# VENEZUELAN CAVE MINERALS: A REVIEW

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## RESUMEN

*Minerales de cavidades venezolanas: una revisión*

Se presenta una revisión de los minerales secundarios identificados en cavidades venezolanas, señalando su localidad, una breve descripción de las características del yacimiento y su posible origen. Al igual que en todo el mundo, en cavidades de rocas carbonáticas predominan la calcita, yeso y aragonito, mientras que en cuevas de cuarcitas está el ópalo. Se reportan los siguientes grupos de minerales: carbonatos (con 6 especies), haluros (1), nitratos (2), óxidos-hidróxidos (5), fosfatos (12), silicatos (5), sulfatos (6), arseniatos (1) y minerales orgánicos (1).

Todos los minerales mencionados se forman por reacciones químicas a temperatura y presión ambiente, pero el factor más importante para explicar su diversidad es la disponibilidad de los distintos componentes químicos involucrados, algunos de los cuales pueden provenir de la disolución o meteorización química de los minerales mayoritarios de la roca caja (ejm. carbonato, sílice), otros de constituyentes minoritarios o trazas de la misma roca caja (ejm. sulfato de la oxidación de pirita), algunos del suelo suprayacente (ejm. nitratos), mientras que el fosfato y sulfato provienen principalmente de la descomposición del guano de murciélago.

*Palabras claves*: minerales de cuevas, mineralogía, sulfatos, silicatos, fosfatos, carbonatos

## ABSTRACT

A list of Venezuelan cave minerals and the localities where they have been found is given together with a brief description of the occurrence and its possible origin. Like in other caves from carbonate rocks throughout the world the most abundant minerals are calcite, gypsum and aragonite, while opal is the most common in quartzite caves. The following mineral groups are reported: carbonates (6 species), Halides (1), nitrates (2), oxide-hydroxides (5), phosphates (12), silicates (5), sulfates (6), arseniates (1) and organic minerals (1).

All minerals species reported form at normal environmental temperature and pressure, but the most important factor that explains their diversity is the availability of the constituent chemicals. Some components come from the main bedrock constituents (e.g. carbonate, silica), while others from minor or trace bedrock minerals (e.g. sulfate from pyrite oxidation), or from the overlaying soil (e.g. nitrate), while phosphate and sulfate develop mainly from the decomposition of bat guano.

*Key words*: cave minerals, mineralogy, sulfates, silicates, phosphates, carbonates.

## INTRODUCTION

Once cave passages are formed, secondary minerals may deposit on the internal space. Such forms are called speleothems (*spelaion* = cave, *thema* = deposit) (Urbani, 1967b), so the usual stalactites and stalagmites that strike most cave visitors are speleothems subject of study by cave mineralogists. The first mineralogical work of Venezuelan speleothems is that of William B. White, J. F. Haman & G. L. Jefferson (1963) in Guácharo Cave describing several types of calcite speleothems and also being the first to identify gypsum in several types of occurrences. Since 1967 different studies have been carried out by the author and more recently in cooperation with Jacques Martini and Paolo Forti. The structure of this work follows that of the book *Cave Minerals of the World* (Hill & Forti, 1986). A summary of the reported occurrences is presented in Table 1.

## CAVE MINERALS

### a. CARBONATES

Carbonates are the constituents of the most frequent speleothems in caves opened in carbonate bedrock (calcite or dolomitic limestones or marbles), they appear in many different shapes.

#### Aragonite $CaCO_3$

- *Cueva de Baruta* (Mi.11), Caracas, Miranda. Urbani (1967ac, 1968).

  This is an unique 200 m long "crystal cave" or geode opened in January 1956 during quarry work and very soon vandalized. Aragonite was very abundant as anthodites with transparent or white needles as long as 5 cm, some transformed to dolomite. Chemical analyses show that the aragonite crystals have higher strontium content than adjacent calcite and dolomite speleothems. It is possible that this element promoted the aragonite crystallization (see under dolomite). The bedrock is a dolomitic marble. A photograph of these speleothems is shown in Urbani (1973b, fig. 13 lower part). Chemical analysis of some samples can be seen under dolomite.

- *Cueva La Guairita 2* (Mi.16), Caracas, Miranda. Urbani (1972b, 1980).

  It was found in a single anthodite flower with needles of up to 15 mm long and 1 mm in diameter growing at the very tip of a 1½ cm long and upward calcite helictite.

- *Cueva Cantera Sur de Baruta* (Mi.28), Caracas, Miranda. Urbani (1967c, 1972b).

  Also as a single anthodite flower developed directly on a visible fracture on the dolomitic marble bedrock, with 1½ cm diameter in its base and 2 cm long needles.

- *Cueva Ricardo Zuloaga* (Mi.42), Miranda. Urbani *et al.* (1995b).

  Included in a cauliflower shaped assemblage associated with sepiolite in which the aragonite crystals appear as well formed needles.

- *Cueva de Iglesitas* (Mi.50), Caracas, Miranda.

  As a white powdery and irregular 1-2 mm thick crust of a few tens of $cm^2$ on the surface of an old sediment fill. Crystals are acicular.

- *Cueva La Peonía* (La.2), Lara.

  Very similar to the previous occurrence but on limestone bedrock.

- *Cueva de Tiburcio*, Yaracuy. Pereira Leopoldo (pers. comm., 1982).

  Contains aragonite in centimeter sized anthodites.

- *Cueva sin nombre al sur de Caracas*, Miranda. Hernández Ramón (pers. comm., 1967).

  This is a small "crystal cave" or geode discoveded by R. Hernández and not revisited since then. The internal surfaces are covered with abundant aragonite anthodites.

**Azurite $Cu_3(CO_3)_2(OH)_2$**

- *Cueva de Baruta* (Mi.11), Miranda. Urbani (1967a, 1972b).

Azurite and malachite were found together in a small nest 3 cm in diameter surrounded by calcite crystals on a wall of this "crystal cave". In this locality pyrite is found in the bedrock so it seems quite possible that chalcopyrite could be present and the necessary copper provided from its oxidation.

