Zeolites and associated minerals in the vacuoles of some of the Campo de Calatrava volcanoes - Ciudad Real, Spain -

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INTRODUCTION

Rocks of the Calatrava Volcanic Field have been extensively exploited. In the case of volcanoes with effusive eruptions, vast and thick lava flows formed, sometimes kilometers long. Given its hardness and tenacity, this compact basalt was used throughout the nineteenth century and the first half of the twentieth to make cobblestones for paving and street curbs.

In the early 1930s about 2 million cobblestones were produced each year, enough to pave 40 km of road (González Cárdenas, 1991). In more modern times, its main use has been for crushed rock for railway ballast, especially for the new high-speed lines. Between 1987 and 1988 seven new workings were opened, and in the early 1990s there were 23 active quarries, some of them illegal, from which 765,000 tons of basalt were quarried each year (González Cárdenas, 1991). Strombolian eruptions lead to the formation of pyroclastic cones, which in Campo de Calatrava can reach up to 100 meters high, and also lava flows whose structure and extent depends on the viscosity of the magma. Some of these lava flows have also been widely exploited. Other pyroclastic materials, such as pozzolans, known locally as "hormigones", "picones" or "carbonillas" were extracted for improvement of agricultural soils or for road paving. In recent years, many of these workings were surreptitiously recorded as "pumice" mines, a material that in reality is not found in the Campo de Calatrava, for legal advantages (González Cárdenas, 1991).

Arzollar volcano, Ciudad Real

The Arzollar volcano (or Arzollar fountain) is located to the left of the road from Ciudad Real to Piedrabuena, about 3 km after the last houses of Ciudad Real. It is a strombolian-type volcano and the type of rock found here is melilitite.

The volcano consists of a cone created from pyroclastic and basaltic flows that sometimes can be more than 20 meters thick. Some outcrops of these materials are exploited in Las Urracas quarry, owned by the company Hormigones de Ciudad Real Inc. ("Horcisa"). This quarry, operated since 1988, is accessible by several tracks that deviate to the left from the road that goes from Ciudad Real to Piedrabuena, about 2 km before the bridge over the Guadiana river.

Cerro Moreno volcano, Almagro

Volcan del Cabezuelo, located in the area generally known as Cerro Moreno, was formed in a strombolian-type eruption, generating limburgitic rocks and also pyroclastic accumulations. Some limestone blocks can be found within the lava, incorporated during the ascension of the magma. These flows have been exploited extensively since 1978, reaching 250,000 tons of rock removed per year.

The quarry of Cerro Moreno volcano is located 1 km NE of Almagro, near the border with the municipality of Bolaños, and was operated by the Basaltos de Almagro, Inc. company.

Las Herrerías volcano, Bolaños de Calatrava

Las Herrerías volcano is located about 1 km SSE of the town of Bolaños de Calatrava. The lava here is melilitite-nephelinite, quite fluid.

The eruption that created the deposit was effusive. Inside the vacuoles of the lava predominantly miarolitic minerals can be found, particularly nepheline, melilite and hydroxylapatite, while zeolites are relatively rare.

In these lava flows a quarry called Las Herrerías is located, which was exploited by the company Ubladesa Inc. since 1987, especially to obtain ballast for the construction of the high-speed railway between Madrid and Seville.

It was the largest basalt quarry of Ciudad Real and it produced up to 325,000 tons a year. In 2001 that same company obtained the concession for Herrerías II over the area of the aforementioned quarry.

From 2008, the north zone of the gap left by the extraction of basalt was transformed into a treatment and waste disposal plant, managed by the Ignea Medio Ambiente Inc. company, which is filling the gap with waste materials.

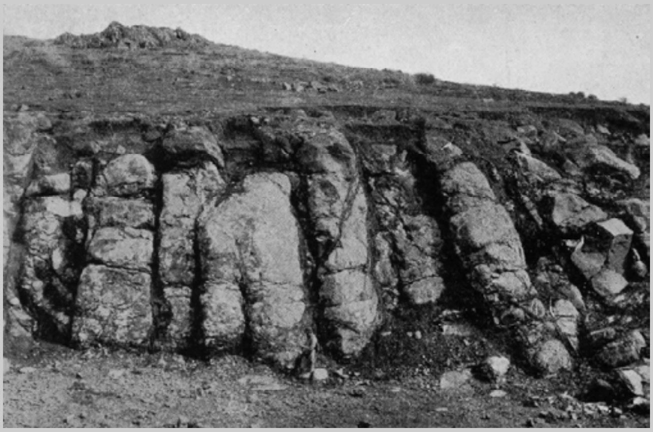
MINERALOGY

The lavas of the volcanoes of the Campo de Calatrava include vesicles in which minerals produced in two separate stages can be found: miarolitic minerals formed at high temperatures during the solidification of the magma, and the ones formed later, by hydrothermal processes at much lower temperatures.

The former include diopside, augite, magnetite, apatite, nepheline and melilite, and among the latter there are zeolites and some carbonates and sulfates. Zeolites present here were formed at low temperatures, most of them formed at a later stage than phillipsite-Ca. Further evidence of the low-temperature hydrothermal mineral formation is the absence of stilbite.

ZEOLITES

In Spanish classical mineralogy, zeolites went almost unnoticed. Calderon (1910) only highlights the presence in Spain of analcime, chabazite and natrolite, relying solely on petrographic studies. Apparently, there were no specimens of Spanish origin of this family of minerals in the various museums whose collections he examined to prepare his book. The most important deposits of zeolites in peninsular (mainland) Spain that are known so far, in terms of variety of species and quality, are those of the Campo de Calatrava volcanoes. These volcanoes were studied extensively by Hernández Pacheco (1932), who surprisingly only mentions a few of the zeolites, mainly from a petrographic point of view.



Front of the flow of the volcano El Arzollar. Hernández Pacheco (1932)

Natrolite

Natrolite, identifiable only under the petrographic microscope, is the only zeolite mentioned by Hernández Pacheco (1932) in his extensive work on the volcanic area of Campo de Calatrava.
In the workings on Arzollar volcano, natrolite appears as microcrystals with prismatic development with a square cross-section with {110} as the dominant face; the crystals are also well shaped and with well-defined terminations, with {111} faces. The terminal area of the crystals is usually colorless and transparent, often with a central white and opaque zone.
The crystals are found in aggregates forming groups of divergent subparallel associations, natrolite being the only type of zeolite present or sometimes associated with phillipsite.
In the workings on Cerro Moreno, in Almagro, natrolite also appears as white needle-like spherules that have formed tapestries over phillipsite crystals.
It is also found in the Las Herrerías volcano, over thomsonite-Ca spherules, which is likely to be an epitaxial growth, very common among these minerals.

