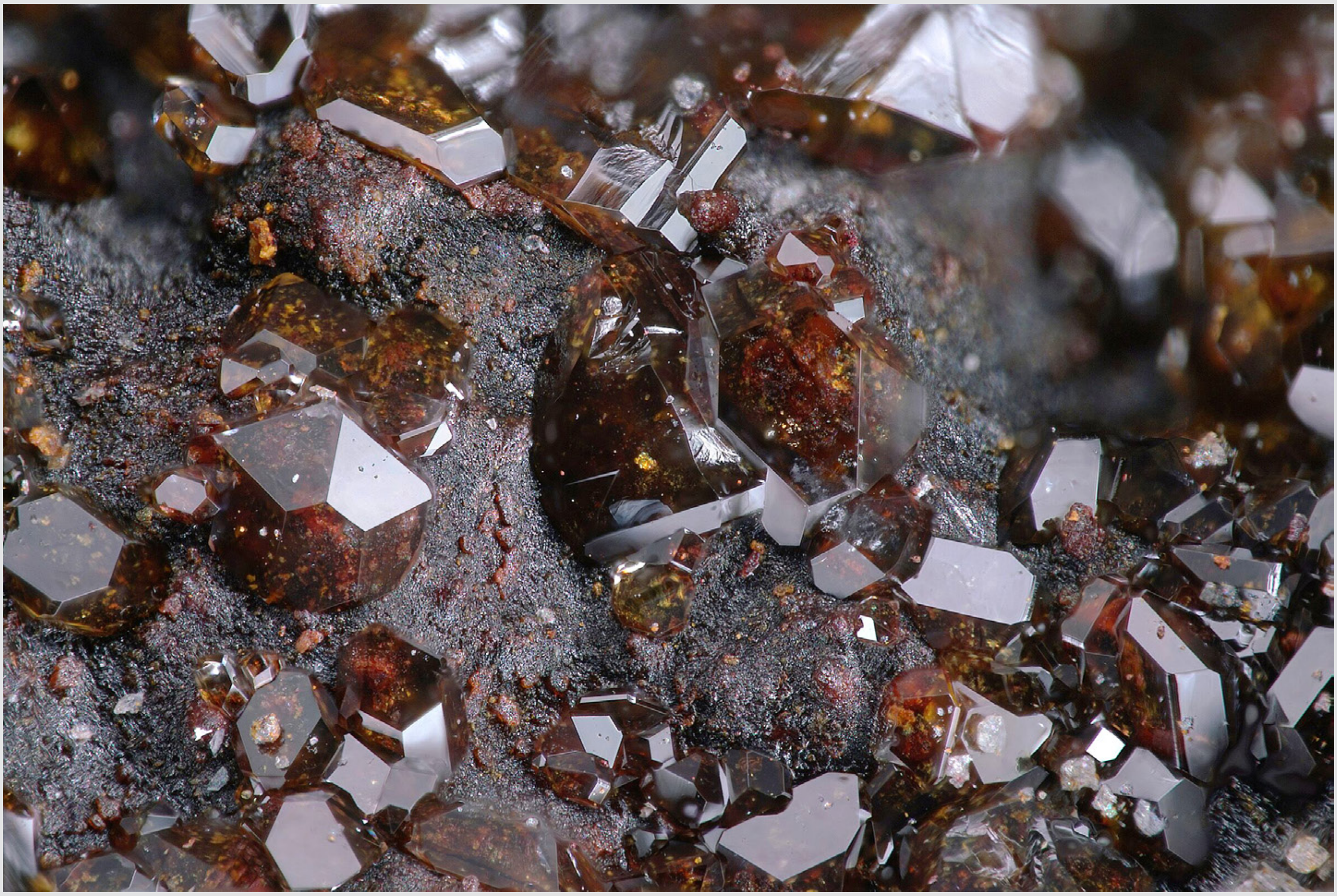
Waterclear **caracolite** twin. FOV 0.3 mm.

Caracolite. Twins with the appearance of a hexagonal prism modified by large dipyramid faces. FOV 0.3 mm.



Caracolite tabular twins with slightly altered surface. FOV 0.2 mm.

Caracolite crystals on goethite.
Left: FOV 0.8 mm.
Top: FOV 5 mm.
Below: FOV 3.5 mm.
Andreas Schloth photos.