**Calcite $CaCO_3$**

The most common cave mineral can adopt adopt many different shapes, such as stalactites, stalagmites, coatings and crusts, conulites, coralloids, cups, draperies, flowstone, helictites, moonmilk, cave pearls, rafts, rimstone dams (gours), cave clouds, shelfstone, cave shields and spar. Very few works have been done on calcitic speleothems.

- *Cueva del Guácharo* (Mo.1).

This is the cave with the greater variety of calcite speleothems from Venezuela, but have been little studied. Stalactites, stalagmites, draperies, flowstones, rimstone dams, helictites, cave pearls, spar and cups are common in this cave. Monocrystalline stalactites and helictites were studied by White *et al*. (1963). Some orange to red colored stalactites were studied by White (1981), who found that the colour is due to organic compounds. Stalactites with concentric layers of calcite and detrital clay formed by periodical flooding were reported by Urbani (1969). Small stalactites of up to 3 cm long with coralloid tips were described by Urbani (1973a).

- *Cueva Alfredo Jahn* (Mi.35), Miranda. Urbani (1973a).

Pisolites of different shapes were described, some formed around small rock fragments, pieces of roots and centipedes.

- *Cueva Quebrada Marasmita* (Mi.6), Miranda. Urbani (1973a).

Here there is a rimstone dam with rims that partially cover the pool due to accumulation of raft calcite in one side due to air currents.

- *Cueva de la Discordia 1* (Fa.34), Falcón. SVE (1974a).

This cave shows the best cave shields found in Venezuela.

- *Cueva de la Gruta* (Mi.12) and *Cueva del Refugio* (Mi.30), Miranda. Urbani (1973a).

As conulites 5 to 8 cm deep.

- *Cueva del Cerro Autana* (Am.11), Amazonas. Urbani (1976).

Calcite appears in this cave as a minor phase interlayered with opal and chalcedony.

- *Cueva de Baruta* (Mi.11), Miranda. Urbani (1967c, 1968, 1970).

  As bothroidal shapes with concentric laminae of radial crystals, compenetration twinning forming "lance points", dogtooth spar, flowstone and dripstone.

- *Cueva Walter Dupouy* (Mi.2), Miranda. Urbani (1972a).

  It has meter-sized rimstone dams in an active stream

- *Cueva del cañón de Sorotamia* (Zu.72), Río Socuy. Zulia. Lagarde Joris (pers. comm.)

  This locality shows the best developed cave pearls found in Venezuela. There is a nest with 20 to 30 shiny pearls almost perfectly spherical and with a mean diameter of 2-4 cm.

- *Cueva Los Encantos*, Zulia. Carreño Rafael (pers. comm.).

  In its middle passage and for about 100 m there are large, not active, rimstone dams, they may cover an area of up to approximately 15 m² and 2.5 m deep. In other locations in the cave smaller rimstone dams are also observed. Several conulites of up to 15-20 cm deep and an upper diameter of 8 cm have also been observed in this cave.

**Calcite, var Lublinite $CaCO_3$**

- *Cueva La Milagrosa* (Mo.22), Monagas. Urbani (1977d).

  This variety of calcite coats the walls and ceiling in the main passage of this cave as a soft deposit with external bothroidal shape. The individual lumps are in the scale of 5-10 cm in diameter covering areas of up to 10-20 m² while the thickness varies from a few millimeters to 20 cm. Under the optical microscope and SEM it is seen that such masses are formed by needles some of which perfectly formed, with a few tens of microns long and with an almost constant diameter of near one micron. Another type also has the external form of needles but as small crystals in an *en echelon* pattern. These speleothems originated by water condensation and/or very slow seepage from the wall fractures.

**Dolomite $CaMg(CO_3)_2$**

- *Cueva de Baruta* (Mi.11), Caracas, Miranda. Urbani (1967ac, 1968).

In this "crystal cave" dolomite speleothems are less abundant than calcite and aragonite. One of the samples had a morphology of a lathlike tip and in thin section showed concentric structures with aragonite in its center (about 5% of the total sample). Other specimens did not have aragonite. The insoluble residue of these speleothems is opal. It is believed that dolomite was formed by alteration of aragonite under the influence of seeping water with high magnesium content coming from the dolomitic marble bedrock. A photograph of these speleothems is shown in Urbani (1973b, fig. 13 upper part). This is the second cave locality worldwide in which well ordered dolomite was found. The chemical composition of some samples of this assemblage is as follows:

| ***Minerals*** | ***Mg (%)*** | ***Sr (ppm)*** |
|---|---|---|
| Aragonite | 1.32 | 507 |
| Aragonite | 0.88 | 470 |
| Aragonite | 0.51 | 400 |
| Aragonite, dolomite | 9.00 | 216 |
| Dolomite, aragonite | 13.0 | 302 |
| Dolomite | 13.1 | 59 |
| Calcite | 0.86 | 23 |

- *Haitón de Sabana Grande* (Fa.52), San Luis, Falcón. Urbani (1977a, 1980).

  Found in a moonmilk assemblage over a clay sediment, the material also contains about 40% of micron-sized gypsum crystals. The crystal size of dolomite was below the resolution of the optical microscope and its origin is not clear.

**Magnesite $MgCO_3$**

- *Cueva Quebrada Ocumarito*, Distrito Federal. Urbani (1980).

  This is a 10 m long cave developed along a fault zone in serpentinite bedrock. The mineral fills the multiple fractures of the rock producing a wedging effect that promotes the passage enlargement. The crusts thickness may vary from a few millimeters up to 6 cm thickness.

**Malachite $Cu_2CO_3(OH)_2$**

- *Cueva de Baruta* (Mi.11), Caracas, Miranda. Urbani (1967a, 1972b).

  Already mentioned under azurite.

## b. HALIDES

### Halite NaCl

- *Cueva Alfredo Jahn* (Mi.35), Birongo, Miranda. Forti & Urbani (1996)

  Forms a sub-millimeter gray coating on the walls at the far end of the Chaguaramo Saloon. It is associated with koktaite.