Gonnardite

Gonnardite is a zeolite that can be easily mistaken for others such as natrolite, mesolite and phillipsite.
In fact, although it is relatively common (around 150 locations are known worldwide), nearly sixty years passed between its discovery in Chaux de Bergonne (France) and the discovery of a second location by Meixner *et al.* (1955).
In the quarry of Arzollar volcano, gonnardite is quite common, forming hemispherical aggregates, often incomplete, having a form rather like sheaves. They have a diameter of 5 mm and a radiated internal structure.
This mineral can also appear as subparallel aggregates. In the outer zone of the aggregates the termination of the crystals can be seen.
The terminations are more or less irregular, but they always have a certain brightness. The crystals are formed by bipyramid faces {111} or, less commonly, {001}.
When they do not complete the spherical shape, {110} faces can be seen on individual crystals, which are typically somewhat flattened. Gonnardite appears associated with phillipsite-Ca. It has also been found associated with amicite, in both cases having been formed later. In the Cerro Moreno quarry, gonnardite appears either alone, without other associated zeolites, or growing over tapestries of phillipsite microcrystals.
In all of the sites studied, gonnardite is always white and milky, almost opaque, which allows it to be differentiated from other zeolites, especially from thomsonite-Ca and phillipsite, which are colorless and transparent.
Divergent clusters of gonnardite spherules are often among the latter minerals formed in the vacuoles.
The only zeolite which seems to have formed later is thomsonite-Ca, which appears on separate beads or growths over gonnardite, in the latter case they could be possibly epitaxially associated.

Thomsonite-Ca

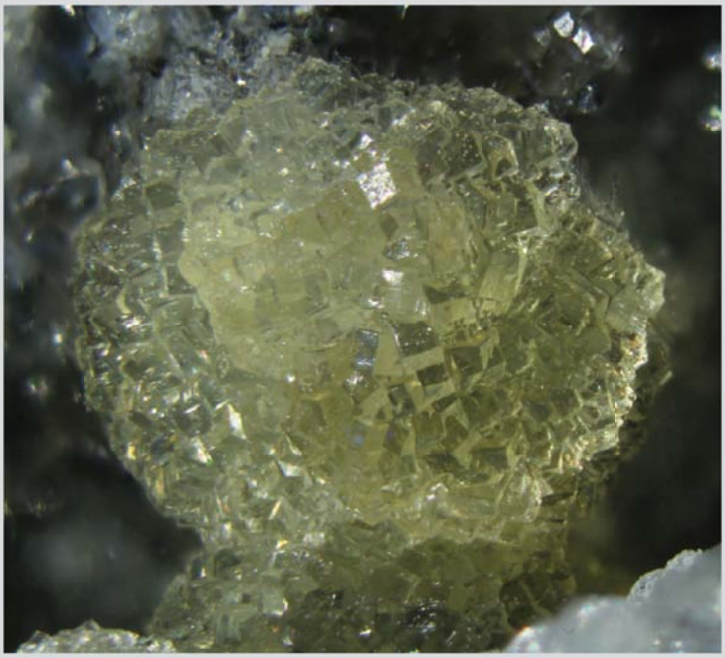
Thomsonite-Ca has been found quite frequently in the Cerro Moreno workings, in Almagro, as spherules formed by the association of prismatic crystals arranged in a radial form. The outer surface of the spherules is formed by the combination of the {001} faces of the individual crystals. These crystals may have a tabular aspect, with {100} more developed than {010}, or nearly with a square section if both pinacoids reach similar development.

View of the El Arzollar Quarry. Photo by Agustin Sanz.

Natrolite. 1.1 mm FOV. Las Herrerias Quarry.
J. A. Soldevilla collection and photo.

Gonnardite with phillipsite. 3.5 mm crystal group.
El Arzollar. Joan Viñals coll. Photo by J. Callén.

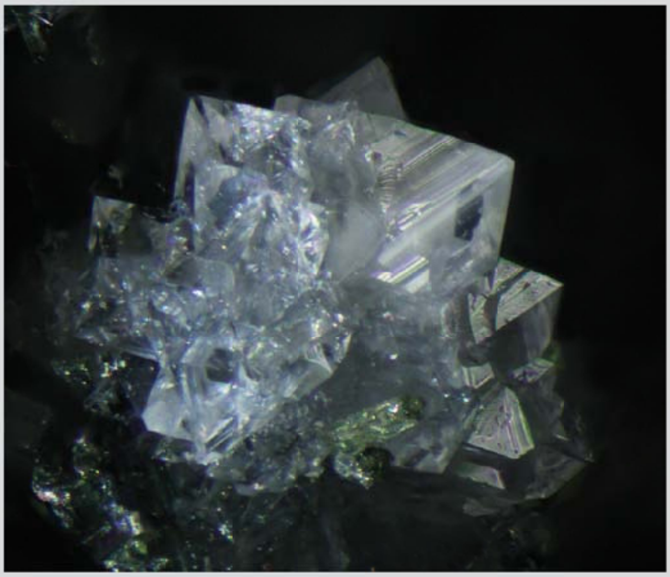
Gonnardite. 2 mm FOV. Las Herrerias Quarry.
J. A. Soldevilla collection and photo.



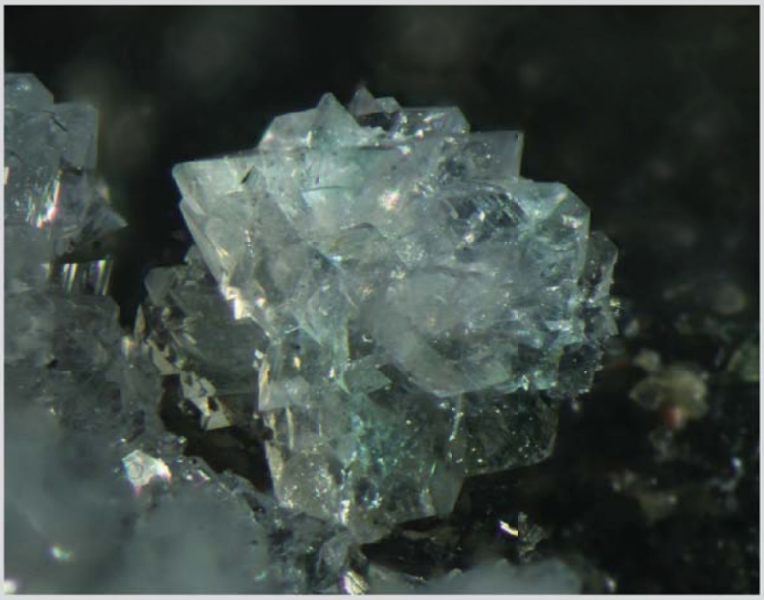
Gismondine. 2.3 mm FOV. Las Herrerias Quarry.
J. A. Soldevilla collection and photo.

