

# Pseudomorphs: when the mineral is not what it was

Jesús Fraile and Miguel Calvo

## Introduction

The word pseudomorph derives from the Greek «ψευδο» (pseudo) and «μορφωσις» (morphōsis), from «μορφή» (morphē), for “false shape”, that is to say, essentially we can talk of pseudomorphism when a mineral exhibits the morphology of a preexisting one, which it has replaced in some way. Haüy (1801) was the first to use the term “pseudomorphoses”, to designate “those bodies with a false and deceptive form,” a shape that had been “stolen from other bodies that had received it from nature.” Although that referred mainly to fossils, formed by calcite and pyrite, it also included pseudomorphs in the “mineral kingdom”, in which “there are some substances of this kingdom whose crystalline forms are merely borrowed, and it is very probable that, at least in some cases, the new substance has gradually replaced the one that ceded its space.”

With the development of mineralogy, pseudomorphs were studied systematically. Blum (1843) compiled in a monograph data on all the cases of pseudomorphism known up to that time, extending his initial work with two appendices, published later (Blum, 1847; 1863). And Naumann (1846) proposed the definition of pseudomorph that is still used today: “Crystalline or amorphous body that shows the crystal shape of another mineral”. So in a pseudomorph a certain mineral is altered by changing its internal structure and/or its chemical composition to that of another mineral, although its initial external form remains.

There have been several proposals regarding the most correct way to designate one pseudomorphic mineral from another. Currently the most accepted form is to first designate the existing mineral, followed by “pseudomorph after” and then the mineral species that it replaced, and whose shape it maintains.

There is no single universally accepted classification for pseudomorphs. Basically they can be divided between those formed by structural or chemical alteration of the original mineral, and those formed as molds by occupying cavities or covering surfaces. These two categories can be subdivided in different ways, delimiting more or less arbitrarily what is really considered a true pseudomorph and what are just accidental shapes produced by contact between different minerals.

The most recent classifications (Strunz, 1982, Klopogge and Lavinsky, 2017) basically coincide in the substantial points, although with some differences such as the inclusion in the latter of metamict minerals and exsolutions as pseudomorphs. In this paper we will follow a classification that mostly coincides with those cited, although introducing some modifications.

Pseudomorphosis can occur mainly in four ways: by structural changes without chemical modifications, by chemical modifications in which elements are gained or lost, by processes of displacement by infiltration or filling of previously formed cavities, without any constituents of the previous mineral remaining, and by coating a mineral that later disappears, leaving the mold formed by the new mineral. In this article we will examine the main pseudomorph formation pathways and some significant examples, showing that several hundred different types of pseudomorph are known.

## Pseudomorphs without change in chemical composition (paramorphs or alomorphs)

As already indicated, some pseudomorphs can occur without chemical changes taking place, due to changes between the structures of polymorphic minerals. In some cases the original mineral is unstable and the difference between the structures is small, so that the alteration always occurs when the conditions of formation changed, so that the initial species does not really ever exist under normal environmental conditions. In others, the mineral is metastable, so that alteration to a new species will depend on the existence of changes in pressure and/or temperature.

## Acanthite pseudomorphs after argentite

In the classical treatises of mineralogy of the nineteenth and early twentieth centuries two species of silver sulphide were distinguished, cubic “argentite” and monoclinic “acanthite”. But the first study performed by X-ray diffraction (Ramsdell, 1925) showed that argentite and acanthite had identical structures, and that therefore it was a single mineral species, which had crystallized in the cubic system as “argentite” when formed at a temperature above 173°C, but always becoming acanthite, the monoclinic polymorph, when cooled below that temperature.

Obviously, these pseudomorphs are common in deposits around the world, instead of the nonexistent argentite. Acanthite formed as a primary mineral also exists, but it is much rarer than the pseudomorph one. The locations where the most typical pseudomorph acanthites have appeared are Schneeberg-Schlema in Obersachsen (Germany), Fresnillo in Zacatecas and San Juan de Rayas in Guanajuato (Mexico) and more recently Bou Azzer and Imiter in Ouarzazate (Morocco).

At Schneeberg, veins of Bi-Co-Ni and Ag were mined since the 12th century, which produced many classic examples of these pseudomorphs, present in old collections. However, these mines had ceased production by the time of World War II. In 1946 the Russian occupation undertook the systematic investigation and exploitation of the associated uranium deposits by underground workings even under the very city of Oberschlema itself, which finally had to be relocated in 1952. By 1955 the new company discovered huge deposits of polymetallic veins around Hartenstein

and Alberoda, to the north and east of Schlema, producing many quality specimens, until mining ceased in 1991. The acanthite specimens appeared as cubes, octahedrons and cuboctahedrons of a lustrous metallic gray, up to 1 cm in size, grouped in formations of several centimeters (Moore, 2016).

In Fresnillo (Cerro Proaño), mining the silver deposits began with the Spaniards in the sixteenth century. The oxide ores near the surface were so diligently exploited

that in 1970 Fresnillo seemed to be exhausted.

In 1975, the Santo Niño and Santa Elena veins were discovered, and later the San Guillermo vein, which, besides being very rich, had not been discovered before because they did not outcrop on the surface. Large amounts of pyrargyrite, stephanite, polybasite and acanthite appeared, so that since 1980 Fresnillo has become the richest silver mine in the world, in addition to providing excellent crystallized specimens

of silver minerals.

Acanthites were found in the form of very sharp cuboctahedra of up to 3-4 cm size from the beginning of the 90s and into the early 2000s as aggregates of elongated crystals from the more recent San Carlos vein. The San Juan de Rayas mine in Guanajuato also provided fairly abundant acanthite specimens in the 70s and 80s, with bright black cubes measuring 1 to 5 cm and forming aggregates of several centimeters (Moore, 2016).

In Morocco, the Bou Azzer mine, already very famous for other minerals, did not yield specimens of acanthite until 2013 when very lustrous, metallic gray,

1 cm crystals on massive calcite were offered at the 2014 Tucson show. The Imiter mine began its modern production period in 1970, although the deposit had already been discovered and worked from the 8th to the 13th centuries. It only produced massive acanthite until 2004, when 1 cm crystals appeared, with rough surfaces and a subdued metallic luster. Since 2005, 3-4 cm octahedral crystals were found, generally in groups (Moore, 2016).



**Acanthite.** 2 cm. Jáchymov (Sankt Joachimsthal), Karlovy Vary, Bohemia, Czech Republic. Benjamin Calvo coll. . Foto J. Callén.

### Quartz pseudomorphs after beta-quartz

Beta-quartz-beta is a high temperature quartz (over 573°C), that crystallizes in the hexagonal system as bipyramids, generally with little or no prism faces. It formed by solidification in a melt. Given its temperature, it can not occur in hydrothermal environments, so it is found in magmatic rocks.

It is unstable at surface conditions, so that it is always transformed into common quartz (alpha-quartz).

These pseudomorphs are found in porphyritic granites, such as those exposed in the Vallibierna ravine, in Benasque, Huesca (Spain), in the acidic subvolcanic rocks of the Val

stream, in Luesma, Zaragoza (Spain), in the Stephanian rhyolites that outcrop next to the La Estrella mine, in Pardos, Guadalajara (Spain) or in the ignimbrites of Amadores beach, in Mogán, Gran Canaria, Canary islands (Calvo, 2016). As classic localities, in which individual crystals and twins up to 2 cm in size occur, we can mention the Esterel massif, between Fréjus and Mandeliue-La Napoule (France) (Drugman, 1922) and Wheal Coates, in St.

Agnes, Cornwall (Great Britain) (Drugman, 1927).

One should clarify that crystals composed of two rhombohedra, with little or no prism development, often brown or black in color, that appear in sedimentary calcite or gypsum in many localities, are not beta-quartz, since they formed at low temperatures. In addition, the difference in development between the faces of the two rhombohedra means that their morphology is frequently distinguishable by the naked eye.

### Djurleite and chalcocite

Digenite,  $\text{Cu}_9\text{S}_5$ , djurleite,  $\text{Cu}_{31}\text{S}_{16}$ , and chalcocite,  $\text{Cu}_2\text{S}$ , are the copper-rich members of a series of minerals with compositions ranging from  $\text{CuS}$  (covellite) to  $\text{Cu}_2\text{S}$  (chalcocite). The monoclinic chalcocite is unstable at high temperatures, becoming a hexagonal polymorph at 103° C. The upper limit of stability of djurleite is 96° C and digenite is not stable at room temperature, unless it contains small amounts of Fe (Pósfai and

Buseck, 1994). It has been suggested that since the compositional ranges of chalcocite and djurleite often overlap, that a transformation without chemical variation between one and the other would be possible merely by the effect of heat. The transformation occurs due to the electrochemical reactions caused by the flow of electrons within the crystal. Cu atoms move and rearrange themselves in a different pattern from the previous grouping. In this way the copper atoms change their position, not only creating the structures of alternatively djurleite and chalcocite, but even forming several variants of djurleite according to their atomic

orientation. As Evans (1979) said: “even nature has difficulties achieving a stable association between them”.

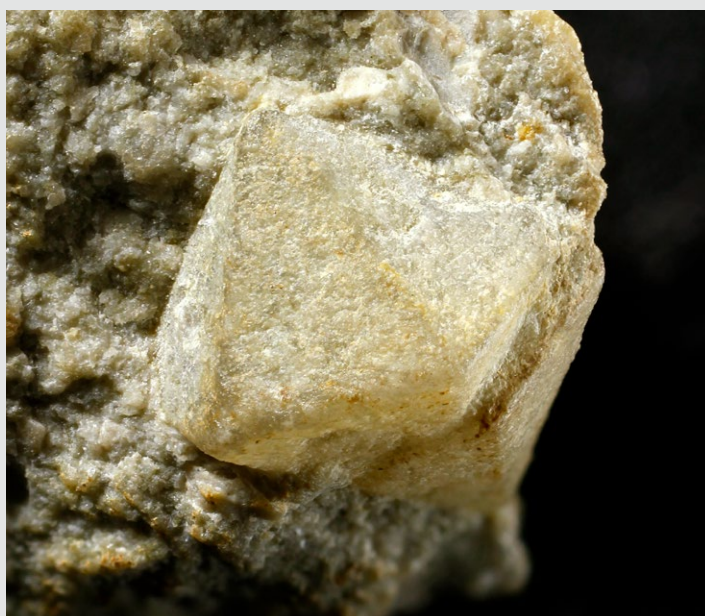
The most famous locality for this type of pseudomorph is the Dzhezkazgan mine, in Dzhezkazgan oblast, Kazakhstan.

This copper deposit was discovered in 1908 and worked since 1920, although there were no specimens from there in the western market until the 1990s. Dzhezkazgan djurleite crystals

are the best in the world, and have the characteristic of being morphologically indistinguishable from chalcocite, with both species appearing intermingled in a chemical intergrowth that does not affect the external form. They appear in the habit of elongated thin black crystals up to 4 cm in length (Moore, 2016).

### Kyanite pseudomorphs after andalusite

Two types of mineral transformations occur in the pseudomorphosis of andalusite to kyanite. One type of transformation consists of the formation of a mantle of muscovite around a nucleus of chialstolite-type andalusite that is later partially altered to fine-grained kyanite within a matrix particularly rich in quartz and biotite. The other type consists of biotite-andalusite altering to muscovite-kyanite within the matrix. These two types of mineral transformations involve similar reactions between the fluid and the local mineral paragenesis and they both progress simultaneously.



Quartz pseudomorph after beta quartz. Near Luesma, Zaragoza, Spain. 6 mm crystal. Miguel Calvo coll.

Each of the initial minerals acts as a source of ions and the intermediate mineral phases are consumed, so that a combination of individual reactions produce the transformation of andalusite to kyanite. This reaction is catalyzed by the muscovite and biotite in the matrix, whose dehydration provides the chemical driving force necessary to break the Si-O bonds (Sánchez-Navas, 2012).