## c. NITRATES

### Nitrammite $NH_4NO_3$

- *Sima Aonda Superior* (Bo.54), Auyán-tepui, Bolívar. Forti (1994).

  Forms a very small patch in a well-aerated and protected niche on the wall of this quartzite cave. The components are believed to come from the decaying organic matter of the surface.

### Sveite $KAl_7(NO_3)_4Cl_2(OH)_{16}.8H_2O$

- *Cueva del Cerro Autana* (Am.11), Amazonas. Martini (1980), Martini & Urbani (1980, 1984), Urbani (1977b).

  This is the first new mineral for science discovered in a Venezuelan cave. It occurs in a quartzite cave where it forms crusts and efflorescences on the walls in patches of about 0.5 to 1 cm thickness and up to a few square meters extent. In some cases it is clearly seen that the forming solutions seeped from the bedding planes. Under the optical microscope and SEM (Urbani, 1977b), the mineral consists of an aggregate of contorted flakes. It is possible that the nitrate, chlorine and part of the potassium, come from the organic matter from the vegetation and soil at the top of the mountain, while the aluminum and potassium come from the weathering of the trace amounts of plagioclase and micas disseminated in the rock. As the solutions are very diluted its formation requires the evaporation of large amounts of water.

## d. OXIDES AND HYDROXIDES

### Goethite a FeO(OH)

- *Cuevas del Cerro María Luisa* and *Cueva de Conejero*, Ciudad Piar, Bolívar. Urbani (1980).

  These caves are developed below the hard lateritic iron crust that covers the surface of the hill. Goethite speleothems are present as centimeter long stalactites, small stalagmites, flowstones and coatings.

- *Sima de la Lluvia de Sarisariñama* (Bo.3), Bolívar. Urbani *et al.* (1976), Urbani (1977c).

  Present as coatings and stalagmites including the largest reported goethite stalagmite in the world with about 3 m height and 1 m diameter.

- *Sima Aonda 3*, Auyán-tepui, Bolívar. Urbani (1996a)

  Crust of a few square decimeters in area and up to 4 cm thick on the wall of the weathered quartzitic bedrock.

### Ice $H_2O$

- *Cuevas de los glaciares de Timoncitos y del pico Bompland*, Mérida. Pérez (1978).

  In 1978 several small caves where visited in those glaciers and ice stalactites were observed. Currently, most of those glaciers have melted.

### Lithiophorite $(Al,Li)MnO_2(OH)_2$

- *Sima Menor de Sarisariñama o Martel* (Bo.2), Bolívar. Urbani *et al*. (1976), Urbani (1977bc).

  Appears in wrinkled and earthy stalactites up to 15 cm long and 20 cm in diameter at its base. It is black, clearly contrasting with the reddish colour of the quartzitic bedrock. A chemical analysis gives the following components in order of abundance: MnO 42.1%, $H_2O$ 8.4%, $Al_2O_3$ 6.2%, $SiO_2$ 5.2%, $Na_2O$ 2.1%, $P_2O_5$ 1.0%, $Fe_2O_3$ 0.2%, LiO2 0.2%, with trace amounts of MgO and $K_2O$.

### Maghemite ? a $Fe_2O_3$

- *Cueva La Milagrosa* (Mo.22), Monagas. Urbani (1977d, 1980).

Appears as crusts of up to 4 mm thickness covering the limestone walls with a shiny and botryoidal shape and near bat guano deposits. A partial chemical analysis shows CaO 15.2%, $Fe_2O_3$ 12.4%, $SiO_2$ 9.8 %, $P_2O_5$ 5.4%, $Al_2O_3$ 4.4 %, with smaller amounts of $Na_2O$, $K_2O$ and MgO (MnO was not determined). The sample is amorphous by X rays but the heated sample studied by P. J. Bridge (Australia) suggests it to be maghemite, possibly by alteration of goethite which is also probably present.

**Mn-Fe (Amorphous oxides-hydroxides)**

- *Cueva El Santuario*, Trujillo. Buzio & Forti (1994).

  Forms black pisolites in a nest of more than a hundred of them, mainly of 3-5 mm in diameter but one reached 3 cm. The origin of such rare speleothems is related to the reducing and acid environment of the forest soil surrounding this limestone cave, which allows for the migration of Fe and Mn in the reduced state and their precipitation as chelated-metallic compounds in the aerated cave conditions.

- *Cueva Alfredo Jahn* (Mi.35), Miranda. Forti & Urbani (1996).

  In this cave two different occurrences of these compounds are found: There are millimetric-sized black pisolites having iron is the major constituent element and lesser amounts of manganese, with up to 30% of organic matter, and with an XRD peak of hydroxyl-apatite. The second occurrence is under the active stream near Salón del Chaguaramo the rock is covered with red to black 1-2 mm thick crusts. They are composed mainly of iron and minor amounts of manganese, also with 20-35% organic matter and minor amounts of mangano-berzelite.

- *Cueva El Samán* (Zu.30), Zulia.

  Has been found in two occurrence types. The first as a 0.5-1.5 mm thick dark-brown to black and shiny coating on the limestone floor and stream clasts on a passage that during the rainy season must be under water. Under the optical microscope it is seen as multilayers. A qualitative EDX analysis shows the presence mainly of Mn, Fe with minor amounts of Al, Si and Ca. The second type is mixed with hydroxyl-apatite and will be explained under this mineral.

- *Cueva Los Encantos*, Fundo Los Encantos, Zulia.

  Same as in the first type of the previous occurrences.

- *Sumidero Los Cantos* (Zu.70), Fundo Los Encantos, Zulia

Appears as 0.5 cm thick black and earthy coating on the limestone bedrock in a place that is under water during the rainy season.

- *Cueva La Peonía* (La.2), Lara

  Same as the previous occurrence but colour is rather reddish and purple.

## e. PHOSPHATES

### Ardealite $Ca(HPO_4)(SO_4).4H_2O$

- *Cueva Ricardo Zuloaga* (Mi.42), Miranda.

  Identified as a constituent of a dusty deposit of decomposed bat guano associated with whitlockite and gypsum.