Thomsonite. 4 mm ball size. Cerro Moreno, Almagro.
Joan Viñals coll. Photo by J. Callén.

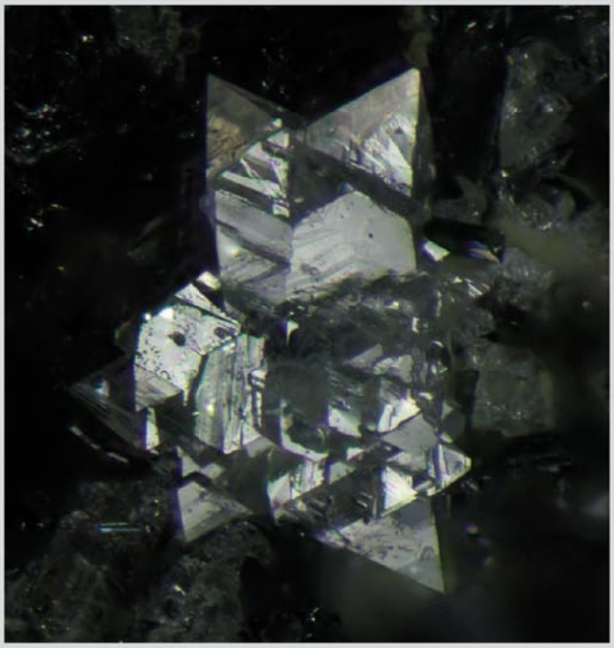
Gismondine. 0.7 mm FOV.
Las Herrerias Quarry.
J. A. Soldevilla collection and photo.



Amicite.
1 mm crystal group. Arzollar.
Joan Viñals.
Photo by Joaquim Callén.



Amicite. 1.3 mm crystal group. El Arzollar.
Joan Viñals coll. Photo by J. Callén.



Amicite. 0.9 mm crystal group. El Arzollar.
Joan Viñals coll. Photo by J. Callén.

Phillipsite.
0.5 mm FOV.
Las Herrerias Quarry.
J. A. Soldevilla collection and photo

Phillipsite. 1.7 mm FOV.
Las Herrerias Quarry.
J. A. Soldevilla collection and photo.

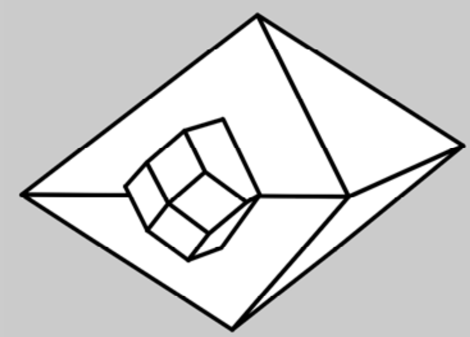
Sometimes the crystals have parallel growth of the {100} and {010} faces, and although occasionally single crystals can be observed, generally they form groups of divergent spherules. The edges and faces are sometimes slightly rounded, with the appearance of irregular smaller faces, which, considering that the flattening takes place on the {100} faces, probably correspond to {110} and {101}.
The thomsonite-Ca that can be found in these workings is completely transparent, with a color ranging from light yellow to almost colorless, but almost always with a light yellowish tone. It usually appears on calcite, but it has also been found associated with gismondine and phillipsite.
In Las Herrerías volcano, in Bolaños, it appears as spherules formed by colorless and transparent crystals, deposited on a thin crust of opaline material overlying the basalt. It can also be found in the Arzollar volcano, as oriented growths on gonnardite. The habit of the thomsonite crystals from the Ciudad Real volcanoes is not the most common for this species, which is more commonly found as clusters of bladed crystals.

Yugawaralite

The presence of this species is doubtful, since it has been observed only as one possible specimen in the Arzollar quarry and has not been analysed.

Gismondine-Ca

Gismondine is a mineral that crystallizes in the monoclinic system and generally, in the volcanoes of Ciudad Real, it is found as tetragonal bipyramidal crystals, which are really interpenetrating twins formed by two perpendicularly twinned individuals on (100). The visible faces belong to $\{\bar{2}32\}$, four faces corresponding to each individual of the twin (Nawar, 1980). The twins may be found as individuals or as disordered groups, but parallel association of two or more crystals is very frequent.
In the Cerro Moreno volcano quarry, in Almagro, gismondine was relatively abundant. It appears associated with calcite crystals, which it sometimes covers completely, and phillipsite.
In most cases, gismondine and phillipsite must have crystallized almost simultaneously, since they form growths on one another even in the same vacuole. Specimens where gismondine forms epitaxial growths with phillipsite were also found, both as gismondine twin crystals growing on phillipsite twins and the converse. These epitaxial growths have also been observed at other sites, such as Osa, Italy (Tschernich, 1992) and John Day River, Oregon, USA (Howard, 1994).

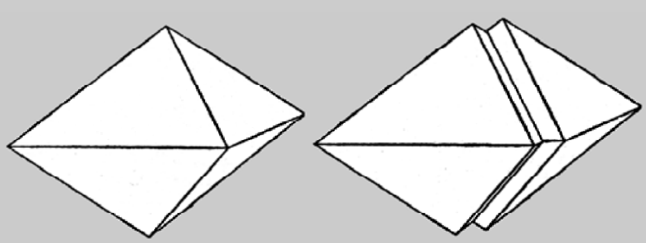


Gismondine-Ca and phillipsite-Ca epitaxial growth. Cerro Moreno.