The most characteristic specimens of this pseudomorph started to appear in 1986 in Altavista, Campbell County, Virginia, where pseudomorphed crystals were more common than unaltered andalusite. The crystals were completely embedded in matrix, elongated and sharp, with relict andalusite in the innermost part of the crystals. The kyanite here is colorless or pale blue. It also occurs on the Keivy plateau, Kola peninsula (Russia) in the form of dark blue or blue-green crystals, sometimes covered by massive white quartz (Moore, 2016).

In Spain, specimens of kyanite pseudomorphs after andalusite are very common in O Pino municipality, La Coruña, where alluvial

deposits of cobbles composed of pseudomorphic kyanite after andalusite have been commercially exploited. The mineralization is found in colluvium and alluvium from the Mera, Brandelos and Quintás rivers. Crystals of andalusite pseudomorphed in part to kyanite have also been found in Sierra Albarrana, Hornachuelos, Córdoba (Calvo, 2018).

### Graphite pseudomorphs after diamond

In some areas in the SW of the Serranía de Ronda peridotitic massif, in Málaga, Spain, and in the Beni Bousera massif, Morocco, pyroxenites with garnet are found in which pseudomorphs of diamond after graphite occur (Davies et al, 1993).

Identification as pseudomorphs was confirmed by finding unaltered relict diamond within the graphite as extremely small crystals, between 0.5 and 2 microns in size (El Atrassi *et al.*, 2011). The pseudo-crystals of graphite have an octahedral shape, with planes {0001} of graphite parallel to those that would correspond to the {111} octahedron faces in the original diamonds. They are found as individual crystals and as aggregates, and the maximum size found so far, around 1 cm

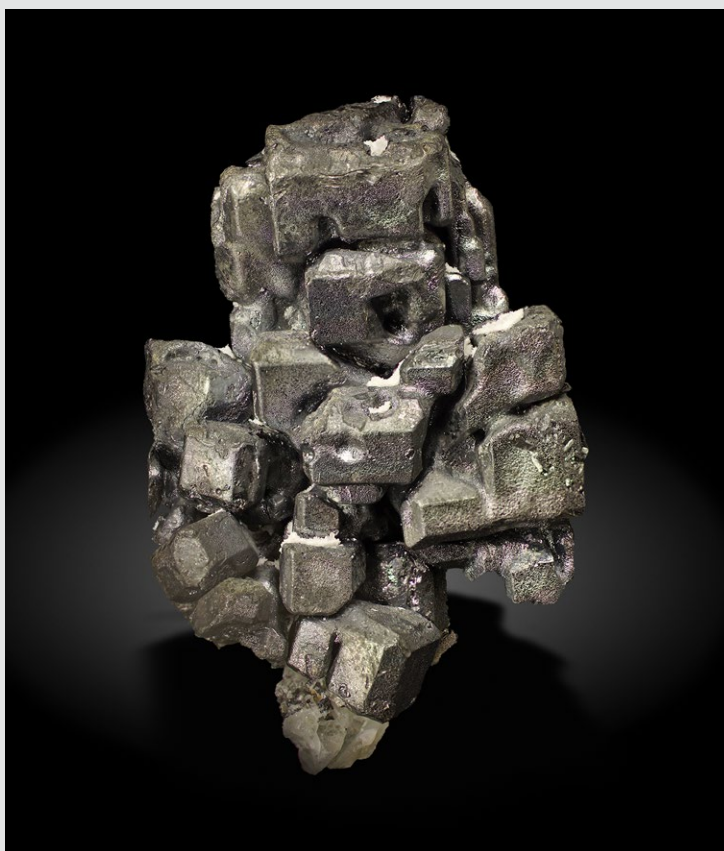
on edge, would correspond to a diamond octahedron of up to 8 carats, and the abundance of graphite implies a diamond content of up to 15% in the original rock (Davies, 1993). The existence of these pseudomorphs indicates an origin for the peridotites inside the mantle, at a depth of about 200 km (Medaris, 1999).

### Calcite pseudomorphs after aragonite

This pseudomorph should in principle be very common since, of these two dimorphic minerals, calcite is the one that is stable in external conditions. However, no example of this has been found

among the many dozens of Keuper aragonite deposits in Spain. In fact, the formation of the aragonite requires a series of special conditions, which occur precisely in this geological formation, and which contribute to stabilize the aragonite against later diagenetic phenomena (Jiménez Martínez *et al.*, 2005).

In geological environments other than the marls and gypsum of the Triassic these pseudomorphs have indeed been found. They are known in the sulfur deposits of Sicily, where they accompany the large sulphur crystals. The best specimens probably come from the Coszzodisi mine, in Casteltermini. They have also found in the Merehead quarry in England, and in the Tsumeb mine, Namibia.



Group of **acanthite** pseudomorphs after cubic crystals of **argentite**. 72 mm. Fresnillo de Gonzalez, Echeverrie, Fresnillo municipality, Zacatecas, Mexico. Bryan Lees, The Collector's Edge.

Well known pseudomorphs of tabular cyclic twins, individual or forming groups, a few centimeters in size, known among local collectors as “Indian coins”, appear in various places in the United States, such as Las Animas, Bent Co., and Owl Canyon, Larimer Co., both in Colorado, and in Buffalo Creek, Selman, Harper Co., Oklahoma, and in various locations in Texas. Another locality in which this pseudomorph appears is the Monolith quarry, in Albany Co., Wyoming. This last locality is characterized by the calcite appearing in compact form, and not as aggregates of crystals or easily visible crystalline grains as in the previous cases. At the Santa Isabel mine, in Almendricos, Lorca, Murcia (Spain), cyclic aragonite twins in hexagonal prismatic habit up to 4 cm in length, covered with calcite and partially or totally transformed into it have been found (Calvo, 2012).

### **Pseudomorphs with change in chemical composition**

In this case there is a modification of the composition, transforming the mineral into another species with a different chemical formula. In the simplest cases, the modification is produced by the action of surface agents, through oxidation processes or the incorporation or loss of water and/or carbonate, and progresses from the internal to the external zone. Pseudomorphs due to water loss are very frequent, especially among uranyl phosphates and arsenates, although this loss is usually reversible, at least in the early stages. The great majority of such specimens present in collections are dehydration products, for example the pseudomorphs of metatorbernite after torbernite. If the change in structure is greater, the hydrated mineral is only stable under very special conditions, and the water loss is not reversible, as in the case of pseudomorphs of calcite after ikaite. In other cases, the alteration processes are more complex, involving hydrothermal conditions or metamorphism of varying degrees.

### **Calcite pseudomorphs after ikaite**

Ikaite, calcium carbonate hexahydrate that crystallizes in the monoclinic system, only exists at temperatures lower than 4-7 °C, losing water and immediately turning into calcite if the temperature exceeds that figure. Its formation also requires special chemical conditions, mainly high concentrations of phosphate (Zhou *et al.*, 2015). The first specimens, used to describe the species, were found in 1962 in an underwater formation in Ika fjord, in the Ivigtut area, Greenland (Pauly, 1963). Subsequently, Suess *et al.* (1982) found well-crystallized specimens in Antarctica, which lead to the realization that the morphology of the mineral corresponded to the pseudomorphs of calcite after

an unknown mineral that had been found in diverse localities, in formations of all geological ages from Permian to Quaternary. These pseudomorphs had been called “glendonites”, “thinolites”, and “chrysanthemum stones”, among many other names, and their original mineral had been hypothesised to be glauberite, thenardite, gaylussite, aragonite, celestine, anhydrite, or many others (Selleck *et al.*, 2007).

These pseudomorphs had been described for the first time by Freiesleben (1827), from specimens coming from Sangerhausen, Thuringia (Germany), who considered them pseudomorphs of calcite after gaylussite, for which reason he called them “pseudogaylussite”. Later Dana used the name “glendonite”, derived from Glendon, a farm in Hunter Valley, New South Wales, Australia, specimens of which were given to him on his trip to this continent in 1840 (Selleck *et al.*, 2007). The so-called “thinolites”, found in Quaternary tuffs in the Mono and Lahontan lakes basins in the United States, are also pseudomorphs of the same type (Council and Bennet, 1993). The transformation of ikaite into “glendonite” involves a very important decrease in volume, so the pseudomorphs are at first spongy and very fragile. If a new generation of calcite is deposited in the pores then the morphology of the pseudomorphs is very well conserved, and they can be extracted from the enclosing rock. The pseudo-crystals are usually centimetric in size, but some have been found even in decimeter sizes. The most characteristic specimens are the individual pseudocrystals or divergent crystal “pineapples”, common in collections and museums, coming from Neogene sediments near the mouth of the Olenitsa River, White Sea coast, Murmansk, Russia. They are also found in Permian terrain in the Sydney basin, Australia (Selleck *et al.*, 2007) and in the Lower Cretaceous in the Eromanga basin, also in Australia (Sheard, 1990).

### **Iron oxide pseudomorphs after pyrite or marcasite**

Oxidation of metal sulphides is a complex process, which includes several types of reactions (oxidation-reduction, hydrolysis, formation of ionic complexes, solution-precipitation, etc.). In the case of iron sulphide, some oxidized form of iron is produced, together with sulphate anions and a lot of acid, 2 moles of acid per mole of pyrite. One type of pseudomorph known for a long time are the ones formed of iron oxides (goethite mainly) produced by alteration of pyrite crystals. These pseudomorphs, which may be total or still maintain relict sulphides in the center of the crystals, are common in superficial zones of deposits in which pyrite is found in relatively porous rocks, such as marls and sandstones.

Due to the complexity of the process it is not known with certainty which reaction predominates at a given pH, what the intermediate products are, and how they vary over time.

Pseudomorphs of goethite after pyrite are extraordinarily common. Recently spectacular specimens have been found in Gachala, Cundinamarca department (Colombia), formed by two crystals twinned according to the so called “iron cross” law, up to 10 centimeters in size. In the case of Spain, the specimens found in Montjuic, especially on the SE slopes, in the city of Barcelona, have appeared in the mineralogical literature since the beginning of the 20th century (Calderón, 1910). But the most spectacular finds in Spain so far are those that occur in Llanos de los Arenalejos, about 2 km north of Carratraca. The original cubic crystals of pyrite reach 3 cm, or occasionally somewhat more, and form large groups which can exceed 20 cm in size (Calvo, 2009). In the Cameros basin, between the provinces of La Rioja and Soria, one can also find limonitized pyrite specimens in those deposits that have been exposed by erosion. Although less common, pseudomorphs of goethite after marcasite crystal clusters have been found too. In the Candesa quarry, in Camargo, Cantabria, they appear in the form of rosettes of up to 1 cm, formed of sharp crystals.

#### **Malachite pseudomorphs after azurite**

Malachite is more stable under atmospheric conditions than azurite and for this reason malachite is much

more common than azurite. The malachite-azurite transition is very sensitive to small chemical changes in the environment: equilibrium is reached with partial pressures of CO<sub>2</sub> near normal values, while precipitation of both minerals from solutions containing cupric ions takes place at pH values between 6 and 8, depending on the partial pressure of CO<sub>2</sub>.

Azurite is formed only under relatively acidic conditions and with high bicarbonate ion activity. Since high activity of bicarbonate ions usually implies basic conditions, this explains why malachite is the more common form of copper carbonate in nature, whereas azurite is formed under quite unusual conditions. It also explains the transformation of azurite to malachite due to small changes in bicarbonate activity and therefore the pseudomorphs of malachite replacing azurite (Vinck, 1986).

Specimens of malachite pseudomorphing azurite have appeared at many localities, but the most striking are those from Milpillas in Mexico, those from Tsumeb in Namibia, and those from Morocco, a consequence of the quality and size of the azurite crystals at whose expense they originated. The Milpillas mine exploits a supergene chalcocite vein with large areas in which oxidized minerals appear, especially azurite, malachite and plancheite in cavities filled with clay. The mine began to be exploited in 2006 and, at the 2007 Denver fair, high-quality azurite specimens with an electric blue color, and malachite pseudomorphs after azurite, also of high quality and significant sizes, began to appear for sale.