### Brushite $CaHPO_4.2H_2O$

- *Cueva del Indio* (Mi.24), Miranda. Forti *et al*. (1996).

  Identified in a light orange powder and very light material produced by decomposition of bat guano, associated with gypsum. The material was collected under a calcitic crust in an area previously mined for guano. This and the samples of other minerals of the apatite group from this cave were collected near the contact of the guano material with the dolomitic bedrock.

- *Cueva de San Sebastián o la Gruta de Lourdes* (Ar.3), Aragua.

  Inside a mineralized bat guano deposit as in the previous locality.

- *Cueva Ricardo Zuloaga* (Mi.42), Miranda. Silva (1995).

  Same type of occurrence as the previous locality.

### Carbonate-apatite $Ca_5(PO_4, CO_3)_3$

- *Cueva del Indio* (Mi.24), Miranda. Urbani (1980), Forti *et al.* (1996).

  Also as a powdery material from the decomposition of bat guano.

### Carbonate-fluor-apatite $Ca_5(PO_4,CO_3)_3F$

- *Cueva del Indio* (Mi.24), Miranda. Forti *et al.* (1996).

Same occurrence as carbonate-apatite.

**Carbonate-hydroxyl-apatite $Ca_5(PO_4,CO_3)_3(OH)$**

- *Cueva del Indio* (Mi.24), Miranda. Pallarés & Urbani (1982ab).

  Same occurrence as carbonate-apatite.

- *Cueva de Los Laureles* (Zu.31), Zulia.

  Dark brown and earthy 0.5 cm thick coating on the limestone bedrock. Fresh bat guano is observed nearby. Associated to smaller amounts of chlor-apatite.

- *Cueva de Pardillal* (Ar.15), Aragua.

  As dark-brown crusts and rough centimetric stalactites. Associated with gypsum, hydroxyl-apatite, fluor-apatite, whitlockite and calcite. This cave is inhabited by a large bat colony.

**Chlor-apatite $Ca_5(PO_4)_3Cl$**

- *Cueva del Indio* (Mi.24), Miranda. Forti *et al.* (1996).

  Same as explained under carbonate-fluor-apatite.

- *Cueva de Los Laureles* (Zu.31), Zulia.

  Dark brown 0.5 cm thick coating on the limestone bedrock. Fresh bat guano is observed nearby. Associated to carbonate-hydroxyl-apatite which is the main phase.

**Evansite $Al_3(PO_4)(OH)_6.6H_2O$ (?) Amorphous**

- *Cueva de Urutany 1* (Bo.4) and *Cueva de Urutany 2* (Bo.5), Bolívar. Urbani (1977b, 1980)

  Appears as rough stalagmites (the largest is 60 cm high and 40 cm diameter in its base) and also as coatings and flowstones on the walls of this quartzite cave. Colour is yellow, yellowish brown and reddish with concentric layering and flaky appearance. Under XRD appears mainly amorphous. It is very soft and when exposed for several weeks in the laboratory environment (50-60% relative humidity) it disintegrates at touch. A chemical analysis of this material gave $SiO_2$ 11.0%, $Al_2O_3$ 10.7%, $P_2O_5$ 4.9%, $Na_2O$ 0.6%, $H_2O$ 22.2% and minor amounts of $Fe_2O_3$ and $K_2O$. The remainder, to 100%, is organic matter. Due to the amorphous nature of the mineral its identification is not certain and probably the high silica and organic matter content may be explained by the presence of allophane (hydrous aluminum silicate) and pigotite (organic mineral). The caves develop under a dense forest having a deep organic soil and contain colonies of bats of the family *Phyllostomidae,* which may account for the presence of phosphorous and organic components while Al and Si may be provided by the quartzite weathering.

- *Cueva de Aguapira 9* (Bo.17), Aguapira, Bolívar

  As a flowstone on the inclined floor of the cave with an area of about 1 m². It appears in the field as a resinous material, which when dried is reddish to brown. The surface of the flowstone is covered by many small rimstone dams of 0.5 cm height and with pools of about 1 cm². The identification is not certain and the material may be a mixture of evansite-allophane-pigotite. The cave is small and unlike the Urutany caves, no signs of bats or bat guano was seen, therefore the components needed to form these minerals may come from the decaying vegetation and the weathering of the quartzite which has traces of feldspars and micas.

**Fluor-apatite $Ca_5(PO_4)_3F$**

- *Cueva del Indio* (Mi.24), Miranda. Forti *et al.* (1996).

  Same as explained under carbonate-fluor-apatite.

- *Sumidero Los Cantos* (Zu.70), Fundo Los Encantos, Zulia.

  Appears as 0.5 cm thick light brown crust protruding 1-2 cm from the limestone bedrock wall. Found on the ceiling of the cave in a place that remains as an air-bag at moments of water flood. Appears at the would-be air-water interface above which the rock is coated with calcite, while below it is covered by clay and partially decomposed organic matter. Detrital quartz and illite-mica are mixed with the phosphate.

- *Cueva de Pardillal* (Ar.15), Aragua.

  In a 2 mm thick gray to brown crust associated with calcite, gypsum, hydroxyl-apatite, carbonate-hydroxyl-apatite and whitlockite.

- *Cueva Ricardo Zuloaga* (Mi.42), Miranda.

  Identified as a constituent of a dusty deposit of decomposed bat guano associated with hydroxyl-apatite and gypsum.

**Hydroxyl-apatite $Ca_5(PO_4)_3(OH)$**

- *Cueva del Guácharo* (Mo.1), Monagas. Urbani (1972b, 1980).

  This was the first Venezuelan cave locality where a phosphate was identified. It appears as coatings on calcite flowstones and limestone bedrock in the small passages identified as HI-4, 5 and 6 in SVE (1968). Such passages host have small bat colonies. The crusts are black to dark brown up to 6 mm thickness but usually they are at the scale of 1-3 mm.

- *Cueva del Indio* (Mi.24), Miranda. Urbani (1972b), Forti *et al.* (1996).