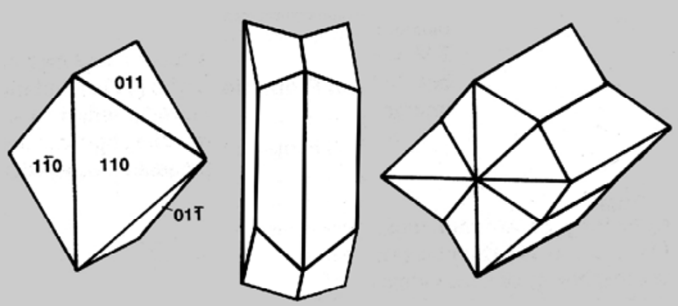
At the other sites studied in Ciudad Real, although it appears very occasionally, it is much scarcer than in Cerro Moreno. In Arzollar volcano, gismondine-Ca has been found associated with thomsonite and tobermorite.

Amicite

Amicite is a very rare species of zeolite worldwide, so far having been found in only a few localities: the type locality, Höwenegg, Egau (Germany) (Alberti *et al.*, 1979), the Kirov mine in Khibiny, on the Kola Peninsula (Russia) (Tschernich, 1992) and mount Koashva, also in the Kola Peninsula (Pekov *et al.*, 2008). In Campo de Calatrava it was found in the spring of 1992, exclusively in one particular area of Arzollar Volcano quarry, in the middle front of the workings, near the main road and the grinding plant.



Morphology of gismondine-Ca crystals twinned on (100) and parallel growth of twins.



Single crystal, a twin formed by two crystals and cyclical twin of amicite.

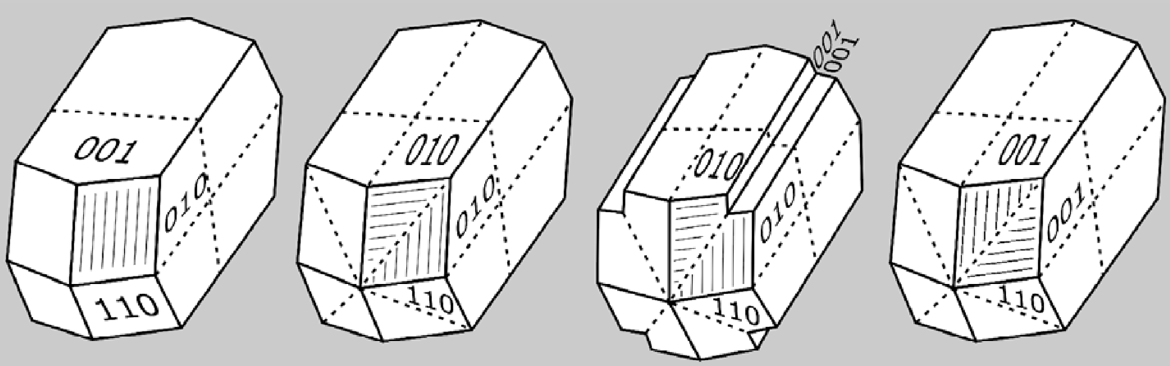
This area disappeared completely within a few months due to the advance of the working face, which exposed deeper levels where this zeolite has not been found.
Amicite crystallizes in the sphenoidal class of the monoclinic system, and appears as crystals with bipyramidal habit, pseudo-tetragonal or pseudo-octahedral, formed by the combination of {110} and {011}. It forms twins on (011) that look very much like the twin of two octahedra following the “spinel law”. The crystals that have been found in Arzollar are colorless, glossy, and about a millimeter or less in size, with quadruple twins being very frequent, identical to those found at the type locality. They can form continuous crusts occupying the entire wall of the vacuoles, sometimes even covering several square centimeters. The only zeolite that has been found associated with amicite in Arzollar is gonnardite, which was clearly formed later.

Phillipsite - Ca

In Campo de Calatrava, phillipsite-Ca seems to be the most abundant zeolite. The phillipsite is never found as single crystals but as twins of different types, which were described in detail by Lacroix (1897), and shown in the figure. Twin planes can be identified on all sides due to the existence of a change in the orientation of the striations. The simple twin, on the left, is formed by two crystals with (001) as the twin plane. It is rare and has not been observed in the phillipsite-Ca of the studied areas. The two central images correspond to the same type of double twin, consisting of four panes, called “Marburg twin” by Lacroix. All specimens studied for this report correspond to this type of twin, with a development that allows observation of the reentrant angle which makes evident the existence of twinning, or without this angle being visible. The right hand figure corresponds to the “Perier twin”.
The distinction between them is relatively simple, observing the striations on the corresponding faces {110}. In the simple twin, all the striations on one side follow the same direction, parallel to the edge formed between the {110} and {010} faces. Marburg and Perier twins, with faces that apparently should correspond to {110}, actually consist of two, from two different crystals, which can be appreciated by the existence of a diagonal division of the striations. Those in which the striations on the two halves are parallel to the edges of {010} correspond to the Marburg twin, and those which are perpendicular to that, to the Perier twin. “Stempel twins”, formed by the association of three double twins following the (110) face, have not been observed.
In Cerro Moreno, phillipsite-Ca appears as single twin associations or as slightly divergent sheaves, which can reach a length up to 5 mm. It appears either alone or associated with other zeolites, predominantly with thomsonite and gismondine. In the Arzollar quarry, phillipsite-Ca appears as twins forming crusts and it is associated with gonnardite. In the Las Herrerías Volcano quarry, zeolites are relatively abundant. The most common one is phillipsite, alone or associated with gismondine, and sometimes gonnardite. It also appears associated with baryte.

Phillipsite-K

Unlike phillipsite-Ca, phillipsite-K is rare in the studied areas. So far it has only been found in the Arzollar Volcano quarry. The appearance of the specimens observed is different from that of the phillipsite-Ca from the same locality, as it appears as parallel growths of many small twins, without clearly distinguishing their individual morphology, covering, sometimes completely, the walls of the vesicle. It appears either as the only zeolite present or else associated with gonnardite.



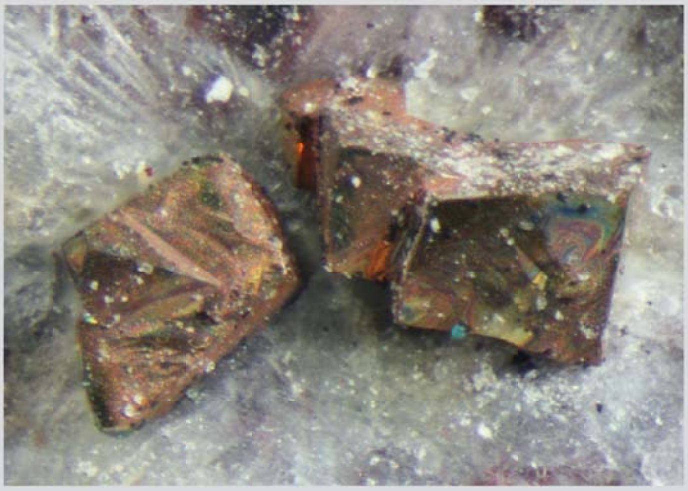
Phillipsite twin. On the left, a twin of two individuals. On the right, four individuals twinned according to the Perier law. The middle two correspond to the Marburg twin, with and without reentrant angles. Striations on the {110} faces serve to differentiate each type of twin.