**Malachite** pseudomorph after disphenoidal **chalcopyrite** crystal. Crystal edge 10 mm. Azcárate pit, Eugi, Esteribar, Navarra, Spain. Miguel Calvo coll.



**Limonite** pseudomorph after **pyrite** crystal. 35 mm. Anlaufstal, Ankogel, Pongau, Salzburg, Austria. Rudolf Watzl, Saphira. Photos J. Callén.



The following year a pocket containing dozens of crystallized samples of azurite and malachite pseudomorphs up to 2.5 cm was found, forming 18 cm groups. At present, spectacular specimens of this pseudomorph continue to appear, with the altered crystals reaching maximum sizes of up to 5 cm (Moore, 2016). The Tsumeb mine yielded specimens of pseudomorphic malachite after azurite and also of other minerals in the superficial oxide zones, especially in the areas mined in the 1920s and 30s. A characteristic of the pseudomorphs from here is that the alteration usually begins at one point on the crystal, extending along it radially (Pinch and Wilson, 1977). Until the closure of the mine in 1996, huge pseudomorphed crystals appeared, up to 20 cm in length (Moore, 2016).

In Morocco, malachite pseudomorphs after azurite crystals have appeared in several localities. The locality of Kerrouchen, near Khenifra, in which azurite specimens had been found occasionally in surface excavations carried out for the extraction of fossils in the early 1970s, is especially worthy of mention. Then from 2003 to 2010 interesting specimens of malachite after azurite appeared in the form of rosette-shaped clusters of dark green color up to 3 cm. They also occur in the Touissit-Bou Becker mines, which have been commercially active since 1907, but which only became famous in 1979 for crystallized azurite specimens of good size and color. In these mines, malachite totally or partially replaces azurite, in crystals of up to 7 cm, implanted in a limonite matrix (Moore, 2016).

In Spain they are found in many localities. Among the best specimens are those from the Milagro mine in Onís, Asturias, which can reach sizes of up to 15 mm and appear as groups. They are also found in the Sol mine, in Cerro de los Guardias, Rodalquilar, Níjar, Almería, and in the La Estrella mine, in Pardos, Guadalajara (Calvo, 2012).

### Malachite pseudomorphs after cuprite

Cuprite is unstable in the presence of carbonate, so that the transformation into malachite occurs readily, giving rise to a more or less thick crust (partial pseudomorphs) or to complete substitution (total pseudomorphs).

The specimens from the Chessy mine in Rhone department (France) have been known for a long time, probably since the beginning of the 19th century. According to Lacroix (1901), during the time of exploitation of this mine, in the first half of the nineteenth century, these pseudomorphs were very abundant, being scattered in a clayey material, loose or associated with azurite crystals, in sizes from a millimeter to about 3 cm.

The crystals from this locality usually have faces with cavities or exhibit skeletal habit, with hopper growths, and generally they conserve relicts of cuprite in their interior.

The specimen in the Museum of the School of Mines of Paris, 4 cm on edge, and found just before 1910, was for a long time (until the appearance of the specimens from Onganja, Namibia) the greatest crystal known of cuprite. It was donated to the museum by Colonel Vésignié, who had acquired it in 1917 for 500 francs (Poullén, 1984), which in those days was around the average salary of a month and a half for a worker. The most spectacular specimens of cuprite transformed into malachite are those that come from the Onganja mine, in Seeis (Namibia) and that began to appear in 1973. The layer of malachite has a thickness of around 1 mm, and it covers crystals of cuprite that can reach a size of 7 cm (White, 1974). This brings up the discussion of whether it is properly a pseudomorph or if it should be considered just a superficial alteration. In some cases, the malachite has been removed by chemical treatment, leaving the crystals of the cuprite still sharp but with a rough surface.

In Spain there are several localities in which cuprite crystals transformed into malachite have also been found, but without reaching the sizes described above. The best ones, which very rarely reach sizes greater than 5 mm, appeared at the end of the 1970s during mining of the San Valentín open pit, Cartagena, Murcia, on cutting through ancient, possibly Roman, workings belonging to the San Juan Bautista concession. The pseudomorphs are associated with azurite crystals that have generally not been altered. Millimeter-sized pseudomorphs also occur in the El Valle-Boinás mine, in Begega, Belmonte de Miranda, Asturias (Calvo, 2012).

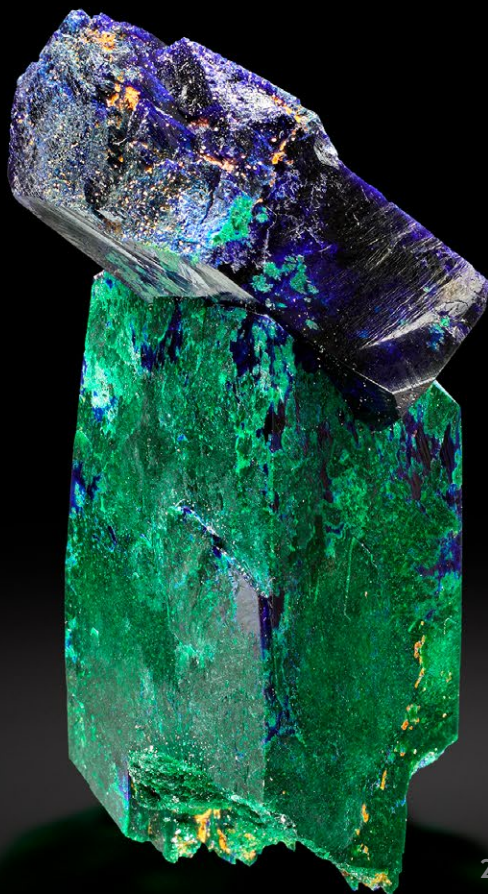
### Gypsum pseudomorphs after glauberite

The transformation of gypsum into glauberite represents an interesting case of pseudomorphism, since it is quite common in Spain, and also because the first specimens of gypsum pseudomorphs after glauberite from the Tertiary basin of Madrid gave rise to a scientific controversy about what the original mineral was.

- 1.- **Malachite** pseudomorph after **azurite**. 95 mm. Tsumeb, Namibia. Anton Watzl.
- 2.- **Malachite** pseudomorph after **azurite**. 4cm. Kerrouchen, Khenifra, Morocco.
- 3.- **Malachite** pseudomorph after **azurite**. 7 cm. Tsumeb, Namibia. Kristalle.
- 4.- **Malachite** pseudomorph after **azurite**. 7 cm. Milpillas mine, level 1140, Cuitaca, Santa Cruz, Sonora, Mexico. [fabreminerals.com](http://fabreminerals.com)  
Joaquim Callén photos.



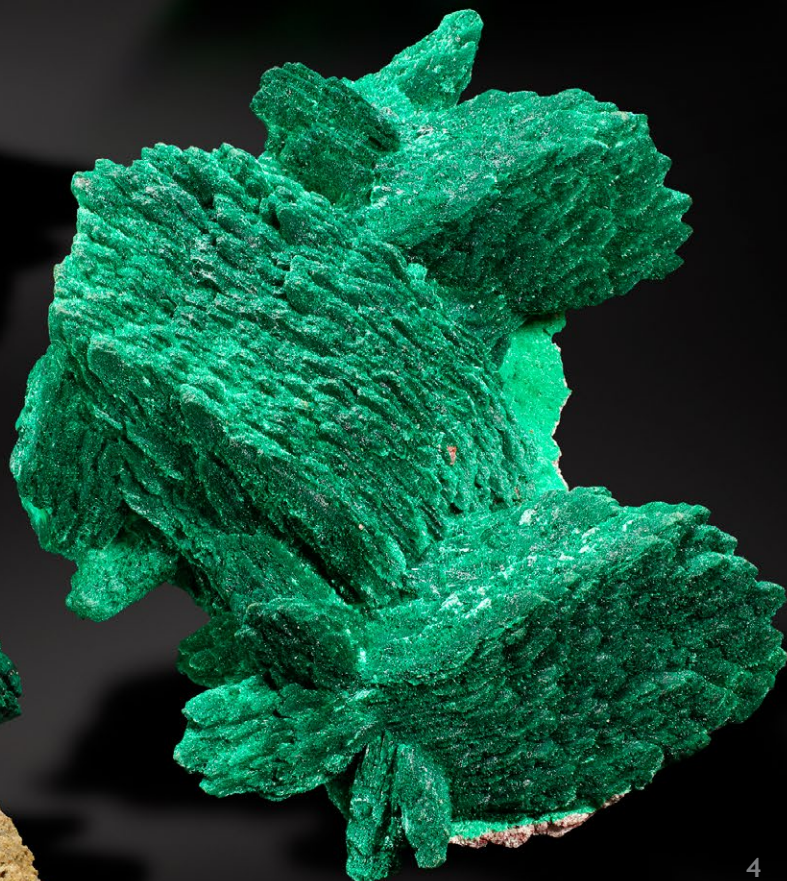
1



2



3



4

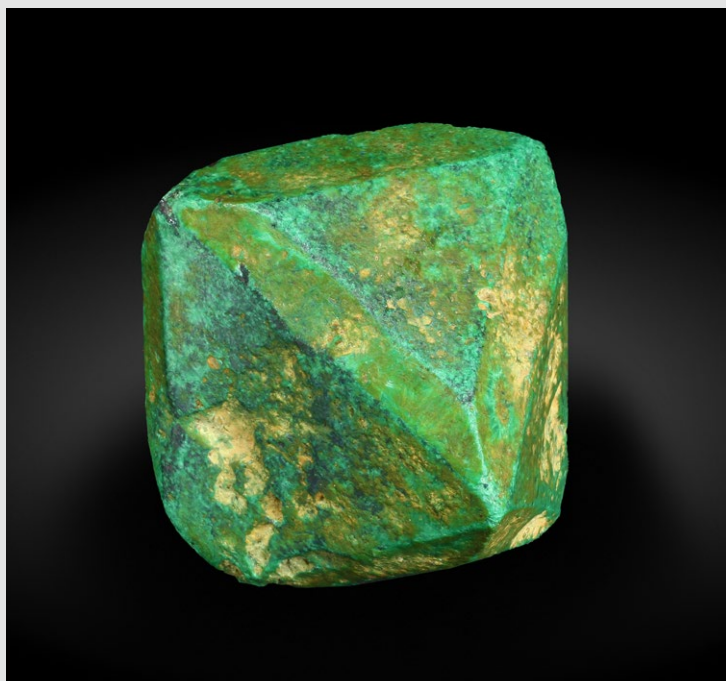
The first example of this type, a piece of gypsum in the shape of a rough rhombohedron, about 7 centimeters in size, was found by Quiroga (1890) in the Manzanares Canal, who supposed it was a pseudomorph after calcite. When Hernández Pacheco y Royo (1916) studied the quarries of the SW slope of Cerro de los Ángeles, in Getafe, they found similar specimens, indicating in their description that, although internally they were composed of irregular aggregates of gypsum lamellae, they indeed comprised authentic crystals, of a morphology different from usual, in which the crystals, monoclinic, would be formed by the prism faces  $\{110\}$  combined with  $\{001\}$  and with some small hemipyramid faces  $\{111\}$ . The easy availability of specimens meant that other mineralogists could study them and discuss their nature. Pardillo (1917) reiterated the hypothesis of calcite pseudomorphs, which was rebutted by Hernández Pacheco y Royo (1917) based on the absence of calcite crystals in this type of terrain and in the crystallographic differences. Pardillo (1918) insisted on the hypothesis of calcite pseudomorphism, considering that the “pseudo-crystals” were formed by the combination of the less developed  $\{021\}$  and  $\{110\}$  rhombohedra and with only part of their faces. Finally, Fernández Navarro (1919) determined that they were pseudomorphs after glauberite crystals, formed by the prism  $\{110\}$ , the pinacoid  $\{001\}$  and in some specimens the hemipyramid  $\{111\}$ .

