

## MINERALOGICAL RECONNAISSANCE OF CAVES FROM MALLORCA ISLAND

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### Resum

S'han fet prospeccions des d'un punt de vista mineralògic a divuit cavitats de l'illa de Mallorca. Han estat identificats, mitjançant anàlisis de difracció de raigs-X, infraroigs, tèrmics i microscopia electrònica (SEM), 16 minerals que s'engloben dins de quatre grups químics diferents. La calcita ha estat l'únic mineral present a totes les cavitats prospeccionades. En espeleotemes de quatre coves diferents s'ha identificat aragonita, guix i hidroxilapatita. Endemés, també han estat identificats alguns altres minerals dels grups dels carbonats, fosfats i silicats, presents en forma de crostes, cristalls diminuts o masses terroses. Els mecanismes responsables de la deposició mineral en les coves de Mallorca són: (i) precipitació a partir de l'aigua de percolació, (ii) precipitació en la zona de mescla (aigua dolça – aigua marina), (iii) reacció entre la roca encaixant i diversos espeleotemes, i les solucions enriquides en fosfats procedents del guano de les rates pinyades, i (iv) transició de fases minerals.

Des del punt de vista de la mineralogia, la Cova de sa Guitarreta i la Cova de ses Rates Pinyades s'han confirmat com a dues de les coves més destacables; cada una d'elles presenta vuit autèntics minerals de cova. L'associació de fosfats que contenen és diversa i interessant.

### Abstract

Eighteen caves on the Mallorca Island were investigated with respect to their mineralogy. Sixteen minerals, divided into four chemical groups, were identified and described using X-ray diffraction, infrared, thermal, and scanning electron microscope analyses. Calcite is the only mineral found in every sampled cave. Aragonite, gypsum, and hydroxylapatite occur in speleothems from four different caves. In addition, a few other carbonates, phosphates, and silicates were identified in crusts, minute crystals, and earthy masses. The mechanisms responsible for deposition of minerals in the Majorcan caves are: (i) precipitation from percolating water, (ii) precipitation in the freshwater/seawater mixing zone, (iii) reaction between the bedrock and various speleothems, and the phosphate-rich solutions derived from bat guano, and (iv) mineral phase transition.

Cova de sa Guitarreta and Cova de ses Rates Pinyades were confirmed to be two outstanding cavities with respect to their mineralogy, both hosting eight true cave minerals. Their phosphate association is diverse and interesting.

## Geographic and geologic setting

The island of Mallorca is located in the western Mediterranean Sea. The island is the largest and the most central in the Balearic Archipelago. From a karstic point of view, the island is divided into four main physiographic provinces. These are the Mesozoic limestone units of Serra de Tramuntana, Serres Centrals, Serres

de Llevant, and the Marines de Migjorn i de Llevant, which corresponds to the Upper Miocene carbonates (Figure 1). All sampled caves are shown in Table 1 under their corresponding physiographic unit.

*Serra de Tramuntana* forms a NE-SW-oriented medium-high mountain range in the northwestern part of the island and consists mainly of Mesozoic rocks (including thick limestone beds). The province is famous for its karren fields, deep canyons, and vertical caves.

*Serres Centrals* occurs in the central part of the island and includes the elevated carbonate hills of Jurassic age. Within this unit, a number of medium-size

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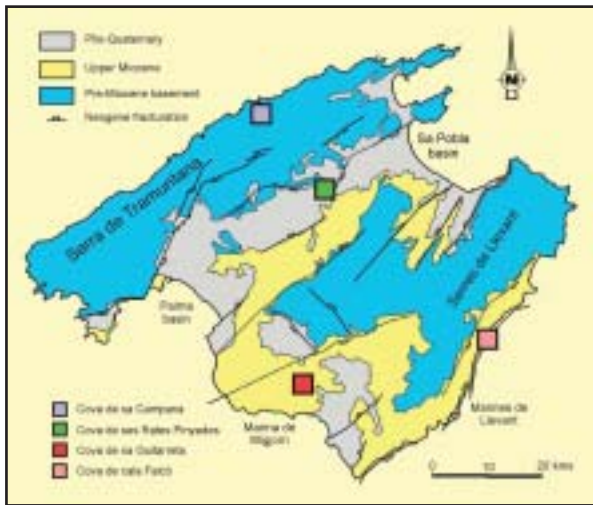


Figure 1: Geological map of Mallorca with the location of the most important caves.

Figura 1: Mapa geològic de Mallorca amb la localització de les coves més importants.

caves were explored and mapped, the most important of them being Cova de ses Rates Pinyades.

*Serres de Llevant* are the heights in the eastern part of the island that are composed of Mesozoic deposits that experienced the same alpine tectonic influence as those in the *Serra de Tramuntana* unit. The topography, however, of *Serres de Llevant* is less rugged. The karst (with very few exceptions) shows an inconspicuous development due to the predominance of dolomites and marls.