Epitaxy of phillipsite on gismondine. 4 mm crystal group . Cerro Moreno. Miguel Calvo coll. Photo by J. Callén.

Phillipsite-Ca. 3 mm crystal. El Arzollar. Joan Martí coll. Photo by J. Callén.

Levyne. 0.9 mm FOV. Las Herrerias Quarry. J. A. Soldevilla collection and photo.

Chabasite and phillipsite. 1 mm FOV. Las Herrerias Quarry. J. A. Soldevilla collection and photo.



Copper. 0,5 mm crystals. El Arzollar.
A. Barahona coll. Photo by J.Callén.

Copper. 0,5 mm crystals. El Arzollar.
A. Barahona coll. Photo by J. Callén.

Brucite. 2.7 mm FOV. La Encomienda Quarry.
J. A. Soldevilla collection and photo.

Opal. 2.2 mm FOV. Las Herrerias Quarry.
J. A. Soldevilla collection and photo.

Calcite.
8 mm crystal group.
Miguel Calvo coll.
Photo by Joaquim Callén.

Calcite covered by **gismondine**. 10 mm crystal. Cerro Moreno.
Miguel Calvo coll. Photo by J. Callén.

Chabazite-Ca

In the Cerro Moreno Volcano workings, in Almagro, chabazite-Ca is relatively common. It appears in the form of lenticular twins known as "phacolite". The twins have a rounded aspect, with individual crystal faces not well defined, and can appear isolated, forming intertwined aggregates in the form of "roses" or as curtains completely covering the rock. In all three cases it may be colorless or milky white and in some specimens there is zoning in which the center part of the dome is white.
The edge view of the crystals shows a colorless transparent central band between opaque areas, and viewed vertically, they have a transparent outer part and a central milky part. It is usually associated with phillipsite-Ca. The same happens in the Las Herrerías quarry, where this mineral also appears. In Arzollar volcano, chabazite-Ca appears as roses formed by aggregates of lenticular twins, transparent or translucent. Its appearance is very similar to certain aggregates of lenticular crystals of calcite, but in the quarries that we studied, calcite does not appear with this morphology. It occurs associated with gismondine crystals.

Levyne-Ca

In Las Herrerías quarry, in Bolaños, levyne-Ca appears with the typical morphology for this mineral, as thin tabular crystals of hexagonal shape, which are actually twins consisting of six crystals, corresponding to the division of the hexagon into six equal sectors.
The wider face corresponds to the pinacoid {0001}, which is highly developed, while the outline is formed by rhombohedral faces $\{10\bar{1}1\}$.
The twins are generally of small size, less than a millimeter. It occurs associated with gismondine and chabazite. In specimens from this locality the presence of another zeolite in epitaxial growth on the {0001} faces is frequently observed, but not on the $\{10\bar{1}1\}$ faces, probably offretite or erionite.
The consequence of this is that, looking at those faces, the twins are opaque and have a silky luster, while looking through the other faces, the twins are transparent.
This epitaxial growth is common in many worldwide locations and is characteristic for this species, which facilitates its identification (Tschernich, 1992).
It is also found in Cerro Moreno as small transparent twins, without obvious epitaxial growths, located over colloform crusts covering the other minerals.

Other hydrothermal alteration minerals

Native copper

In the Arzollar Volcano quarry, specimens with small crystals of native copper associated with phillipsite have occasionally been found.

Opal

Opal is found as thin crusts of glassy transparent aspect, the variety "hyalite", in the workings on Las Herrerías volcano.

Brucite

In the La Encomienda workings, located 4.5 km NE of Corral de Calatrava, brucite is found as colorless or orange or brown crystals, with a prismatic or tabular development, with {0001} as the main face, with a characteristic pearly luster and hexagonal outline, with $\{11\bar{2}0\}$ faces, or twelve-sided, formed by the combination of $\{11\bar{2}0\}$ and $\{10\bar{1}0\}$.

Calcite

Calcite is a relatively common mineral in the vesicles of the volcanic rocks of Campo de Calatrava. In Arzollar volcano, globular calcite formations up to a centimeter in diameter appear.
It is also found as crystals of scalenohedral habit, colorless and transparent, several millimeters in size.
In the Cerro Moreno quarry calcite appears as spherules up to 5 mm in diameter, as transparent crystalline crusts on phillipsite-Ca and as pale orange crystals with rhombohedral or scalenohedral habit.
They are often wholly or partially covered by zeolites, particularly gismondine and gonnardite. In Las Herrerías calcite is also found, as small crystals on crusts of twinned phillipsite-Ca.

Aragonite

For a long time the existence of aragonite in the volcanic rocks of Ciudad Real has not been clear. Quiroga (1879) indicated that it appeared forming concretions in vugs and fissures of nepheline basalts, without specifying the location, and this was also repeated by Calderón (1910). However, Castro (1919) indicated that in all cases it was in reality calcite, not aragonite.
Calcite is much more abundant than aragonite, but the latter, although rare, does really appear. It is found in the form of fusiform individual crystals or aggregates of crystals of several millimeters size, colorless, divergently grouped inside vesicles in the Azollar basalt. In some cases, aragonite crystals are coated by calcite crystals of smaller size (Calvo, 2012).
Acicular aragonite microcrystals also appear as divergent groups in Cerro Gordo volcano, located about 3.8 km N of Granátula de Calatrava (Calvo, 2012).
The presence of aragonite as microscopic inclusions in the olivine of the leucitic lava of the El Morrón quarry was also mentioned, located 3 km NNE of Villamayor de Calatrava. This finding has been interpreted as the first evidence of aragonite crystallization in the mantle at depths greater than 100 km (Humphreys, 2010).

Hydrotalcite

Hydrotalcite is found very occasionally in Cerro Moreno. This mineral appears as thin tabular crystals of hexagonal form, in sub-millimetric sizes, with {0001} as the dominant face (Calvo, 2012). The crystals can appear as more or less disordered aggregates or, preferably, forming rosettes.