This type of pseudomorph is quite frequent in the Tertiary evaporite basins. The largest pseudo-crystals, up to 30 centimeters long, were found during construction of the M-50, between Getafe and Pinto, within the municipal boundaries of Getafe, Madrid. There are also notable examples of these pseudomorphs on the walls of the Torcal de Valdemayor, a doline located SW of San Juan lagoon, about 8 km west of Chinchón. In the El Consuelo mine, in Chinchón, there is a one meter thick layer, above the exploited glauberite bed, in which this mineral has been transformed into gypsum (Ordóñez *et al.*, 1982). They also appear in the slope on the right hand side of Valdehorna arroyo, 5 km NW of Chinchón (Calvo, 2014). In some outcrops of the Miocene age Zaragoza Formation, in the vicinity of the city of that name, there are gypsum pseudomorphs after glauberite as aggregates of centimetric crystals in which the morphology of the original mineral is conserved very well. Notable specimens appear in Salinas ravine, in the municipality of Remolinos, and in the Camino de la Plana, in Valmadrid municipality (Calvo, 2014).

#### Calcite pseudomorphs after gypsum

On the other hand, gypsum can give rise to pseudomorphs too, mainly by its transformation into calcite, which happens by chemical reaction with surface water loaded with  $\text{CO}_2$ .

**Malachite** pseudomorph after **cuprite**. 2 cm. Chessy, France. C. Gonzalez coll. Joaquim Callen photos.



Right hand page:

**Malachite** pseudomorph after **cuprite**. 10 cm. Onganja, Namibia. Ricardo Prato.

**Gypsum** pseudomorph after **glauberite**. 11 cm. Road to the Invencible mine, Remolinos, Zaragoza, Spain. Miguel Calvo coll.





The most spectacular calcite pseudomorphs are those that appear on the slopes of Pico de Uris, next to the road from Villabáñez to Renedo de Esgueva, with the characteristic shape of gypsum roses, with the pseudo-crystals being hollow inside. The interior cavities formed because of the reduction in volume that gypsum undergoes when it is transformed into calcite (Calvo, 2012).

### Hematite pseudomorphs after magnetite

The transformation of magnetite into hematite is called “martitization”, with “martite” being the mineral variety formed by this transformation. The reverse transformation, from hematite to magnetite, can also occur, although it is much less frequent, and is known as “mushketovitzation”. The transformation of magnetite to hematite can be expressed in terms of a redox (oxidation-reduction) reaction in equilibrium, producing the oxidation of magnetite to hematite by oxygen. However, other authors have indicated that the availability of reductants and oxidants is too low to explain the large-scale conversion of magnetite to hematite through fluid-rock interactions in some giant mineral deposits, so some other mechanism must be involved. Ohmoto (2003) proposed that the transformation of Fe oxides in near-surface environments occurred mostly through non-redox reactions. In this model hematite is formed simply by the removal of  $\text{Fe}^{2+}$  from magnetite, so that no Fe oxidation reaction need be involved. Recent studies suggest that the replacement reaction depends on several factors, including reaction temperature, time, and chemistry of the solution that are specifically related to the solubility of  $\text{Fe}^{2+}$ .

The addition of oxygen to the system causes the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  only on the surface, resulting in hematite growth on the outside of the mineral. The replacement of magnetite by hematite is a rapid process at moderate temperatures (200° C) but is still fast in geological terms even at low temperatures (Zhao *et al.*, 2019).

Among the localities in which this type of pseudomorph occurs, the one that has probably provided the most good quality specimens in recent times is Payún Matru volcano, Malargüe, Mendoza province, (Argentina). The specimens are found in volcanic ash and are elongated, in the form

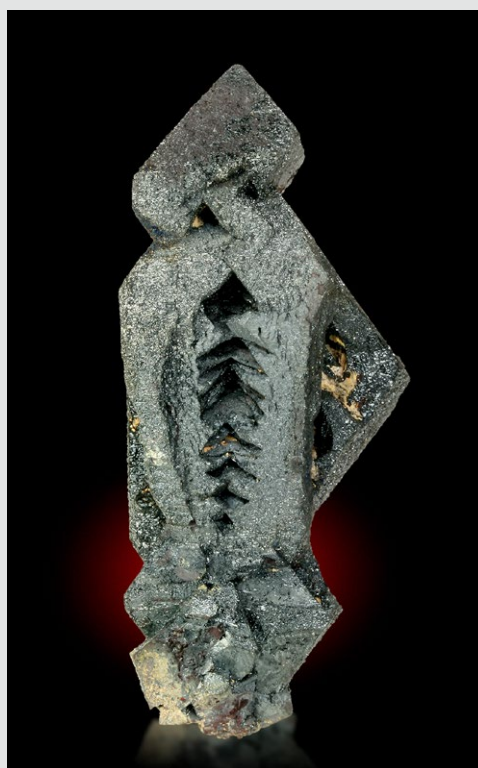
of a skeletal hopper crystals, with predominance of the octahedron face. They measure several centimeters in length and have a very intense metallic black luster on some faces, although on other faces they have a granulose aspect and a light brown color. The first specimens were found around 1990 (Robinson and King, 1991), although good quality specimens did not become common until the early 2000s. Octahedra up to 5 centimeters across have been found, within groups of crystals up to 30 centimeters. But the exact volcanic cone where they were extracted has still not been revealed (Moore, 2016).

### Smithsonite pseudomorphs after calcite

Another type of pseudomorph from a Spanish locality described in old scientific literature is smithsonite

pseudomorphs after calcite. Blum (1863) reported the presence of “Zinkspat pseudo Kalkspat” in Torre la Vega, Santander, which probably refers to the Reocín deposit, which at that time was being worked on a large scale in its upper zones, where carbonates predominate. Also Arce (1880) mentions these pseudomorphs, coming according to him from the Picos de Europa, and stating that samples were sent to the School of Mines in Madrid. Calderón (1910) also indicates the occurrence of smithsonite pseudomorphs after scalenohedral calcite crystals, in this case “around Puente Viesgo”.

In modern times, these pseudomorphs have come from the Pozobal mine, located in the area of the same name, 2.7 km SW of Cabanzón, in Herrerías municipality, near the border with Asturias. This mine is accessible by road from Casamaría. Partially



**Hematite pseudomorph after magnetite**, 7 cm. Payún volcano, Altiplano de Payún Matru, Mendoza, Argentina. Zona Minera.

accessible underground workings remain.

Pseudomorphs after groups of scalenohedral calcite crystals have a finely botryoidal surface, and are partially hollow, filled with scoriaceous smithsonite and clay. They are cream or very pale brown, and specimens whose original calcite crystals reached 5 centimeters have been observed.

This type of pseudomorph also appeared in the San Antonio mine, in Santa Eulalia, Chihuahua (Mexico). In the year 2000, good specimens were found on level 8 of the mine, with a cream to bone-white color, sometimes

yellowish or orange, which in some cases were just epimorphs, with a surface coating, but in many others had replaced the initial calcite crystal completely. Sometimes the individual crystals reached 10 cm, forming crystal crusts up to 30 cm, on a matrix of iron oxides. In 2013 lots of these pseudomorphs appeared again with the calcite completely replaced. In this case, the color was rather yellowish green with a satiny luster, and formed flattened groups of scalenohedral crystals with the initial calcite shape but of a smaller size (up to 2 cm) (Moore, 2016).

### Plumbogummite pseudomorphs after pyromorphite

Pseudomorphs of plumbogummite replacing pyromorphite seem to be quite common, and they have been known since the 19th century. Miers (1900) describes them from Roughten Gill, in Caldbeck, Cumberland (Great Britain) and Huelgoat, in Brittany (France). In Spain these pseudomorphs have been found in the El Horcajo mines, in Monte Bedures, Vegadeo, Asturias, and in the Antonina mine, in Sobrado, León (Calvo, 2015). Practically all are hollow, so we can not be certain whether they are true pseudomorphs or rather epimorphs.

Nevertheless, specimens of this type of pseudomorph did not attract much attention until the appearance in 2005 of plumbogummite pseudomorphs supposedly after mimetite, from the Daoping mining area in China. In 2014, at the Denver show, spectacular specimens of plumbogummite came on the market, in which this mineral formed thin blue-gray layers over pyromorphite, as partial replacements or even complete pseudomorphs

**Cerussite pseudomorph after anglesite on goethite.** Cavernous pseudocrystal in whose interior one can see the typical cyclic cerussite twins. San Valentín open pit, La Unión. Murcia, Spain. Pseudocrystal 11 mm. Miguel Calvo coll.



that conserved the original crystal shape. In 2015, several large specimens with good crystallization appeared again at the Tucson show. The location was initially not revealed in detail although it was known to be close to the Yangshuo - Daoping mining area (famous for its pyromorphite crystals) in Guilin prefecture, China. The Daoping deposit is a hydrothermal lead-zinc deposit in an area with fractures and faults in a north-northwest direction, appearing only in very specific areas of the large secondary pyromorphite deposit (Liu, 2005).

### Talc pseudomorphs after dolomite

The talc deposits of Puebla de Lillo, León, were formed during the Mesozoic, by hydrothermal metasomatism that transformed into talc the dolomites that had previously been formed at the expense of Carboniferous limestones. In some spots there were large rhombohedral dolomite crystals, which were altered to talc, maintaining the morphology very well, even the facial growth details. These crystals were found in workings mined around 1995, and they reach sizes up to 8 cm on edge (Calvo, 2018).

The transformation of dolomite or magnesite into talc is precisely the way in which most deposits of this latter mineral originate, and which in many cases retain characteristics of the original material, such as traces of cleavage planes. But the presence of well-formed crystals is rare. In addition to the Spanish locality, there is one known in Germany since the 19th century, the Johannes mine, in Göpfersgrün, Wunsiedel, Fichtelgebirge, Bavaria, and another in the United States, the Cadillac mine, in Ennis, Madison Co, Montana. In the latter two, specimens of talc pseudomorphs after quartz are found too, which have not been found in Puebla de Lillo, at least not with sufficient definition.



**Calcite** pseudomorph after **gypsum**. 11 cm. Road to Villaváñez, Renedo de Esgueva, Valladolid, Spain. Miguel Calvo coll. J. Callen photos.

### Galena pseudomorphs after pyromorphite

Specimens of galena pseudomorphs after pyromorphite are among the European classics, highly valued for their rarity. The most important and well-known locality is the Kautenbach mine, Rhineland-Palatinate (Germany). Significant specimens are also known from four other localities, the Dreifaltigkeits mine in Saxony (Germany), which seems to have been the first locality known for these pseudos, the Himmelsfürst mine, also in Saxony, the Huelgoat mine in Brittany (France), and the Wheal Hope mine in Cornwall (England) (Keim and Markl, 2017). These rare pseudomorphs became famous in the period 1790-1820

for their frequent appearance in the Wheal Hope lead mine in Perranzabuloe, Cornwall (England), as short, slightly rough prisms of dark gray color. In 1993 some more specimens seemed to have turned up in the dumps, but in this case some of the original crystals remained unaltered, and it was discovered that instead of pyromorphite the initial mineral was mimetite. This suggested that at least in this case the pseudomorphs initially described as galena pseudomorphs after pyromorphite were actually galena pseudomorphs after mimetite (Moore, 2016).

Since the volume occupied by galena is less than that corresponding to pyromorphite, if all the lead came from the pyromorphite, these pseudomorphs would have a spongy internal texture. This is indeed the case, except for those from Huelgoat, which are massive, suggesting an extra supply of lead, which greatly complicates their mechanism of formation, given that due to the insolubility of the galena, sulphur and lead can not be transported by the same fluid, so probably the galena was deposited within a plumbogummite paramorph on pyromorphite (Keim and Markl, 2017).