  As brown to black 1-3 mm thick crusts directly on the dolomitic bedrock and other calcite speleothems. The cave hosted a large bat population. This mineral and other five phosphates reported in this cave also occur in the contact between bedrock and the guano deposit.

- *Cueva El Samán* (Zu.30), Zulia.

  In one of the farthest northwestern passages of this cave, now the largest in Venezuela, there is an irregular black to very dark brown mass of up to 5 cm thick and covering about 0.5 $m^2$. The XRD pattern is that of a Mn-Fe rich amorphous mineral associated with well-crystallized hydroxy-apatite. Qualitative EDX analyses show the presence of Mn, Fe, Ca, Al, P and Si.

- *Cueva Los Laureles* (Zu.31), Zulia.

  Appears as dark brown to black 1-3 mm thick crusts on the limestone bedrock. Qualitative EDX analysis shows that the external surface is rich in Mn and Fe, but inside only Ca and P were detected. Under XRD the hydroxyl-apatite pattern shows broad peaks suggesting a low crystallinity.

- *Cueva Ricardo Zuloaga* (Mi.42), Miranda. Urbani (1972bd, 1996b), Silva (1995).

  As brown to black 1-3 mm thick crusts on calcite speleothems in "Salón del Arpa" and on the dolomitic marble bedrock. Gypsum is also identifiable but rather than a chemical *in situ*, it comes from the large amount of dust raised by the visitors of this very dry and dusty cave. A detailed study of the fresh to decomposed bat guano is under way and a 3 m deep exploratory pit was excavated and sampled in which this mineral has been identified associated with whithlockite and gypsum.

- *Cuevas La Torre 1 & 2* and *Cueva Narices del Diablo*, Valle de Guanape, Anzoátegui.

As brown 1-1.5 mm thick crusts on calcite speleothems and on the limestone bedrock.

- *Sima del Peñón de Ocumare*, Ocumare del Tuy, Miranda.

  Same as previous occurrence.

- *Cueva del Riíto*, La Aguadita, Churuguara, Falcón.

  Same as previous occurrence but yellowish brown.

- *Cueva de Lizardo o La Cuevita* (Fa.26), Falcón.

  Same as previous occurrence but associated with whitlockite.

- *Cueva de San Sebastián o la Gruta de Lourdes* (Ar.3), Aragua.

  As brown to black and sometimes reddish 1-3 mm thick crusts directly on the calcite bedrock. The mineral is found in the contact between the calcite bedrock and what was the former guano deposit which was exploited as fertilizer.

- *Cueva de Pararille*, Santa Cruz, Churuguara, Falcón.

  As brown to black-brown 2 mm thick crusts covering a 1 m² stalagmitic form found in the higher part of an ascending passage inhabited by a large bat colony with air temperature of 35°C. Under SEM, diatoms are visible and also many filaments (fungus and algae).

- *Cueva de Pardillal* (Ar.15), Aragua.

  As brown to gray 2-8 mm crusts associated with calcite, gypsum, fluor-apatite, carbonate-hydroxyl-apatite and whitlockite.

- *Cueva de Iglesitas* (Mi.50), Miranda.

  As dark brown to black 1-1½ mm thick crust directly on a calcite flowstone. Found in the uppermost passage inhabited by bats.

**Hydroxyl-apatite, chlorian $Ca_5(PO_4)_3(OH, Cl, F)$)**

- *Sima del Peñón de Ocumare*, Miranda.

  Dark brown coating 2 mm thick on calcite flowstone. Related to bat guano.

**Leucophosphite $KFe_2(PO_4)_2(OH).2H_2O$**

- *Cueva de los Culones de Caoma* (DF.10), Distrito Federal. Urbani *et al*. (1995a).

  This is a 30 m long cave in weathered garnet amphibolite. Leucophosphite is found as roughly 0.1 mm sized rounded nodules concentrically interlayered with opal in coralloid fingers. Under the binocular microscope the mineral shows bright yellowish to red colours.

**Struvite $(NH_4)MgPO_4.6H_2O$**

- *Cueva Ricardo Zuloaga* (Mi.42), Miranda.

  Identified as a contituent of a dusty deposit of decomposed bat guano associated with hydroxyl-apatite, whitlockite and gypsum.

**Whitlockite $Ca_9(Mg,Fe)H(PO_4)_7$**

- *Cueva Ricardo Zuloaga* (Mi.42), Miranda.

  As orange brown moist and soft coatings, 5 mm thick and covering small areas of a few square centimeters on the cave walls. Under SEM it appears as an accumulation of 5-10 m m apple-shaped forms. Another type of occurrence is inside a decomposed bat guano deposit associated with gypsum, hydroxyl-apatite, brushite, ardealite and struvite.

- *Cueva de Pardillal* (Ar.15), Aragua.

  Identified in a 5 cm long stalactite with concentric layers associated with gypsum and calcite. Also in dark brown crusts with calcite, gypsum, hydroxyl-apatite, fluor-apatite and carbonate-hydroxyl-apatite.

- *Cueva de Lizardo o La Cuevita* (Fa.26), Falcón.

  As 1-2 mm orange-brown crusts on flowstone with hydroxyl-apatite.

- *Cueva de los Vencejos*, Peñón de las Guacas, Mi.

  Associated with gypsum in a small guano deposit formed by droppings of birds (Swifts) under their nest.

## f. SILICATES

### Allophane (amorphous hydrous aluminum silicate)

See comments under Evansite.

### Chalcedony $SiO_2$

- *Cueva del Cerro Autana* (Am.11), Amazonas. Urbani (1976).

This was the first Venezuelan cave where coralloid opal speleothems were studied. Under thin section crystallized fibrous quartz (chalcedony) are seen intermixed with the opal and minor calcite layers. The speleothems are active.

### Opal-A $SiO_2.nH_2O$

- *Cueva de Baruta* (Mi.11), Miranda. Urbani (1967c, 1972b).

This is the first opal occurrence found in a Venezuelan cave but as a very inconspicuous HCl insoluble residue of dolomite speleothems.