Baryte

Although baryte is a rare mineral in the volcanic rocks of Campo de Calatrava, it is occasionally found in the quarry on Las Herrerías volcano and in Cerro Moreno.
It appears as colorless crystals of tabular habit, up to 3 mm long and well developed. The crystals have well developed pinacoid faces {001}, limited by {110} and {102}, and sometimes with tiny modifications, probably due to {011} faces. Baryte crystals are generally sitting on a silica crust that covers other preexisting minerals, such as zeolite or calcite. In Las Herrerías volcano, baryte is also found associated with nepheline and hydroxylapatite, which are partially altered and covered with a colloform looking material. Baryte crystals are extremely small in this case, with a white color, and they form treelike aggregates. Both baryte and the accompanying zeolites, mainly phillipsite, were formed later than the colloform deposit and do not exhibit any alteration.

Morphology of the baryte crystals of the La Herrería and Cerro Moreno volcanoes.

The volcanic rocks of Campo de Calatrava contain a significant proportion of baryum, between 445 and 1600 parts per million (Cebriá and Lopez, 1995). This element is usually part of the feldspars. However, baryte is not the only barium mineral identified in the volcanic area of Campo de Calatrava. Sharygin *et al.* (2011) found oxykinoshitalite, with a high content of titanium, inside melilitites with olivine in the Vaqueriza volcano, in Aldea del Rey, and also in nephelinite with olivine in the Asdrúbal volcano, Puertollano.

Ettringite

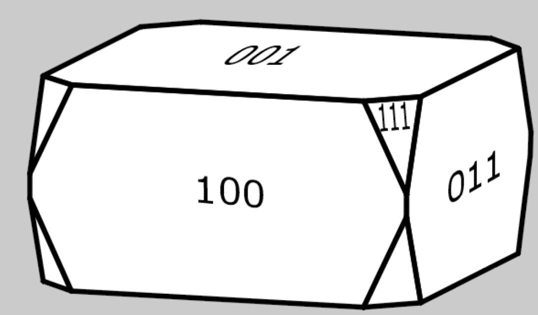
The quarry located in Las Herrerías volcano, in Bolaños, is so far the only Spanish locality for ettringite. It is mostly found in subparallel aggregates of prismatic crystals, translucent and white, curved so that the association has the form of barley grains. The terminations of the individual crystals are generally confusing.
The ettringite crystal aggregates are between 0.5 and 2 millimeters in size. In some cases they form radial and divergent aggregates, and they can also appear scattered disorderly on a carpet of phillipsite-Ca crystals.
Ettringite has also been found, although less frequently, as skeletal hollow crystals, in which the bipyramid dominates, combined with small prism faces.
These crystals usually appear as parallel aggregates of a few individuals (Calvo *et al.*, 2010).

Thaumasite

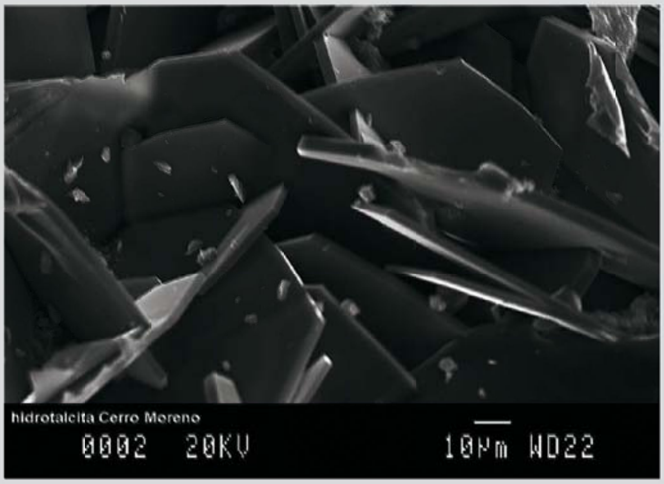
In Las Herrerías volcano, thaumasite appears forming felted, subparallel, divergent aggregates, or as disordered thin crystals, between 5 and 20 micrometers thick, but which are comparatively long, up to 2 cm in length (although usually only of millimetric size) (Calvo *et al.*, 2010), with the prism $\{10\bar{1}0\}$ as the principal face. In some cases, with the scanning electron microscope, we can observe a termination corresponding to the bipyramid, probably $\{10\bar{1}2\}$. It is associated with small crystals of phillipsite-Ca and, less frequently, with gismondine-Ca crystals. It has also been found as relatively compact chalk-like masses on a macroscopic scale, with a slightly silky luster, which is due to the presence of needle-like crystal sections. The outside of these masses appears covered by individual acicular thaumasite crystals, without any other associated minerals. In Cerro Moreno, thaumasite appears as centimetric compact masses, covered by filiform microcrystals. It has occasionally been found in Arzollar volcano too.
In the vacuoles of the basalts of the Campo de Calatrava, thaumasite and ettringite were the last minerals to form. Despite their chemical and probable genetic similarities, these two minerals have not been found directly associated with each other.

Apophyllite-(KOH)

Apophyllite-(KOH) has been found in Arzollar volcano, but is not very common. It appears as thick tabular crystals, single or grouped, in sizes up to 3 mm.



Morphology of apophyllite-(KOH) crystals from Arzollar.



Hydrotalcite as hexagonal plates.
Cerro Moreno Quarry. J. Viñals coll and photo (SEM).

Hydrotalcite. 3 mm FOV. Cerro Moreno Quarry.
J. A. Soldevilla collection and photo.

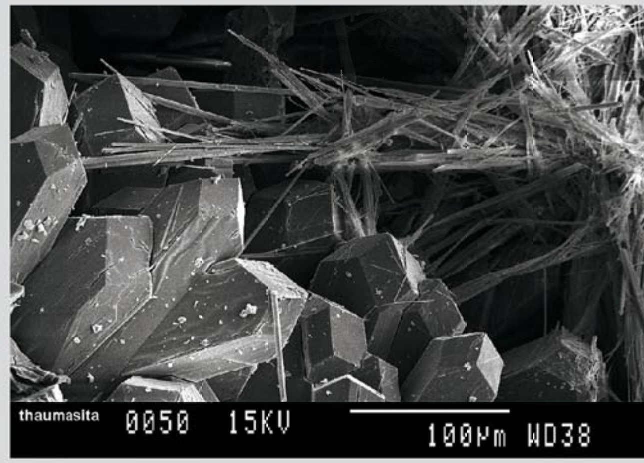
Baryte. 6 mm crystal group. Cerro Moreno.
Miquel Calvo coll. Photo by J. Callén.