### Demantoid garnet pseudomorphs after fossils

In the vicinity of the village of Antetetzambato, in the north of Madagascar, there is a deposit of artisanally

exploited andradite garnet of the demantoid variety, both for use as a gem and for collectors. The garnet was formed by metasomatic alteration of fossiliferous sandstones due to lamprophyre intrusions, which gave rise to fine grained skarn veins, with cavities with crystals. The fossils that are occasionally present, corals and molluscs, have also been replaced by skarn minerals (Pezzotta *et al.*, 2011).

### Amphibole pseudomorphs after pyroxene

The replacement of primary pyroxenes by

amphiboles, generally of the actinolite series, is called “uralitization”. Since pyroxenes are anhydrous minerals, while amphiboles are hydrated, the presence of water is necessary, which can come from external fluids or be contributed by minerals from the original rock, such as chlorites (Fagan *et al.*, 1997). Notable specimens of such “uralite” pseudomorphs appeared from 1967 onwards from skarns on Prince of Wales island, Alaska.



**Talc pseudomorph after dolomite.** Puebla de Lillo, León, Spain. M. Calvo coll.

The prisms of uralite resemble the texture of wood, forming groups that included crystals up to 5 cm size. Good specimens also occurred at the Calumet mine, Turret district, Chaffee county, Colorado, where iron ore was mined until 1900, but which since 1960 has provided good epidote and diopside crystals in addition to these interesting pseudomorphs. Spain has yielded some important specimens in the mines on the Burguillos del Cerro skarn (Monchi mine, Milucha mine) in Badajoz, whose wooden appearing “uralite” pseudomorphs form groups of several centimeters.

They also appear in the Aguablanca mine in Monesterio, Badajoz, worked for nickel from 2004, in which pseudo-crystals of gray green “uralite” with internal fibrous structure can reach 5 cm high by 2 cm wide (Calvo, 2018).

### Mica pseudomorphs after andalusite

When andalusite occurs in pegmatites it usually gets replaced by micas due to the late pegmatitic fluids. The aluminum-rich minerals of pegmatites are particularly easy to transform into muscovite. The muscovitization of andalusite is also frequent in metamorphic environments. This muscovitization of the polymorphs of  $\text{Al}_2\text{SiO}_5$  increases in the sequence: kyanite, andalusite, sillimanite (Ahn, 1988). Muscovite pseudomorphs replace andalusite at Small Point, Phippsburg, Sagadahoc Co., Idaho, as well-formed pseudocrystals

measuring up to 3 cm and which are also associated with unaltered andalusite, with staurolite, biotite, quartz and cordierite, as a consequence of late metamorphism. They also appear in Quartz Creek, King County, Washington, in the form of the muscovite variety called “sericite”, as twinned prismatic pseudocrystals with a bronze color, up to 2 cm size (Moore, 2016).

Andalusite crystals of the “chiastolite” variety present in many slates are actually in many cases mixtures of phyllosilicates rather than true andalusite.

Those found in the slates of the metamorphic aureole of the Boal pluton, Asturias, are transformed in part or totally into a mixture of muscovite and margarite. The degree of alteration can be visually roughly judged in thin sections, by the pink color and crystalline aspect of the relict andalusite (Lozano *et al.*, 2011; Jiménez Martínez, 2015).

### Chlorite and mica pseudomorphs after cordierite

Pseudomorphs composed of phyllosilicates (micas, chlorites, and clay minerals, mainly) after other silicates, especially cordierite but probably also others of prismatic habit, such as schorl tourmaline, attracted attention from the beginning of scientific mineralogy,

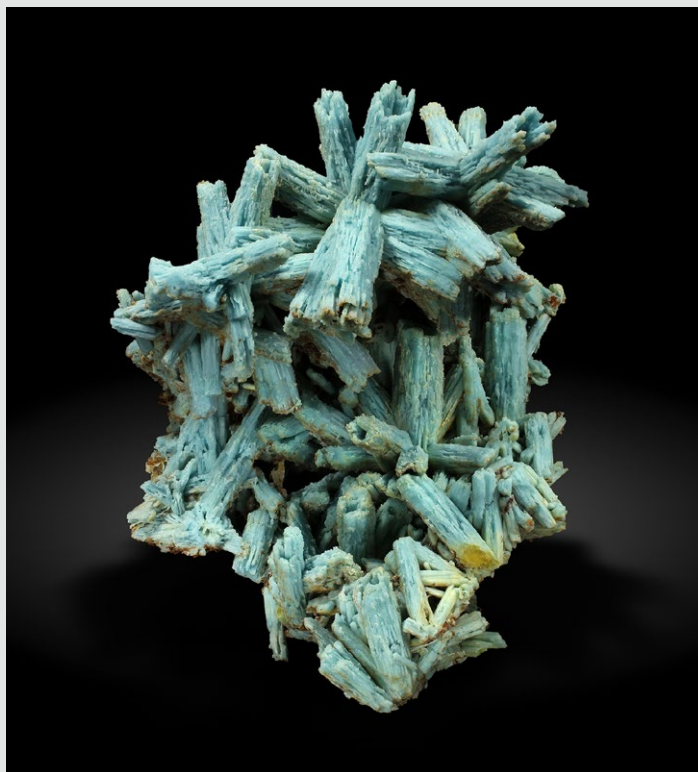
but their heterogeneity caused them to receive different names according to their place of origin and the researcher who studied them. So we ended up with a cacophony of names like gigantolite, cataspilite, pinite, dysintribite, gongylite, hygrophyllite, iberite, oncosine, oösite, parofite, and polyargite.

In the 1840s, Jacobo María de Parga y Puga, a prominent politician and amateur mineral collector, provided Carl Gustaf Mosander, a Swedish chemist and mineralogist, with samples of material from San Martín de Montalbán, Toledo (Spain), which was studied by

Mosander himself and analyzed by Norlin. As it was considered a new mineral, they proposed naming it “iberite” (Svanberg, 1844). The differences between this and “gigantolite”, another previously supposed mineral, were simply morphological, although both are pseudomorphs after cordierite.

Later, Blum (1847) also described the specimens from San Martín de Montalbán, identifying them as “chlorophyllite” pseudomorphs after cordierite. He considered “chlorophyllite” to be an independent mineral species, with its own chemical formula. Later, in the fourth appendix of

his work on pseudomorphs (Blum, 1879) he used the name “iberite”. It has also been found at other localities. Fernández Navarro (1905) reported the existence of “iberite” in the La Torera mine, next to San Rafael, Segovia, and Calderón (1910) reported it in the Puerto de la Fuenfría, also in the province of Segovia. In recent times specimens of chlorites and micas have been found pseudomorphizing cordierite crystals in the altered granite exposed along the road to Fitor, 1.2 km to the W of the exit loop to Palafrugell on the motorway from Palamós, in the municipal limits of Mont-ras. These pseudo-crystals are up to 2.5 centimeters long and 1 centimeter thick, dark brown in color, with a fairly sharp prismatic morphology (Calvo, 2018).



**Plumbogummite** pseudomorph after **pyromorphite**, 17 cm.  
Yangshuo mine, Guangxi, Zhuang autonomous region, China.  
Bryan Lees, The Collector's Edge.

### Achтарagdite

Achтарagdite is the name given to grayish pseudo-crystals with complex morphology but belonging to the cubic system, which can reach sizes up to 15 cm, but usually between 2 and 4 cm, which come from the mouth of the Achтарagda river, in the Vilyui river basin, in Yakutia, Siberia. Its internal structure has been studied in detail, revealing that it is formed by concentric growths of hydrogrossular with an external zone of hydroandradite, forming a porous matrix in which other minerals are deposited too (Galuskin and Galuskina, 2002). The original mineral was probably wadalite, comprising part of rodingites that have undergone alteration, maintaining its form in the pseudomorphed crystals (Galuskina et al, 1998).

### Rutile pseudomorphs after ilmenite

Some rutile aggregates, classically considered “elbow twins”, are instead topotaxial replacements (transformation of one crystalline substance into another in which the orientation of the lattice is maintained) of ilmenite or other hexagonal titaniferous precursors. True twinned rutile can be distinguished from pseudomorphilic ilmenite rutile by the angle of the prism intersections, the morphology of the join and the general shape of the aggregate.

Rutile is more commonly epitaxial (association of two minerals between which there exists a structural

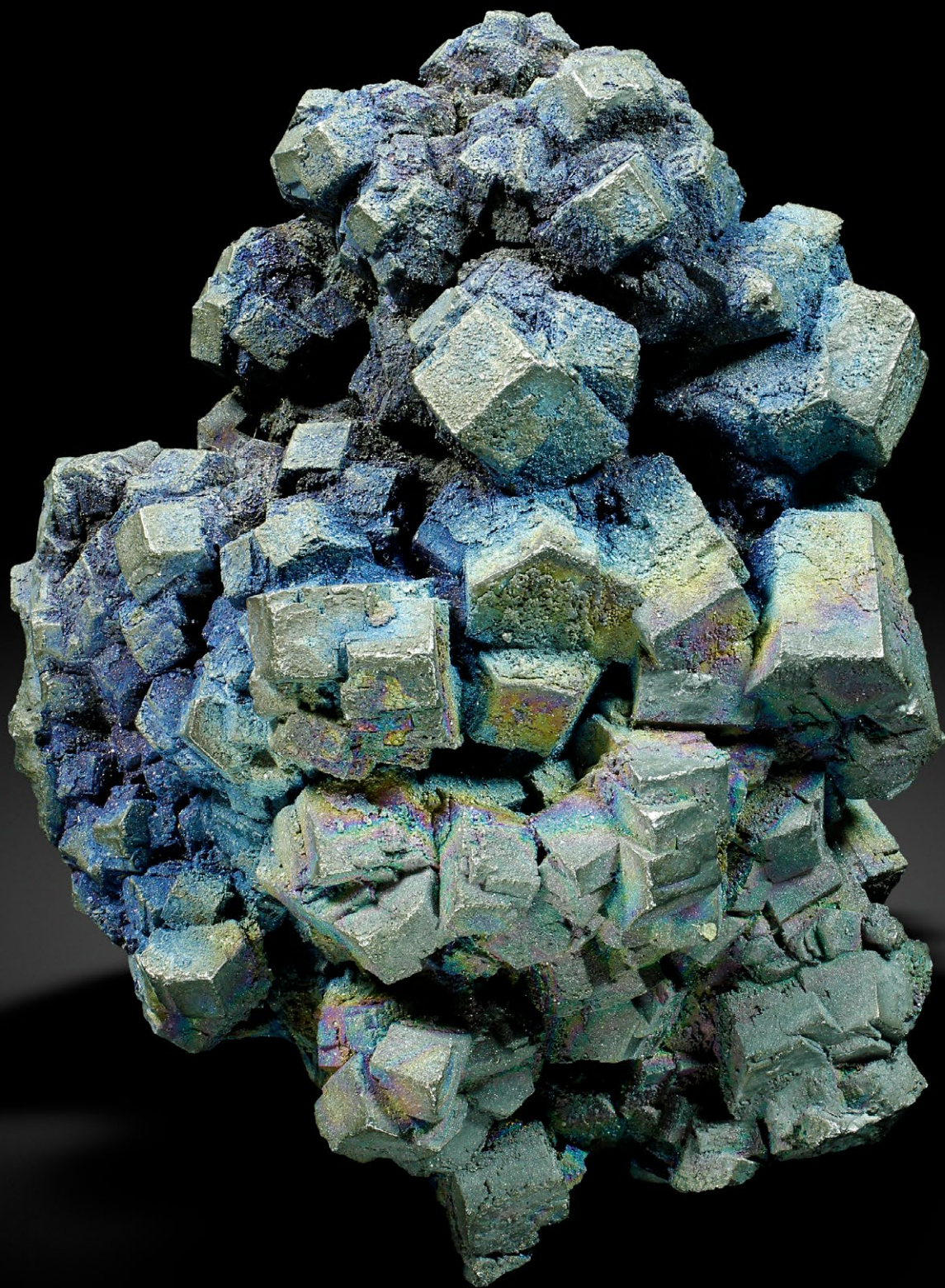
compatibility by which the crystals of one are developed on the other in certain spatial directions) on ilmenite that sometimes has been pseudomorphed into hematite (Armbruster 1981) or less frequently topotaxial after ilmenite in altered rocks. Such growth is governed by the spacing and arrangement of the oxygen atoms. The rhombohedral symmetry of the ilmenite (whether altered or not into hematite) results in the association of rutile prisms that are arranged on the basal plane of the ilmenite with which they join at an angle of 60° or 120° to form equilateral triangles (Force *et al.*, 1996).