- *Sima de la Lluvia de Sarisariñama* (Bo.3), Bolívar. Urbani (1980).

With a wide variety of coralloid and cauliflower forms of up to several square meters of coverage. Also as metric flowstones mainly covered with coralloid surfaces. The most spectacular forms are soda-straws and stalactites as much as 35 cm long with a diameter of 2.5 cm at the upper part. This stalactitic opal is translucent and glassy in comparison with the usual darker and grayish coralloids. Under SEM all show filament structures suggesting an origin induced by biologic activity (Fig. 1).

- *Sima Mayor de Sarisariñama o Humboldt* (Bo.1), Bolívar. Urbani (1977d).

Same type of occurrence as the previous locality but with rather rare stalactitic forms.

- *Sima Menor de Sarisariñama o Martel* (Bo.2), Bolívar. Urbani (1980).

Same features as Sima de la Lluvia occurrence but here a complete sequence has been documented from soft, wet and dark bacterial mats of up to 25 cm in diameter and 1-3 cm thick on the walls where some seeping water was available, to dryer parts with some small coralloids, to very dry and older parts with well-developed coralloids, suggesting a biologic induced precipitation of the opal. The bacteria were studied by Kunicka-Goldfinger (1982).

- *Cueva del Cerro Autana* (Am.11), Amazonas. Urbani (1976).

  See under chalcedony.

- *Cueva El Abismo* (Bo.7), Bolívar. Urbani (1977b).

  As coralloid and cauliflower forms.

- *Sima Aonda Superior* (Bo.54), Bolívar. Forti (1994).

  Mainly as coralloid forms, some of several square meters in area. Here the study of a thin section of a coralloid reveals the presence of former living beings that also suggests a biologic origin.

- *Sima Aonda* (Bo.8), Bolívar. Urbani (1996ac).

  At the caves of the Aonda Platform opal coralloids are always more frequently found near the entrances in the penumbra zone with algae covering parts of the bedrock. Those coralloids are the ones that show more abundant filament structures under SEM (Fig. 2, a,b,c,d), but they also also occur in samples collected deeper inside the caves (Fig. 2,e,f). One SEM image (Fig. 2f) shows a tube structure which suggests that the opal precipitaded around a filament when the organism was alive. Similar structures have been recently found related to the deposition of iron, manganese and gold (Ghiorse & Hirsch, 1979; Bischoff *et al*., 1992).

- *In all other caves explored in the Precambrian quartzites of the Roraima Group*: Kukenán, Chimantá, Urutany, Aguapira, Tramen, Roraima, Yuruaní, Auyán-tepui. Bolívar and Amazonas. Lagarde J. & C. Galán (pers. comm.).

  As coralloid speleothems. Under SEM all samples viewed show numerous organic structures, usually filament-shaped, suggesting a biologic induced origin.

- *Most caves in sandstones of the Tertiary Mirador Formation, Páramo del Tamá and Fila de Capote*, Táchira-Apure: Cueva del Loto (Ap.1) and others. Urbani (1996c), González Freddy (pers. comm.).

  As millimeter-sized rough coralloids, mainly near the entrances of the caves (Fig. 3).

- *Cueva de los Culones de Caoma* (DF.10), DF. Urbani *et al*. (1995a).

  Found as 0.5-1.5 cm long coralloids developed in a weathered garnet-amphibolite. See under leucophosphite.

**Palygorskite $(Mg,Al)_2SiO_4O_{10}(OH).4H_2O$**

- *Cueva Las Úrsulas* (Mi.47), Miranda. Urbani (1975ab).

As 1 mm thick leathery sheets and crusts on the walls and fractures. This cave developed along a joint in quartz-mica-albite-schists. The sheets are light brown but also reddish due to iron-oxide staining. They are flexible and associated with minor amounts of calcite.

**Sepiolite $Mg_4Si_6O_{15}(OH)_2.6H_2O$**

- *Cueva Ricardo Zuloaga* (Mi.42), Miranda. Urbani *et al*. (1995a).

Appears in an elongated deposit following a fracture in the ceiling of the cave. The mineral shows a cauliflower-shaped deposit in a 1 m long section and about 3 cm wide and 1-1.5 cm thick. It is soft, humid and plastic. By XRD it appears with low-crystallinity. Qualitative EDX analysis shows the presence of Si, Ca and Mg and the sample when heated to 1200°C is transformed to diopside (Ca, Mg-pyroxene). Ranging out from the moist to drier and older parts of the occurrence sepiolite becomes more crystalline and becomes associated with increasing amounts of aragonite.

## g. SULFATES

**Aluminite $Al_2SO_4(OH)_4.7H_2O$**

- *Cueva del Indio*, Pipe, D.F.

It occurs as a 4 mm thick white and chalky efflorescence on the wall of a small tectonic cave opened on quartz-feldspar metasandstone and metaconglomerate bedrock.

**Ammonium-jarosite $(NH_4)Fe_3(OH)_3(SO_4)_2$**

- *Cueva Alfredo Jahn* (Mi.35), Miranda. Forti & Urbani (1996).

This mineral is present in light-blue spots on the marble wallrock of the Chaguaramo Saloon, it has millimetric thickness and mixed with hydroxyl-apatite. It is likely that the ammonium required for this mineral and for koktaite is supplied by organic matter carried by the water into the cave from the soil of surrounding forest.

**Bassanite $CaSO_4.½H_2O$**

- *Cueva de San Sebastián o la Gruta de Lourdes* (Ar.3), Aragua.

  Found on top of shale fragments from a collapse inside the middle level of this cave opened in Paleocene limestones. Looks white to slightly brown efflorescences of up to three mm thickness, soft and dusty, no traces of gypsum were found. This level of the cave is very dry and shows temperatures up to 28°C. The finding and analysis took place in 1983 but in 1996 only gypsum was found in the same spot, suggesting that bassanite formed directly in this dry environment and latter hydrated to gypsum.

**Epsomite $MgSO_4.7H_2O$**

- *Cueva de la cantera Sur de Baruta* (Mi.28), Miranda. Urbani (1972b, 1974).