Baryte. 8 mm FOV. Las Herrerías Quarry.
J. A. Soldevilla collection and photo.

Curved ettringite crystals with **phillipsite-Ca**.
Las Herrerias Quarry. J. Viñals coll and photo (SEM).

Ettringite. 2 mm FOV. Las Herrerías Quarry.
J. A. Soldevilla collection and photo.

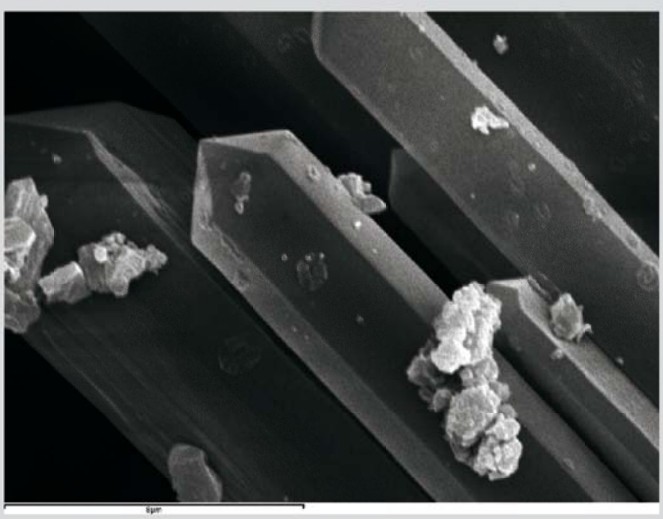
Ettringite. 3.5 mm FOV. Las Herrerias Quarry.
J. A. Soldevilla collection and photo.



Needles of **thaumasite** on **philipsite-Ca**.
Las Herrerias Quarry. J. Viñals coll and photo (SEM).

Ettringite.
0.8 mm FOV.
Las Herrerias Quarry.
J. A. Soldevilla
collection and photo.

Thaumasite. 3 mm FOV. Las Herrerias Quarry.
J. A. Soldevilla collection and photo.



Idiomorphic **thaumasite** crystals. Las Herrerias Quarry.
J. Viñals coll and photo (SEM).

Hydroxylapophyllite. 2 mm crystal aggregate.
Cerro Moreno, Almagro. Joan Viñals coll. Photo by J. Callén.

Apophyllite. 1.2 mm FOV. Arzollar Quarry.
J. A. Soldevilla collection and photo.

The major faces correspond to {001}, with {100} and {111} being present too. These crystals, which may be transparent and colorless or with white colored areas, possibly due to alteration, appear over carpets of phillipsite-Ca crystals.
In some cases microcrystals are very flat, almost lamellar, with {001} being the only visible face, exhibiting its characteristic pearlescent luster. They may occur associated with natrolite.
The Cerro Moreno workings occasionally yield it as subparallel or diverging groups, in rosette or fan shaped habits, formed by lamellar apophyllite-(KOH) microcrystals, colorless and very brilliant.

Tobermorite
Tobermorite has been found so far only in the quarry on Arzollar volcano, and it is not a very common mineral.
It appears either as small white botryoidal scabs, with a felted outer surface and a slightly pearly luster, or as divergent aggregates of needle-like crystals, colorless or white, sometimes with a sheaf-like or hedgehog aspect.
It appears associated with phillipsite-Ca, thomsonite-Ca and gismondine- Ca.

MIAROLITIC MINERALS
These minerals were the first to form, at a relatively high temperature. In some cavities they are the only type of mineral present. In other cavities, later zeolites and other low-temperature hydrothermal minerals were formed, and consequently appear associated with the miarolitic minerals, but they correspond to two different stages.

Perovskite
Hernandez Pacheco (1932) indicates the presence of this mineral, which he considers rare in the volcanoes of Ciudad Real, on a petrographic level. It appear as microscopic grains, which sometimes have contours corresponding to the morphology of individual crystals.
It has also been found occasionally inside vacuoles in the Las Herrerías basalt, as ordered arborescent growths of crystals. It appears associated with magnetite, augite and nepheline.
With this same morphology, it is also found in Arzollar volcano. The perovskite is basically black color, although it frequently exhibits bright iridescence in various colors.

Magnetite
In the Las Herrerías quarry, magnetite appears as octahedral crystals, associated with nepheline and hydroxylapatite. At this site, the crystals have faces with hopper shapes, produced by irregularities in growth.
It is also found in the quarry on Arzollar volcano, associated with nepheline, melilite and hydroxylapatite.

Hydroxylapatite
Hernández Pacheco (1932) indicates the presence of apatite in thin needle shaped crystals, and he considered it a frequent mineral. In Las Herrerías, hydroxylapatite appears as colorless acicular or filiform crystals, formed by the prism $\{10\bar{1}0\}$ and terminated by the pinacoid {0001} and pyramid $\{10\bar{1}1\}$. It appears associated with melilite, nepheline, magnetite and augite in the miarolitic cavities.
It also occurs with the same morphology in Arzollar volcano.

Nepheline
Nepheline is very common in the volcanic area of Ciudad Real, where it is an essential component of the so-called “nepheline basalts”. It occurs as microscopic crystals within the rock mass. In some cases it is so abundant that the color of the basalt is lighter than usual (Hernández Pacheco, 1932).
The lava of Las Herrerías volcano is of nepheline-melilitic type, ie, these two minerals are key components of the rock mass, and they are also abundant inside miarolitic cavities.
The nepheline appears as hexagonal prismatic crystals, under a millimeter in size. The crystals are well defined, formed by the combination of pinacoid {0001} with the $\{10\bar{1}0\}$ prism. Generally they are transparent, with a colorless or greyish tone, though in some cases the outer zone is white, due to incipient alteration. In the miarolitic cavities it is associated with hydroxylapatite and melilite.
The nepheline of Arzollar volcano appears only occasionally inside miarolitic cavities, associated with abundant pyroxene crystals and needles of apatite, but not with melilite. In Cerro Moreno, nepheline is very abundant, but it is not associated with melilite or hydroxylapatite.

Melilite
This mineral was mentioned by Hernández Pacheco (1932) as a component of some rocks, associated with nepheline and calcite. At Las Herrerías quarry, melilite is quite common, associated with nepheline and hydroxylapatite.
It appears as orange tabular crystals, often opaque but sometimes translucent.
The crystals have a thick tabular development with {001} as the main face, with the sides formed by the combination of {110} and {100} faces. When the first of these two faces is proportionally much more developed, the crystals have a square cross section with rounded corners.
In other cases, more equal development of the two faces results in crystals with an octagonal outline, somewhat rounded.
Melilite also appears associated with nepheline and hydroxylapatite in the Arzollar quarry, but it is rather scarce there.