The best specimens of rutile/hematite pseudomorphs after ilmenite come from North-western province, in Zambia. Starting in the second half of 2007 we began to see samples of these pseudomorphs from some site that remains unknown, although located near the city of Mwinilunga and very close to the Zambian border with Congo and Angola. They are loose black crystals, of submetallic luster, with irregular edges and flattened habit that initially were ilmenite and that now are a mixture of rutile and hematite with fine granular masses of hematite occupying the voids in the sagenitic networks of rutile crystals that replaced the interiors of the ilmenite plates. The large basal faces are partially covered by the youngest generation of epitaxial rutile. These curious crystals measure between 1 and 8 cm and were on the market especially in 2007 and 2008.

Demantoid **garnet** pseudomorphing fossils; on the left a gastropod (17 mm), and on the right a coral (55 mm). Antetazambato mine, Madagascar. Julien Raoul coll.

Right hand page: **Galena** pseudomorph after **pyromorphite**. 55 mm. Kautenbach mine, Traben-Trarbach, Hunsrück, Rhineland-Palatinate, Germany. Ian and Diana Bruce, Crystal Classics.





### **Pseudomorphs formed by infiltration and filling**

When a chemical change can not be explained logically, it must be assumed that it is likely to have been processes of infiltration, filling of preexisting cavities, or displacement by dissolution of the previous mineral while the new one is forming.

### **Gypsum pseudomorphs after halite**

The solubility of halite enables it to easily form crystals, often with hopper growths depending on conditions, and these can just as easily disappear again, leaving voids that can be filled by any other mineral, even by clays. Pseudomorphs of gypsum after halite are common in the Glass Mountains, Major county, Oklahoma, as cubes up to 5 cm in size. The initial crystals of halite exhibited cubic shapes with deep hopper on their faces and the pseudomorphs faithfully replicate this shape, or have the shape of a stepped pyramid by way of being an exterior gypsum mold of one of the initial halite hopper faces. The gypsum pseudo-crystals show dark brown colors, some with a younger generation of gray gypsum coating (Moore, 2016).

There are also gypsum pseudomorphs after halite crystals in the Salina ravine, in Remolinos, Zaragoza (Spain), in an evaporitic deposit of halite with very abundant reserves of salt located on the left bank of the Ebro river, in a valley dominated by sedimentary formations of gypsum and halite. At the beginning of the ravine, there are layers containing dark grey pseudomorphs of gypsum after hopped cubes of halite reaching up to 15-20 cm on a side. The cubes are sometimes somewhat deformed by the pressure from the upper strata (Calvo, 2014).

### **Cassiterite pseudomorphs after orthoclase**

Pseudomorphs of cassiterite replacing orthoclase are relatively rare, and have been found in very few localities. The best known are those that come from Wheal Coates, Cornwall. These pseudomorphs have the Carlsbad twin morphology of the original orthoclase, in sizes up to 5.5 cm, as isolated twins or as interpenetrating groups. The first specimens were found in 1828, loose inside a reddish sand. The tin content varied among specimens, indicating that the degree of substitution was different (Davey, 1832). Specimens were even found where substitution had only occurred in half of a twin (Greg and Lettsom, 1858). Apart from the classic specimens that appeared in Wheal Coates, specimens were also found, but only rarely, in the Fowey Consols mine, also in Cornwall (Davey, 1832). Since 1970 this type of pseudomorph has also been found in the Aberfoyle tin mine, Storeys Creek mine, and the Rex Hill mine in the Mathinna district, Tasmania, Australia, as floater specimens of black granular

cassiterite pseudomorphs after Carlsbad twins of orthoclase. These specimens tend to be darker (almost black) than those that previously appeared in Cornwall.

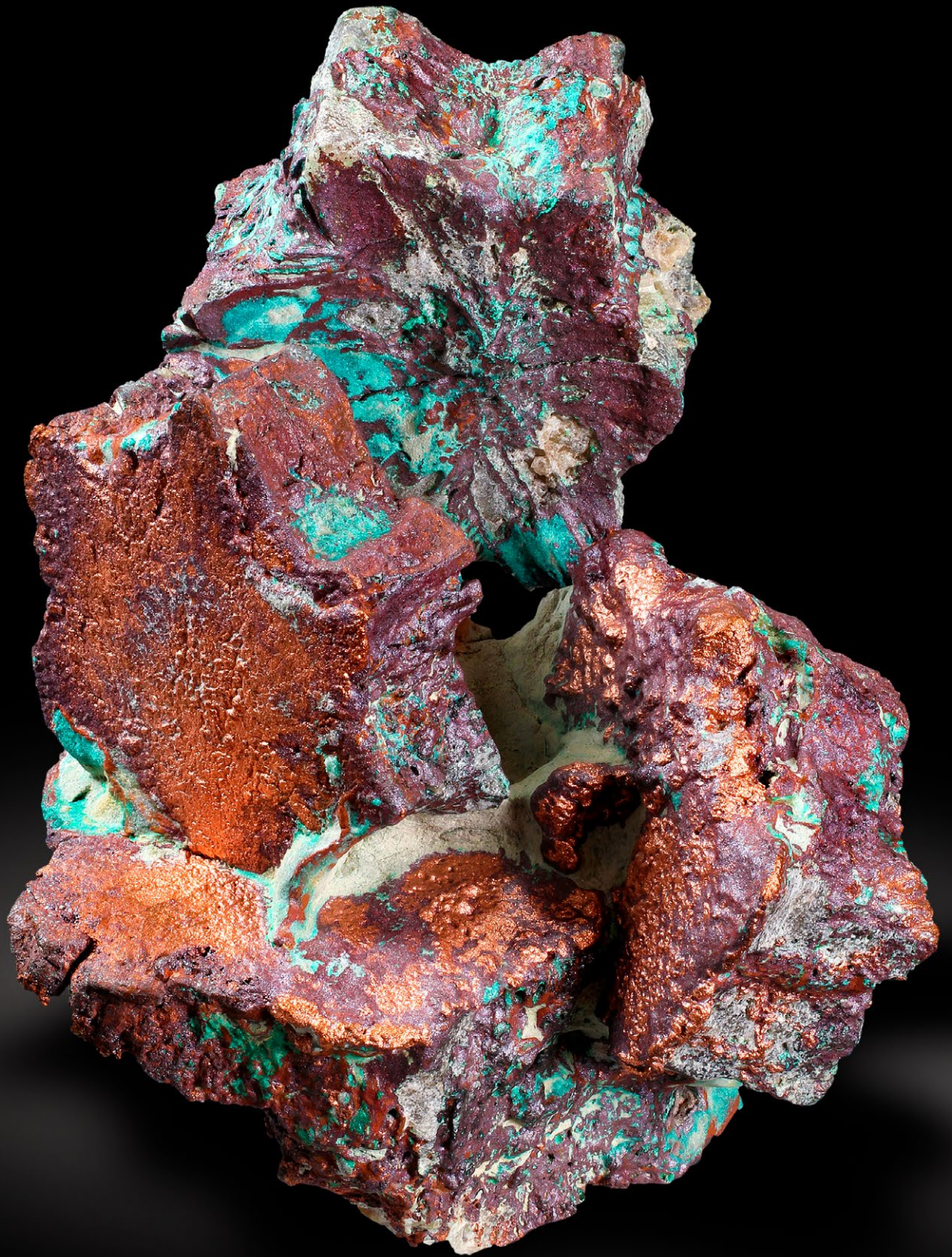
### **Opal pseudomorph after ikaite**

The opal found in the Upper Cretaceous sandstone strata of White Cliffs, in New South Wales (Australia), appears not only as veins and irregular masses, but also as pseudomorphs after various fossils, such as crinoids, bivalves, gastropods, belemnites, and even ichthyosaurus bones. Among the most spectacular mineral specimens from this area are the opal “pineapples” in which opal replaces the crystals of another mineral. It is estimated that between 300 and 500 specimens of this type have been found, and medium quality specimens achieve around \$30,000 at auction (Opal Auctions, 2019). These pseudomorphs of opal replacing a crystallized mineral were already observed by Jaquet (1893), who thought they were pseudomorphs after gypsum. Subsequently, Anderson and Jevons (1905) carefully examined the morphology of the crystals, and based on the facial angles and on the existence of a cleavage plane they identified the initial mineral as glauberite. This identification was maintained for a long time, for example appearing in Frondel’s catalogue (1935), although currently it is thought that they are probably pseudomorphs after ikaite (Pecover, 2007).

### **Copper pseudomorphs after aragonite**

The pseudomorphs of native copper replacing aragonite that come from Corocoro (Bolivia), have been known for a long time, and were already described by Söchting (1858), who noted that in many cases the pseudomorphism was only partial, leaving relicts, sometimes very large, of the original aragonite. Corocoro is the most important copper deposit in Bolivia. It sits in a tertiary sedimentary basin in the northern altiplano. How these pseudomorphs formed is not clear, since at first sight they can not be attributed to either direct chemical alteration nor to a physical substitution by filling cavities. Söchting (1858) suggests that another copper mineral formed first which was later transformed into native copper. This hypothesis could be completed by supposing that the calcium carbonate acted to increase the pH of a solution enriched in copper, which allowed the precipitation of a mineral, possibly cuprite, replacing the aragonite, and that later this mineral was transformed into native copper by the reductive action of the organic matter present in the marls.

**Copper pseudomorphs after crystals of aragonite.**  
45 mm. San Agustín mine, Corocoro, La Paz, Bolivia.  
Luis Miguel Burillo. Joaquim Callen photo.



### Quartz pseudomorphs after carbonates and sulphates

Quartz perimorphs which substitute carbonates and sulphates, such as anhydrite, barite, calcite, and aragonite, are common in hydrothermal veins, but it is often difficult to determine with certainty the initial mineral. Once quartz is formed, it is usually harder to dissolve than most other minerals, so perimorphs of another mineral replacing quartz are much rarer.

### Quartz pseudomorphs after anhydrite

Specimens in which quartz pseudomorphs anhydrite crystals are relatively common in the amethyst geodes of the Rio Grande do Sul/Artigas area (Brazil and Uruguay). Specimens of this pseudomorph began to appear on the collector market around the year 2000. Generally the pseudomorphs, up to 10 cm in size, are grayish white or pale pink (Moore, 2016). Quartz pseudomorphs after anhydrite have also been found in other deposits, among them the Upper New Street quarry, in Paterson, Passaic Co., New Jersey, where small-sized specimens appeared in the 1960s in hollow amygdules with drusy quartz crystals that keep the external shape of the elongated prisms of the disappeared anhydrite, with sizes up to 3 cm. In 1990, specimens of the same type found by local collectors appeared again (Moore, 2016).

The hollow quartz nodules that appear in marly clay layers between Tubilla del Agua and Paramo de Masa have been identified as anhydrite nodules pseudomorphed later by diagenetic processes. The presence of anhydrite inclusions concentrated in the external parts of the nodules is the main argument to infer that the nodules have been formed by the substitution of precursor anhydrite and that this substitution would have occurred from the exterior to the interior. The presence of quartz mosaics with a considerable amount of dispersed anhydrite inclusions may indicate a volume-for-volume replacement of anhydrite by silica in the initial stages. At a later stage, the rate of dissolution of the anhydrite exceeded that of quartz precipitation, producing a secondary porosity so that the increasing dissolution of the sulphate allowed the growth of quartz crystals in a less dense mass. This process has also been observed in the geode-rich formations of Warsaw and Fort Payne in the Upper Mississippi Valley and Tennessee, and in the quartz geode strata of Laño in Treviño, Burgos (Spain) (Elorza and Rodriguez, 1984).