*Marines de Migjorn i de Llevant* unit, is build up of post-orogenic Upper Miocene tabular limestones and calcarenites deposits (POMAR *et al.*, 1990). This unit fringes the *Serres* along the southern and eastern lowlands of the island. Ten of the sampled caves have developed within this unit.

Aspects concerning the karst geography and geology of Mallorca Island have been described by COLOM

(1975), FORNÓS *et al.* (1986/87), GINÉS & GINÉS (1989), RODRÍGUEZ-PEREA & GELABERT (1998), SERVERA (1995), and GINÉS (1995b). In addition, the stratigraphy and structure of Mallorca have been outlined in detail by GELABERT *et al.* (1992), FORNÓS & GELABERT (1995), and FORNÓS *et al.* (2002).

## Caves and types of speleothems

Eighteen caves were investigated. Ten of these caves were formed in the Upper Miocene calcarenites. Eight of the other investigated caves are developed in Mesozoic limestones (see Table 1). From a speleogenetic point of view, GINÉS (1995b) and GINÉS & GINÉS (1987) divided the Majorcan caves and shafts into four categories: vadose shafts, vadose, phreatic, and littoral caves. In the present study, the majority of speleothems investigated were collected from caves assigned to the littoral category.

All types of speleothems formed by dripping, flowing, and seeping water (stalagmites, stalactites, shields, flowstones, crusts, helictites, eccentrics, etc.) are well-represented throughout most of the cavities in the Mallorca Island (GINÉS, 1995a). In addition, the subaqueous speleothems, in particular the so-called phreatic overgrowths, are abundant. These phreatic overgrowths are extremely important in deciphering Mediterranean sea level changes over the last 300,000 years (TUCCIMEI *et al.*, 2000; VESICA *et al.*, 2000; FORNÓS *et al.*, 2002; GINÉS *et al.*, 2003).

Earlier studies pointed out that most of the common speleothems are composed of calcite and aragonite (POMAR *et al.*, 1979; GINÉS *et al.*, 1981). Scanty occurrences of gypsum have also been identified (GINÉS, 1995a). The main goal of this study is to investigate the less spectacular crusts and earthy masses. In searching for phosphates, special attention was paid to those speleothems that were partly or totally covered by bat guano.

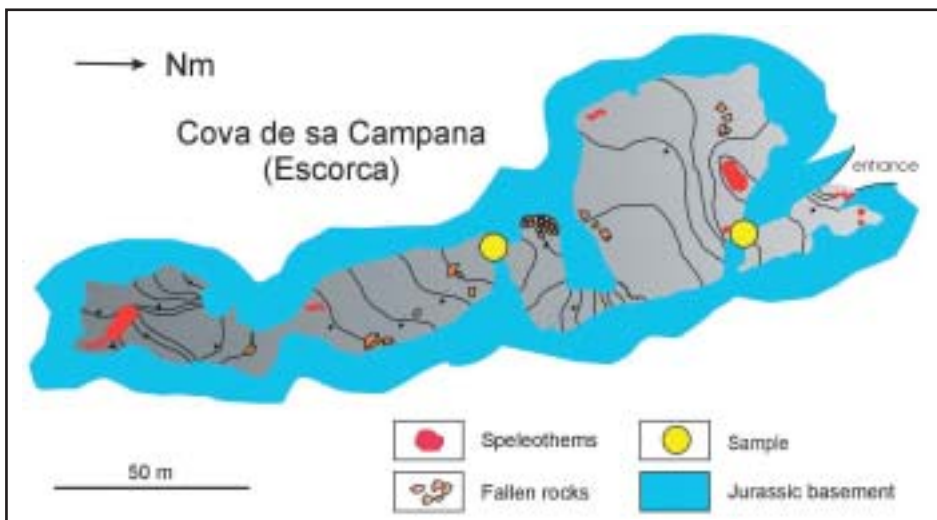


Figure 2: Map of Cova de sa Campana.

Figura 2: Topografia simplificada de la Cova de sa Campana.





## Analytical protocol

All collected samples (40) received a macroscopic characterization and afterwards were examined with the binocular microscope. The identification of minerals was primarily done by means of X-ray diffraction (XRD). Air-dried, whole-speleothem XRD samples were prepared from ground (< 38  $\mu\text{m}$  size) material and run on a Siemens D5000 diffractometer. Diffracted-beam-monochromated Cu K $\alpha$  was used (40 kV, 30 mA). Digitally recorded patterns collected between 3° and 80° 2 $\theta$  (step size of 0.04° 2 $\theta$  and count rate of 2 to 4 second/step) were analyzed with the EVA software (version 7.0.0.1). Silicon (NBS 640b) was used as the internal standard. The overall results of the XRD analyses are tabulated in Table 1 and the representative XRD patterns are shown in several figures throughout the paper.