Leucite

In the Arzollar workings, leucite is found very occasionally as granular aggregates composed of highly deformed trapezohedral crystals of a size between 0.1 and 1 mm. The color of these crystals ranges from creamy white to beige. These aggregates have been found filling the miarolitic cavities.

Augite

In the Las Herrerías volcano, augite appears as nodules of up to 10 centimeters in diameter, porous and with cavities, formed by aggregates of olive green microcrystals.
It occurs associated with forsterite crystals. In this same volcanic quarry, augite appears as black crystals up to two millimeters in size at most, slightly translucent, associated with hydroxylapatite and nepheline.

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The crystals have a simple morphology, and are formed by the combination of {100}, which is quite dominant, giving the crystals a tabular habit, with {110} and {$\bar{1}$11}. With this latter form it also occurs in the Arzollar workings.

Forsterite

Olivine of forsterite composition is a common component of the massive rocks of Campo de Calatrava. Sometimes it appears as grains visible to the naked eye. In the quarry of Las Herrerías, forsterite is also found in some cavities, with crystals of tabular appearance, trapped inside a spongy mass of microcrystals of olive green augite. These forsterite crystals are orange in their outermost zone, while inside they have a very pale color, sometimes even almost colorless.

Diopside

In the Arzollar workings, diopside occurs as disordered aggregates of microcrystals coating vesicles inside the basalt, and which were subsequently themselves covered by zeolites. It is also found as relatively well defined prismatic crystals, with a bottle green color, up to 2 mm in length.

Osumilite-Mg

Osumilite-Mg has been found very occasionally in the basalt of Cerro Moreno quarry, as microcrystals of prismatic habit and hexagonal cross section, formed by the combination of the prism {10$\bar{1}$0} with the {0001} pinacoid. It is usually bluish green or yellowish and is internally zoned.

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Photographies of the locality: Agustin Sanz.

Hydroxylapophyllite. 1.5 mm crystals. Cerro Moreno, Almagro. Joan Viñals coll. Photo by J. Callén.

Tobermorite, **natrolite** and **phillipsite**. 1.1 mm FOV. Las Herrerias Quarry. J. A. Soldevilla collection and photo.

Baryte and **magnetite**. 2.1 mm FOV. Las Herrerias Quarry. J. A. Soldevilla collection and photo.

Perovskite. 1.3 mm crystal aggregate. El Arzollar, Almagro. A. Barahona coll. Photo by J. Callén.

Mellilite, **nepheline**, **hydroxyldapatite**. 2 mm mellilite crystals. Las Herrerias. Joan Viñals coll. Photo by J. Callén.

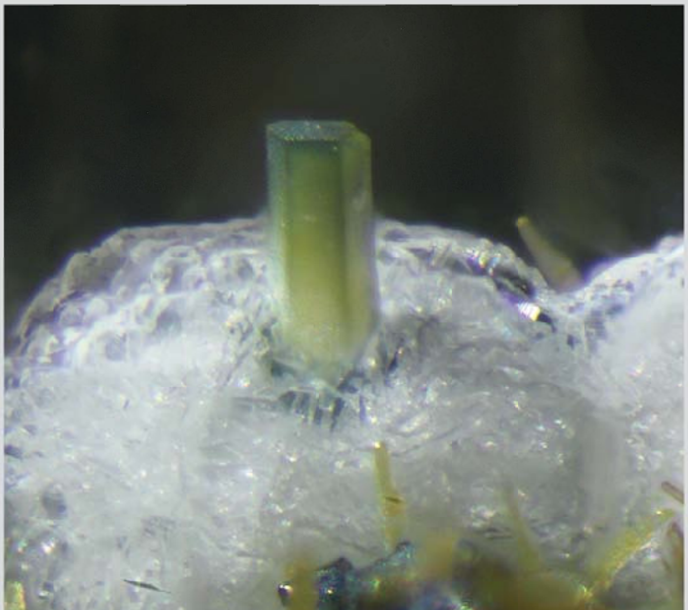
Nefeline and mellilte. 1.7 mm FOV. Las Herrerias Quarry. J. A. Soldevilla collection and photo.

Mellite, **hydroxylapatite**. 1.7 mm FOV. Las Herrerias Quarry.
J. A. Soldevilla collection and photo.

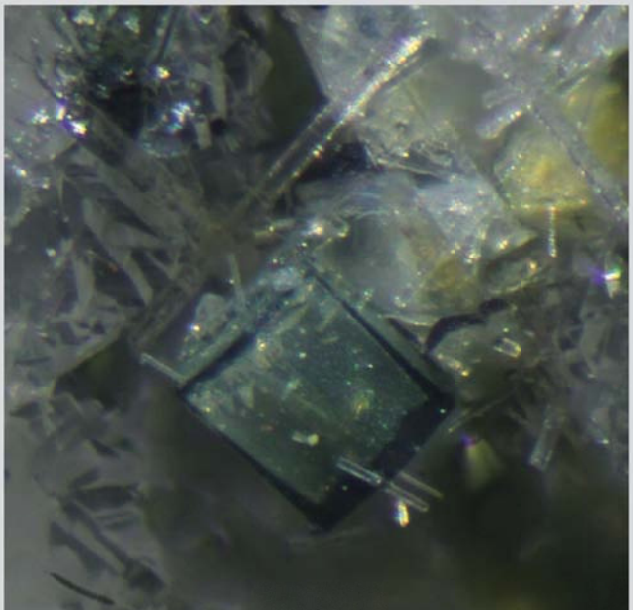
Augite. 1 mm FOV. Las Herrerias Quarry.
J. A. Soldevilla collection and photo.

Forsterite. 3.9 mm FOV. Las Herrerias Quarry.
J. A. Soldevilla collection and photo.

Tobermorite, **diopside** and **phillipsite**. 1,5mm tobermorite spray. El Arzollar. J Viñals coll. Photo by J.Callén.



Osumilite-(Mg). 0,25 mm crystal size.
Cerro Moreno, Almagro. Joan Viñals coll. Photo by J.Callén.



Osumilite Mg. 0,2mm crystal. Cerro Moreno, Almagro.
Joan Viñals coll. Photo by J.Callén.