### Quartz pseudomorphs after calcite

Probably the first Spanish pseudomorphs that entered the scientific literature were those formed by opal (and/or chalcedony) pseudomorphs after calcite

crystals found on the summit of Cerro Almodóvar, located approximately 1.5 km NE of the urban area of the old town of Vallecas, now annexed within the municipal boundaries of Madrid. Andrés Manuel del Río, discoverer of vanadium and author of the first book on mineralogy published in the Americas, points out in the second edition of his work (Río, 1832) that Donato García (who was Professor of Mineralogy in the Royal Cabinet of Natural History during the first decades of the nineteenth century) had found in the formations of “magnesite or sea foam” (old name for sepiolite) from the outskirts of Madrid “octahedral opal”. Leonhard (1833) describes these specimens as opal pseudomorphs after calcite, indicating that they come from the “Cerro de Vallecas”, and making reference to “Amar”. We can assume that this was a personal communication from the Spanish geologist Rafael Amar de la Torre. These pseudomorphs were also described in detail by Blum (1843; 1847). Prado (1864) reports that he found these pseudomorphs in Vallecas, and Fernández Navarro (1904) points out the existence in Cerro Almodóvar of

**Chalcedony and opal, pseudomorphs after calcite.** Cerro de Almodóvar, Vallecas, Madrid, Spain. 35mm high. Obtained in 1975. Miguel Calvo coll.



pseudomorphs after calcite, identifying the siliceous material as chalcedony, although Calderón (1910) considered it to be opal. The pseudomorphs that have been analyzed are formed mainly of microcrystalline quartz, although opal pseudomorphs could exist too, or pseudos composed of both, since they appear on flint masses that exhibit fine coatings of opal. The pseudomorphed calcite crystals are only a few millimeters in size, formed by combinations of an obtuse rhombohedron (“nail head”) with a very sharp rhombohedron, and are either completely replaced by silica or partially hollow. The pseudomorphs are very well defined, white, with a porcelanous luster in some areas (Calvo, 2016).

### **Pseudomorphs by incrustation (epimorphs and perimorphs)**

These pseudomorphs are formed when one mineral grows as a coating on the surface of another mineral that is not directly related, after which the original disappears, and the new mineral maintains the shape as a mold. We can differentiate two main types: those in

which a coating maintains the morphology of the old crystals, and those in which the coating fills up all the space between the crystals of the earlier mineral, and when the older mineral disappears it leaves a negative pseudomorph, with open gaps that maintain the shape of the first mineral. In the first case the pseudomorph can be partially filled by the encrusting mineral, or by others, or even leaving relicts of the older mineral.

### **Quartz epimorphs after calcite**

In the La Viesca mine, in the Olga concession, in Siero, Asturias (Spain), there are specimens with quartz epimorphs of large calcite crystals, up to 25 cm in size, associated with druses of cubic fluorite crystals. These epimorphs can be incomplete, so that the coating occurs only on some of the faces.

The quartz crusts have a thickness of a few millimeters, with the crystals being terminated both on the outside and the inside of the mold. There may be remnants of calcite, or it may disappear completely, and a new generation of fluorite crystals can even form within the epimorphs (Calvo, 2016).

**Quartz epimorph after calcite**, on quartz. Perseverancia vein, El Chaparral concession, Villaviciosa de Córdoba, Córdoba, Spain. Epimorph, 3 cm. Miguel Calvo coll.



**Cassiterite pseudomorph after feldspar**. 4 cm. Wheal Coates, near St. Agnes, Cornwall, England. Chris Mavris coll. J. Callen photos.



Very similar specimens of this type of epimorph have also been found in the Xiefang mine, Ruijin county, Jiangxi province (China), also associated with fluorite; in the Faywood mine, Cookes Peak district, Luna Co, New Mexico, and in the mines of Căvnic, Maramures (Romania).

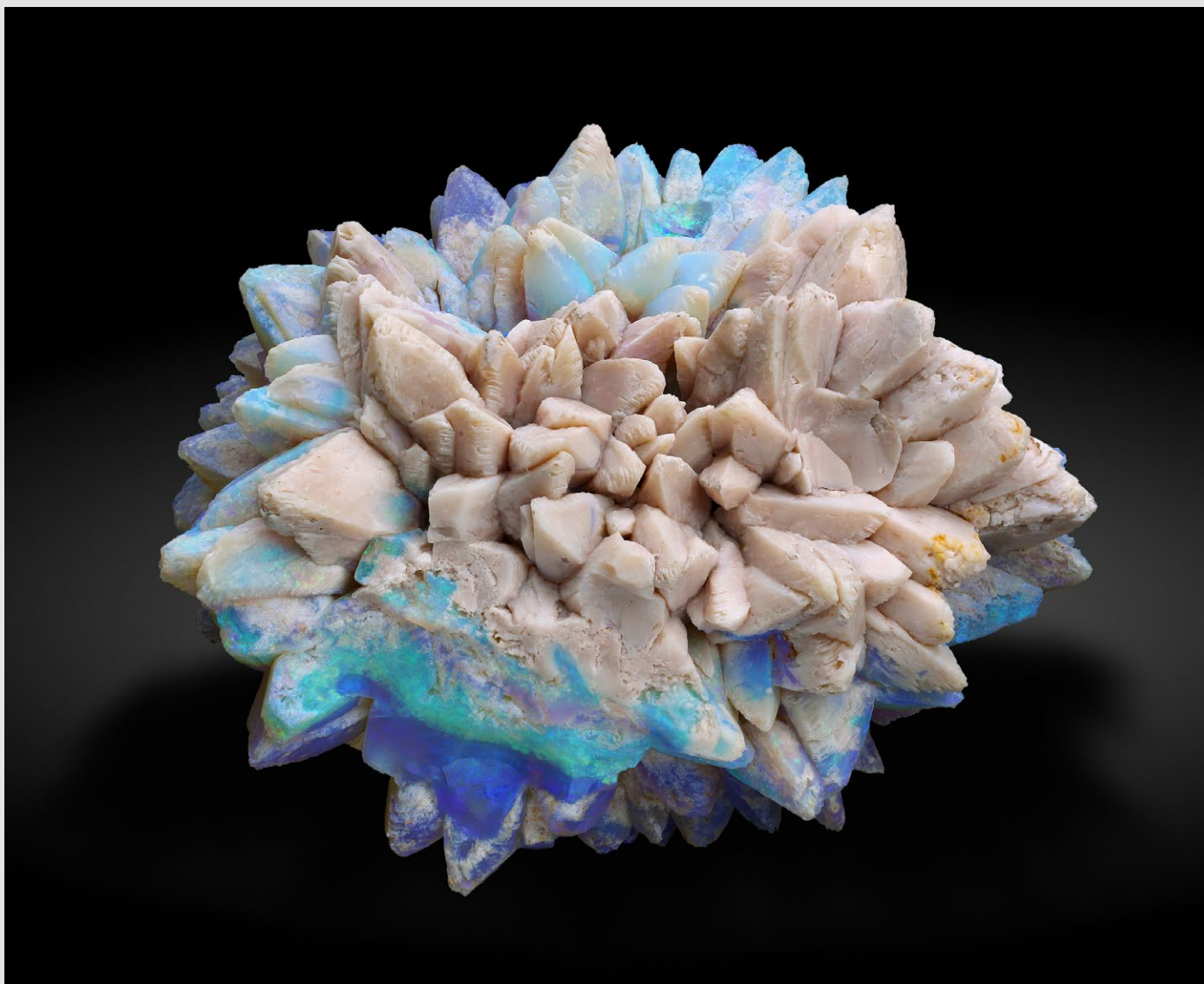
Specimens of quartz epimorphs after calcite have also been found in the Perseverancia vein, in the El Chaparral concession, in Villaviciosa de Córdoba, Córdoba (Spain), which was exploited by both an open cut and underground workings. The epimorphs formed by the substitution of calcite crystals, up to 4 cm in size, which had grown on crusts of quartz crystals, by very fine-grained silica. The outer surface of the epimorphs is smooth and the morphology well defined, but internally they are hollow, partially filled with spongy microcrystalline silica (Calvo, 2016).

## References

- Ahn JH, Burt DM, Buseck PR (1988): Alteration of andalusite to sheet silicates in a pegmatite. *American Mineralogist*, 73: 559-567.
- Alonso-Zarza, A.M., Sanchez, Y., Bustillo, M.A., Sopena, A. and Delgado, A. (2002). Silicification and dolomitization of anhydrite nodules in argillaceous terrestrial deposits: an example of meteoric-dominated diagenesis from the Triassic of central Spain. *Sedimentology*, 49, 303-317.
- Anderson, C. and Jevons, H.S. (1905). Opal pseudomorphs from White Cliffs, New South Wales. *Records of the Australian Museum*, 6, (1), 31-37.
- Arce, B. (1880). Apuntes acerca de los criaderos de calamina y blenda situados en los Picos de Europa, y de la explotación que de los mismos hace la Sociedad Minera La Providencia. *Revista Minera Metalúrgica y de Ingeniería*, 31, 67-68; 75-76; 82-83; 90-91; 97-100; 105-106; 115-116.
- Armbruster, T. (1981). On the origin of sagenites: structural coherency of rutile with hematite and spinel structure types. *Neues Jahrbuch für Mineralogie – Monatshefte*, 328-334.
- Blum, J.R. (1843). *Die Pseudomorphosen des Mineralreichs*. E. Schweizerbat'sche Verlagshandlung, Stuttgart. 378 págs.
- Blum, J.R. (1847). *Nachtrag zu den Pseudomorphosen des Mineralreichs*. E. Schweizerbat'sche Verlagshandlung, Stuttgart. 140 págs.
- Blum, J.R. (1863). *Dritter Nachtrag zu den Pseudomorphosen des Mineralreichs*. Ferdinand Enke, Erlangen. 294 págs.
- Calderón, S. (1910). *Los Minerales de España*. Junta para Ampliación de Estudios e Investigaciones Científicas. Madrid. Volumen I. 416 págs.
- Calvo, M. (2009). *Minerales y Minas de España*. Vol. IV. Óxidos e hidróxidos. Escuela Técnica Superior de Ingenieros de Minas de Madrid. Fundación Gómez Pardo. 751 págs.
- Calvo, M. (2012). *Minerales y Minas de España*. Vol. V. Carbonatos y Nitratos. Escuela Técnica Superior de Ingenieros de Minas de Madrid. Fundación Gómez Pardo. 711 págs.
- Calvo, M. (2014). *Minerales y Minas de España*. Vol. VI. Sulfatos (Seleniados, Telurados), Cromatos, Molibdatos y Wolframatos. Escuela Técnica Superior de Ingenieros de Minas de Madrid. Fundación Gómez Pardo. 653 págs.
- Calvo, M. (2015). *Minerales y Minas de España*. Vol. VII. Fosfatos, Arseniados y Vanadatos. Escuela Técnica Superior de Ingenieros de Minas de Madrid. Fundación Gómez Pardo. 479 págs.
- Calvo, M. (2016). *Minerales y Minas de España*. Volumen VIII: Cuarzo y otros minerales de la sílice. Escuela Técnica Superior de Ingenieros de Minas de Madrid. Fundación Gómez Pardo. 399 págs.
- Calvo, M. (2018). *Minerales y Minas de España*. Vol. IX. Silicatos. Escuela Técnica Superior de Ingenieros de Minas de Madrid. Fundación Gómez Pardo. 767 págs.
- Council, T.C. and Bennett, P.C. (1993). Geochemistry of ikaite formation at Mono Lake, California: implications for the origin of tufa mounds. *Geology*, 21, 971-974.
- Davey, S. (1832). Notice of Pseudomorphous crystals of oxide of tin, found in Huel Coates mine, in St. Agnes, in the year 1828. *Transactions of the Royal Geological Society of Cornwall*, 484-485.
- Davies, G.R., Nixon, P.H., Pearson, D.G. and Obata, M. (1993). Tectonic implications of graphitized diamonds from the Ronda peridotite massif, southern Spain. *Geology*, 21, 471-474.
- Drugman, J. (1922). An example of porphyry-quartz, from the Esterel Mts., France, twinned on face (10-12). *Mineralogical Magazine*, 19, 295-300.
- Drugman, J. (1927). On b-quartz twins from some Cornish localities. *Mineralogical Magazine*, 24, 366-382.
- Elorza, J.J. and Rodríguez, J. (1984). Late Cretaceous quartz geodes after anhydrite from Burgos, Spain. *Geological Magazine*, 121, 107-113.
- Fagan, T.J. and Day, H.W. (1997). Formation of amphibole after clinopyroxene by dehydration reactions: Implications for pseudomorphic replacement and mass fluxes. *Geology*, 25, 395-398.
- Fernández Navarro, L. (1904). Nota sobre el terciario de los alrededores de Madrid. *Boletín de la Real Sociedad Española de Historia Natural*, 4, 271-281.
- Fernández Navarro, L. (1919). Una opinión sobre el yeso del Cerro de los Ángeles. *Boletín de la Real Sociedad Española de Historia Natural*, 19, 260-266.
- Force, E.R., Richards, R.P., Scoti, K. and Valentine, P.C. (1996). Mineral intergrowths replaced by "elbow" twinned rutile in altered rocks. *The Canadian Mineralogist*, 34, 605-614.
- Freiesleben, J.C. (1827). En: *Isis: Encyclopädische Zeitschrift, vorziigl für Naturgeschichte, vergleichende Anatomie und Physiologie*, 10, 333-336.
- Fronde, C. (1935). *Catologue of mineral pseudomorphs in the*