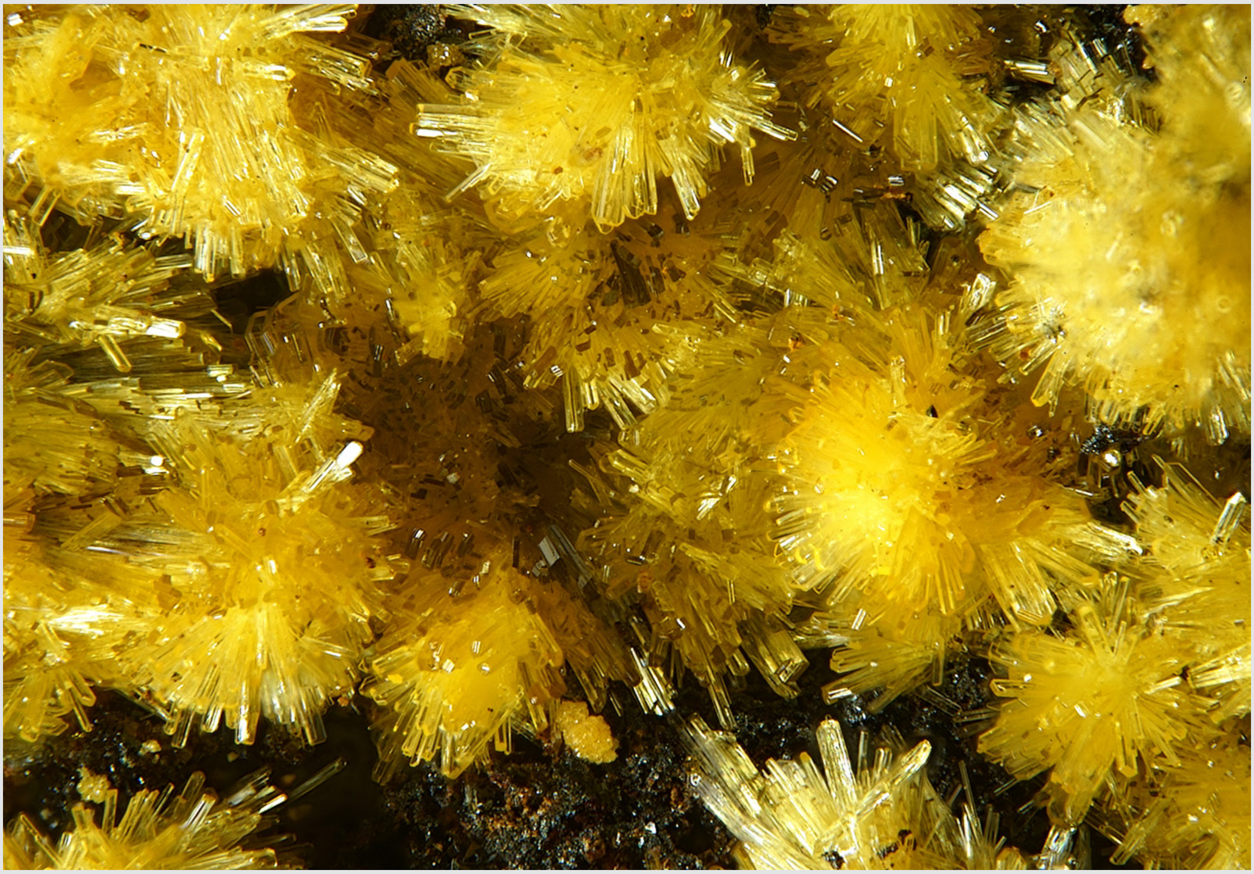
Gypsum $CaSO_4 \cdot 2H_2O$

Gypsum is widespread in the Ferruginosa mine, but only as granular masses or crystalline aggregates of a few millimeters, mainly on goethite or limonite. No significant masses or crystals have appeared. Sometimes the bright crystalline grains are difficult to differentiate visually from other minerals.

Sideronatrite $Na_2Fe(SO_4)_2(OH) \cdot 3H_2O$

The presence of sideronatrite in the Cabo de Palos surroundings, in an unspecified mine, had already been pointed out by Rosell *et al*. (2017). In the Ferruginosa mine, sideronatrite is found as groups of divergent crystals, up to 2 mm size, of different shades of yellow to orange, depending generally on the thickness of the crystals, associated with natrojarosite and less frequently with caracolite. The crystals have tabular morphology, elongated in one direction. The structure of sideronatrite allows this mineral to be transformed into metasideronatrite very easily in a dry environment above a temperature of 35º C, losing two of its three water molecules. This change is reversible, so that under normal conditions of temperature and humidity the mineral is rehydrated to sideronatrite (Ventruti *et al*., 2010). This implies that the metasideronatrite specimens in collections, obtained in tailings exposed to the sun, such as those from most of its Spanish localities (Calvo, 2014) are currently almost certainly sideronatrite.

Sideronatrite. Divergent aggregates of flattened prismatic crystals. FOV 2.5 mm.



Sideronatrite. Divergent aggregates of flattened prismatic crystals. FOV 3.2 mm.

In any case, the specimens from the Ferruginosa mine present a very remarkable quality for this mineral, of the same level as those of the other two mines in which well-formed crystals are known, the Bergwerk West coal mine, of Kamp-Linfort, in Germany, and the Coronel Manuel Rodríguez mine, in Mejillones, Chile.

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