  Shows very delicate white fibrous and powdery efflorescences one cm thick covering areas of several square decimeters in very dry areas near the cave entrance. The bedrock is dolomitic marble.

- *Cueva El Ermitaño* (La.1), Lara. Urbani (1967a, 1972b, 1974).

  Found in two cm thick crusts of massive epsomite with coarsely fibrous nature and transparent crystals. The surface is covered by a white powdery mineral identified as hexahydrite produced by the *in situ* dehydration of epsomite.

**Gypsum $CaSO_4.2H_2O$**

- *Cueva del Guácharo* (Mo.1), Monagas. White *et al*. (1963), Urbani (1967a).

  This was the first Venezuelan cave where this common cave mineral was identified by White *et al*. (1963). This mineral occurs in a very wide variety of morphologies of white to transparent crystals forming flowers, frostworks, needle-like crystals, cotton surfaces, cockscomb stalagmites, crusts on walls and ceilings making up sparkling passages, and extraordinary "hair" hanging more than 3 m that can be moved by air blown onto them.

- *Cueva Cruxent* (Mi.37), Miranda. Urbani (1967a).

  Found in several places of the main passage as gray-colored crusts of up to one cm thick with perpendicular fibers.

- *Cueva del Indio* (Mi.24), Miranda. Urbani (1972b), Forti *et al.* (1996).

Here two types of occurrences are found, one is as very rare layers 1-2 cm thick of almost transparent fibers, the other, more common one, is as white to yellowish powdery material associated with brushite and minerals of the apatite group. Both occur inside a decomposed bat guano deposit which was exploited for fertilizer.

- *Cueva La Peonía* (La.2), Lara. SVE (1974b).

  Appears as centimetric sized flowers.

- *Cueva del Peñón del Diablo* (DF.12), Distrito Federal. Urbani (1980).

  As small efflorescences on the walls near the entrance. The cave is developed in calcitic marble with visible pyrite crystals.

- *Cueva El Ermitaño* (La.1), Lara. Urbani (1972b, 1974).

  As small millimeter-sized white crusts on the walls.

- *Cueva pequeña de la isla El Saco*, Mochima, Sucre.

  Same as previous occurrence.

- *Cueva La Milagrosa* (Mo.22), Monagas. Urbani (1977d).

  As efflorescences up to 2 mm thick at prominent high evaporative places of the bedrock. Colour may vary from transparent to reddish-colored by iron oxides. Individual crystals are about 0.5 to 0.05 mm. The cave opens in the Late Cretaceous black limestones of the Querecual Formation with high pyrite content.

- *Cueva Ricardo Zuloaga* (Mi.42), Miranda. Urbani (1972b), Silva (1995).

  As the most abundant mineral related to a guano deposit and found in light-colored powdery masses and dust. Associated with phosphates.

- *Cueva de San Sebastián o la Gruta de Lourdes* (Ar.3), Aragua.

  Same as the previous locality.

- *Haitón de Sabana Grande* (Fa.52), Falcón. Urbani (1977a).

  Part of a moonmilk assemblage as small crystals of 10-30 m m (40%) associated with dolomite (55%).

- *Sima Mayor de Sarisariñama or Humboldt* (Bo.1), Bolívar. Urbani (1980).

Crusts of up to 2.5 cm thick with transparent to white fibers perpendicular to the cave walls.

- *Sima Aonda Superior* (Bo.54), Bolívar. Forti (1994).

  Same as previous occurrence.

- *Gruta de los Morrocoyes*, Aragua de Maturín, Monagas. Urbani (1996d).

  As crusts of up to 0.5 cm thick, white and relatively hard. Also associated in trace amounts with hexahydrite. The bedrock are subarkoses of the San Juan Formation (Late Cretaceous).

- *Cueva de Iglesitas* (Mi.50), Caracas, Miranda.

  As a 1-2 mm thick powdery and irregular crust on the vertical wall of a 3 m trench on a clay-silt sediment fill formed about 15 years ago (30% smectite, 30% kaolinite, 25% illite-mica, 15% quartz).

- *Cueva de Pardillal* (Ar.15), Aragua.

  Appears in small stalactites and millimetric wall coatings associated with calcite, hydroxyl-apatite, carbonate-hydroxyl-apatite, fluor-apatite and whitlockite.

**Hexahydrite $MgSO_4.6H_2O$**

- *Cueva El Ermitaño* (La.1), Lara. Urbani (1974).

  As an *in situ* dehydration product of epsomite in this very dry cave.

- *Gruta de los Morrocoyes*, Aragua de Maturín, Monagas. Urbani (1996d).

  White and soft eflorescences of 5 mm thick with fibers perpendicular to the cave wall. Since no traces of epsomite have been found, it is assumed that the mineral formed directly under a highly evaporative environment and not as a dehydration product of epsomite as in the previous locality. It is associated with traces of gypsum. The bedrock are subarkoses of the San Juan Formation (Late Cretaceous) with traces of pyrite in some siltstone-shaly interlayers.

**Koktaite $(NH_4)_2Ca(SO_4)_2.H_2O$**

- *Cueva Alfredo Jahn* (Mi.35), Miranda. Forti & Urbani (1996).

Appears mixed with hydroxyl-apatite and halite in pale-gray spots on the marble bedrock. As for the source of the required ammonium see the comment under ammonium-jarosite.

## h. ARSENIATES

### Mangano-berzelite $(Na,Ca)_2(Mg,Mn)_2(AsO_4)_3$

- *Cueva Alfredo Jahn*, Miranda. Forti & Urbani (1996).

This is the first report of this mineral in a cave environment and is found in red to reddish-brown 1-2 mm thick coatings on the limestone bedrock under the influence of an active stream. It is associated with amorphous Fe-Mn oxide-hydroxides. The provenance of arsenic is unknown.

## i. ORGANIC MINERALS

### Pigotite

See comments under Evansite.

## j. RELATED FORMS

### Mud and sand formations

- *Cueva del Guácharo* (Mo.1), Monagas.

"Mud and sand castle" stalagmites have been observed in the Gran Salón del Derrumbe from El Guácharo cave.