## Other epimorphic substitutions by quartz

In mining operations in the Sierra de Cartagena, in the municipalities of Cartagena and La Unión (Spain), epimorphs formed by quartz with a granular appearance (more or less corroded microcrystals) and/or chalcedony replacing crystals of other minerals have been found with some frequency (Calvo, 2016). The Catón mine yields epimorphs composed mainly of quartz microcrystals replacing elongated crystals, probably aragonite, up to 3 cm long, forming large groups. In the Emilia open pit and the San Valentín open pit there are similar epimorphs, of smaller size, in the second case composed mainly of chalcedony. The most well-known and appreciated epimorphs from this area are those in which quartz replaces large crystals of barite or anglesite, with individual sizes up to 3 cm, formed mainly by chalcedony, coming from the St. Valentine open pit, the Tomasa pit, and the Los Blancos pit. They are associated with botryoidal chalcedony, on the typical mineralization of this area, greenalite and siderite with galena.



**Opal** ("Red Earth Opal") pseudomorphing the *glendonite* variety of *calcite*, which had pseudomorphed *ikaite* crystals. 10 cm. Golden Gully, White Cliff, Australia. Robert Sleeczy, Ausrox. Photo J.Callen.

American Museum of Natural History. Bulletin of the American Museum of Natural History, 67, 389-426.

-Galuskin, E. and Galuskina, I.O. (2002). Achtarandit-sponge hibschite pseudomorph after wadalite-like phase: internal morphology and mechanism of formation. Neues Jahrbuch für Mineralogie – Monatshefte, 178, 63-74.

-Galuskina, I.O., Galuskin, E. and Sitarz, M. (1998). Atoll hydrogarnets and mechanism of the formation of achtarandite pseudomorphs. Neues Jahrbuch für Mineralogie – Monatshefte, 49-62.

-Greg, R.P. and Lettsom, W.G. (1858). Manual of mineralogy of Great Britain and Ireland. John van Voorsy, Londres. Pag. 359.

-Haüy, R.J., 1801. Traité de Mineralogie. Chez Louis, Paris. Vol I, 140-145.

-Hernández Pacheco, E. and Royo, J. (1916). Mineralogía, geología y prehistoria del Cerro de los Ángeles (Madrid). Boletín de la Real Sociedad Española de Historia Natural, 16, 533-539.

-Hernández Pacheco, E. and Royo, J. (1917). Acerca del yeso del Cerro de los Ángeles (Madrid). Boletín de la Real Sociedad Española de Historia Natural, 17, 572-574.

-Jaquet, J.B. (1893). Opal mining in New South Wales. The White Cliffs Field. Some interesting particulars. Australian Town and

Country Journal, 27 mayo 1893, pag. 24.

-Jiménez Martínez, R. (2015). Las quialitolitas del Parque Histórico de Navia: Patrimonio mineralógico en el occidente de Asturias. De Re Metallica, 24, 25-32.

-Jiménez Martínez, R., Calvo, M., Martínez, M.A. and Gorgues, R. (2005). Yacimientos de aragonito del Triásico español. Bocamina (16), 28-93.

-Keim, M.F. and Markl, G. (2017). Formation of galena pseudomorphs after pyromorphite. Neues Jahrbuch Für Mineralogie – Abhandlungen. Journal of Mineralogy and Geochemistry, 194 (3), 209–226.

-Kloprogge, J.T. and Lavinsky, R. (2017). Photo-Atlas of mineral pseudomorphism. Elsevier, 281 pags.

-Lacroix, A. (1901). Minéralogie de la France et de ses Colonies. Librairie Polytechnique Ch. Béranger, Paris. Vol. 3, 303-308.

-Leonhard, K.C.R. von (1833). Grundzüge der Oryktognosie. Joseph Engelmann, Heidelberg. Pag. 83

-Liu G, Ottens B (2005). Daoping mine. The Mineralogical Record, 36 (1), 25-33.

-Lozano, R.P., Jiménez, R., González, R., Paradas, A. and Baeza, E. (2011). Revisión de la terminología utilizada en la exposición pública de minerales españoles del Museo Geominero (IGME, Madrid). Boletín Geológico y Minero, 122, 49-70.



**Quartz pseudomorph after calcite.** 78 mm. Huanggang mine, Inner Mongolia, China. Mario Pauwels coll.



**Quartz pseudomorph after anhydrite.** 12 cm. Irai, Rio Grande do Sul, Brazil. Enric Kucera



**Partial quartz perimorphism of a calcite crystal, with later formation of fluorite crystals.** 11 cm. La Viesca mine, Huergo, Siero, Asturias, Spain. M. Calvo coll.

-Maliva, R.G. (1987). Quartz geodes; early diagenetic silicified anhydrite nodules related to dolomitization. *Journal of Sedimentary Research*, 57, 1054-1059.

-Medaris Jr. L. G. (1999). Garnet peridotites in Eurasian high-pressure and ultrahigh-pressure terranes: A diversity of origins and thermal histories. *International Geology Reviews*, 41, 799-815.

-Miers, H.A. (1900). Note on the Hitchcockite, Plumbogummite and Beudantite analysed by Mr. Hartley. *Mineralogical Magazine*, 12, 239-243.

-Moore, T.P. (2016). *Compendium of mineral discoveries (1960-2015)*. The Mineralogical Record Inc, Tucson, Arizona. 813 págs.

-Naumann, C.F. (1846). *Elemente der Mineralogie*. Verlag von Wilhelm Engelmann, Leipzig. Pag.96.

-Ohmoto, H. (2003). Nonredox transformation of magnetite-hematite in hydrothermal systems. *Economic Geology*, 98, 157-161

-Opal Auctions (2019). <https://www.opalauctions.com/auctions/pineapple-with-gem-fire-opal-26773>.

-Ortí, F., Rosell, L. y Ladorcz, A. (1995). Fábricas cristalinas de yeso secundario de reemplazamiento de glauberita: aplicación en prospección de sulfato sódico. *Geogaceta*, 17, 49-52.

-Pardillo, F. (1917). Sobre el yeso del Cerro de los Ángeles (Madrid). *Boletín de la Real Sociedad Española de Historia Natural*, 17, 535-537.

-Pardillo, F. (1918). Algunas consideraciones más sobre el yeso del Cerro de los Ángeles (Madrid). *Boletín de la Real Sociedad Española de Historia Natural*, 18, 126-130.

-Pauly, H. (1963). "Ikaite", a new mineral from Greenland. *Artic*, 16, 263-264.

-Pecover, S.R. (2007). Australian opal resources. *Outback spectral fire*. *Gems and Gemology*, 82, 103-115.

-Pezzotta, F., Adamo, I. and Diella, V. (2011). Demantoid and topazolite from Antetazambato, Northern Madagascar: Review and new data. *Gems and Gemology*, 47, (1), 2-14.

-Pinch, W.W. and Wilson, W.E. (1977). Tsumeb!. *Minerals: a descriptive list*. *The Mineralogical Record*, 8, (3), 17-37.

-Poullen, J.F. (1984). Des collections prestigieuses. *Monde & Minéraux*, (64), 8-25.

-Pósfai, M. and Buseck, P.R. (1994). Djurleite, digenite and chalcocite intergrowths and transformations. *American Mineralogist*, 79, 308-315.

-Prado, C. (1864). *Descripción Física y Geológica de la Provincia de Madrid*. Madrid, Junta General de Estadística. 219 págs.

-Quiroga, (1890). Comunicación en Actas de la Sociedad Española de Historia Natural, 19, 100.

-Rio, A.M. del (1832). *Elementos de Orictognosia o del Conocimiento*

de los Fósiles. Imprenta de Juan F. Hurtel, Filadelfia. Pag 270.

-Robinson, G.W. and King, V.T. (1991). What's new in minerals? Annual world summary of mineral discoveries. *The Mineralogical Record*, 22, 381-393.

-Sanchez-Navas A, Oliveira-Barbosa, R., Garcia-Casco A, and Martín-Algarra A. (2012). Transformation of andalusite to kyanite in the Alpujarride Complex (Betic Cordillera, Southern Spain): Geologic implications. *Journal of Geology*, 120, 557-574.

-Selleck B.W., Carr, P.F. and Jones, B.J. (2007). A review and synthesis of glendonites (pseudomorphs after ikaite) with new data: assessing applicability as recorders of ancient coldwater conditions. *Journal of Sedimentary Research*, 77, 980-991.

-Sheard, M.J. (1990). Glendonites from the Southern Eromanga basin in South Australia: paleoclimatic indicators from Cretaceous ice. *Quarterly Geological Notes*, (114), 17-23

-Suess, E., Balzer, W., Hesse, K.F., Muller, P.J. and Wefer, G. (1982). Calcium carbonate hexahydrate from organic-rich sediments of the Antarctic Shelf: Precursor of Glendonites. *Science*, 1216, 1128-113.

-Söchting, E. (1858). Gediegen Kupfer pseudomorph nach Aragonit. *Annalen der Physik*, 180, 332-334.

-Strunz, H. (1982). Pseudomorphosen-Der derzeitige Kenntnisstand. Versuch einer Klassifizierung. *Aufschluss* 33, 313-342.

-Svanberg, L.F. (1844). *Mineralanalyser. Öfversigt af Kongliga Vetenskaps-Akademiens Förhandlingar*, 4, 219-222.

-Urrutia, M., Graña, J., Garcia-Rodeja, R. and Macías, F. (1987). Procesos de oxidación de piritas en medios superficiales: potencial acidificante e interés para la recuperación de suelos de mina. *Cuaderno do Laboratorio Xeolóxico de Laxe*, 11, 131-145.

-Vinck, B.V. (1986). Stability relations of malachite and azurite. *Mineralogical Magazine*, 50, 41-47.

-White, J.S. (1974). What's new in minerals?. *The Tucson show*. *The Mineralogical Record*, 5, 76-78.

-Zhao, J., Brugger, J. and Pring, A. (2019). Mechanism and kinetics of hydrothermal replacement of magnetite by hematite. *Geoscience Frontiers*, 10, 29-41.

**Jesús Fraile** [jffraile@unizar.es](mailto:jffraile@unizar.es)

**Miguel Calvo** [calvoreb@unizar.es](mailto:calvoreb@unizar.es)