- *Cueva de Baruta* (Mi.11), Miranda. Urbani (1970).

Inside a predominantly sandy deposit that fills one of the passages there are rounded concretions forming grape-shaped accumulations. The cementing material is calcite, which includes detritic quartz, microcline, muscovite, plagioclase, opaque and clay minerals.

### Clay vermiculations

- *Cueva del Pio* (Mi.22), Miranda. Urbani & Pereira (1970), Hill & Forti (1986: 160), Hedges (1993: 4).

  This cave showed the best vermiculations observed in Venezuela, now completely vanished due to touching and rubbing by thousand of persons that visit the cave annually. They were of the hieroglyphic type.

- *Sima del Naranjo* (Mo.41), Monagas. Lagarde Joris (in Hedges, 1993:5)

  Here areas of about 0.5 m² are covered by hieroglyphic vermiculations very near oil-bird (*Steatornis caripensis*) nests.

- *Cueva Ricardo Zuloaga* (Mi.42), Miranda.

  Irregular millimetric to centimetric sized hieroglyphic and leopard's spots types of vermiculations covering several square meters are found on the wallrock at the lower entrance of the cave. The material is composed of clay (illite-mica), some gypsum and green algae.

### Rootsicles

- *Cueva de La Guairita 2* (Mi.16), Miranda

  Plant roots have penetrated the first section of this small cave ataching themselves to the subvertical wallrock; subsequently they were covered by calcite. Since the original root has decayed what remains are pipe-shaped casts attached to the wall. The external diameter varies from 1 to 3 cm while the internal hole is less than 1 cm.

### Carbide related formations

- *Cueva de la Brújula* (Mi.1), Miranda

  This is a cave with many calcite stalactites and flowstones but now mostly inactive and in the process of degradation. During one of the 1965-1966 visits calcium carbide was dumped on the floor of the innermost part of the cave, in 1995 on such dump were observed two irregular 1.5 cm high vertical calcite fingers 3-6 mm in diameter. Under SEM the surface appears like a smooth polygonal pavement (Fig. 4, a,b), while at a broken surface it looks like dogtooth spar crystals of micrometer size (Fig. 4,c,d).

**Guano-fire materials**

- *Sima Fumarola de la isla de Monos* (An.5), Anzoátegui. Galán & Galán (1983).

  Combustion of bat guano started in 1977 with emission of "smoke" at the upper entrance of the cave which was mainly visible during the rainy season. A year later when the cave was visited, at a depth of 0.5 m in the former bat guano deposit the temperature was above 100°C. The residual material was identified as margarite and gypsum.

- *Cueva del Peñón de las Guacas o de los Carraos* (Mi.14), Miranda.

  Here a bat deposit also burned leaving irregular slags masses of up to 15 $cm^3$. The material is very light and porous with a metallic luster and iridescent colors. It is amorphous under XRD.

## MINERALS IN ARTIFICIAL CAVITIES

**Aragonite $CaCO_3$**

- *Túnel 1 de la Quebrada Mapurite*, Distrito Federal.

**Chalcanthite $CuSO_4.5H_2O$**

- *Túnel 3 de la Quebrada Mapurite*, Distrito Federal. Urbani (1980).
- *Túnel de Aroa*, Yaracuy. Urbani (1980).
- *Túnel 1, 2 y 3 de Santa Isabel*, Guárico.
- *Túnel de Uria*, Distrito Federal.

**Calcite $CaCO_3$**

- *Túnel de Carrizal*, Miranda.
- *Túnel 1 del Viaducto 1*, Caracas-La Guaira Highway, D.F.

  As white stalactites of up to 52 cm long with incipient stalagmitic growth. Some other stalactites that grow on ventilation pipes and iron reinforcements are reddish dark-brown and have about 75% calcite, 15 % quartz and 10% illite-mica, the last two minerals of detritic origin. The colour is due to a high iron content as suggested by the increase in the XRD background between 10 and 25°2q under Cu radiation.

- *Túnel 2 de Santa Isabel*, Guárico.
- Also in many highway and old railroad tunnels.

**Epsomite $MgSO_4.7H2O$**

- *Túnel de Uria*, Distrito Federal. Urbani (1980).
- *Túnel 3 de Santa Isabel*, Guárico.

**Fe rich (amorphous oxide-hydroxides)**

- *Túnel 1, 2 y 3 de Santa Isabel*, Guárico.

  Preliminary mossbauer spectroscopy data allows its identification as goethite.

- *Túnel de Aroa*, Yaracuy.

**Goethite a FeO(OH)**

- *Túnel del Junko Country Club*, Distrito Federal. Urbani (1980).
- *Túnel 1, 2 y 3 de Santa Isabel*, Guárico.

**Gypsum $CaSO_4.2H_2O$**

- *Túnel de Uria*, Distrito Federal.

**Hematite a -$Fe_2O_3$**

- *Túnel 1 del Viaducto 1*, Caracas-La Guaira Highway, D.F.

**Magnetite $Fe_3O_4$**

- *Túnel 1 del Viaducto 1*, Caracas-La Guaira Highway, D.F.

**Malachite $Cu_2CO_3(OH)_2$**

- *Túnel 3 de Santa Isabel*, Guárico.
- *Túnel de Aroa*, Yaracuy.

**Melanterite $FeSO_4.7H_2O$**

- *Túnel de Aroa*, Yaracuy.
- *Túnel de Uria*, Distrito Federal. Urbani (1980)

**Mn rich (amorphous oxide-hydroxides)**

- *Túnel 2 de Santa Isabel*, Guárico.

**Pickeringite $MgAl_2(SO_4)_4.22H_2O$**

- *Túnel de Uria*, Distrito Federal.
- *Túnel 3 de Santa Isabel*, Guárico.

**Rozenite $FeSO_4.4H_2O$**

- *Túnel de Aroa*, Yaracuy.

**Siderotile $FeSO_4.5H_2O$**

- *Túnel 3 de Santa Isabel*, Guárico.
- *Túnel de Aroa*, Yaracuy.

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