The phosphate samples were further investigated by means of the infrared (IR) technique using a Bruker IFS 66 instrument in order to better distinguish between various types of phosphates.

For scanning electron microscope (SEM) observations, freshly fractured speleothem fragments or hand-picked aggregates were gold-coated. SEM investigations were made on a JEOL JSM 5510 LV equipped with an energy dispersive spectrometer.

Differential thermogravimetric analyses (DTG) were performed on a Netzsch STA 409 EP instrument, heating about 20 mg of sample up to 1000°C at 10°C/minute.

## Results and discussions

### CARBONATES

Calcite is the only mineral found in every investigated cave, making up the bulk of most of the speleothems. Aragonite is plentiful in Cova de sa Campana



Figure 4: Dolomite crust in Cova de sa Guitarreta (Llucmajor).

Figura 4: Crosta de dolomita en la Cova de sa Guitarreta (Llucmajor).

and Coves de Campanet, but is restricted mainly to the erratic speleothems (helictites and eccentrics). Some of the fossil or recent phreatic overgrowths from Cova del Dimoni and Cova des Pas de Vallgornera are aragonitic (GINÉS, 1995a; TUCCIMEI *et al.*, 2000; FORNÓS *et al.*, 2002). No further details are given for calcite and aragonite due to their common appearance in the cave environment.

Hydromagnesite was identified solely along two narrow, slightly ventilated passages from Cova de sa Campana (Figure 2) where the calcite coralloids are tipped with a loose, dull white, powdery moonmilk. The identification of hydromagnesite as the principal constituent of the moonmilk is based on XRD analyses (Figure 3). The X-ray peaks are sharp indicating that the material is well-crystallized. The Cova de sa Campana hydromagnesite, however, is very fine grained and no euhedral crystals were visible under the SEM.

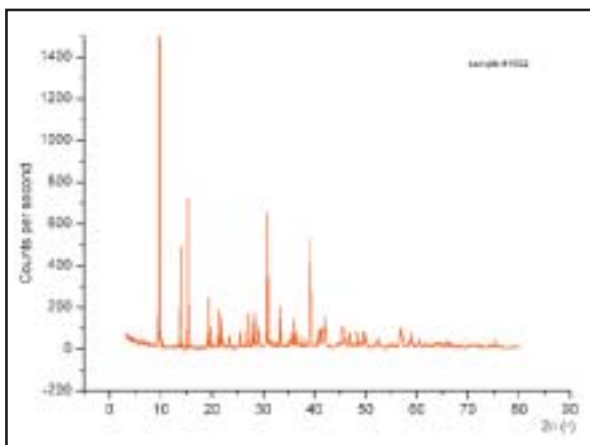


Figure 3: Powder pattern of hydromagnesite moonmilk from Cova de sa Campana (Escorca).

Figura 3: Difractograma de raigs-X corresponent a "moonmilk" de hidromagnesita de la Cova de sa Campana (Escorca).

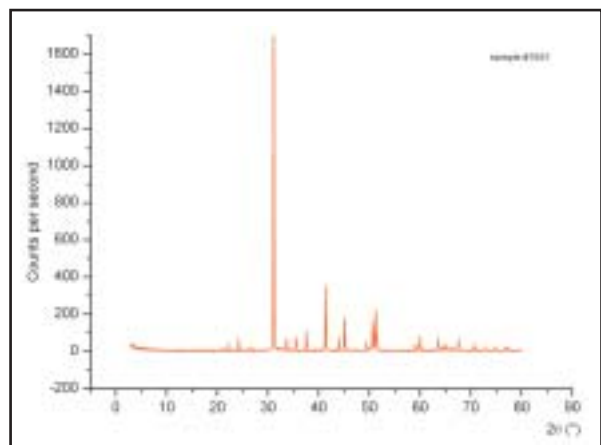


Figure 5: X-ray diffraction pattern of dolomite.

Figura 5: Difractograma de raigs-X de dolomita.

The presence of hydromagnesite in this cave fits into the depositional sequence of carbonate minerals proposed by LIPPMANN (1973), in which, after calcite precipitation, the Mg/Ca ratio increases and hydromagnesite is deposited from Mg-rich solutions. This fact suggests dolomitic rocks occur within the carbonate sequence hosting the cave.

At two different locations within Cova de sa Guitarreta, millimeter and sub-millimeter chalky crusts covering either the bare bedrock or some of the fallen limestone blocks were identified (Figure 4). Occasionally, these crusts are unevenly covered by a brown dust. The XRD investigations indicated the presence of dolomite (Figure 5), a rather common rock type, but a very rare secondary cave mineral (ONAC, 2004). As the host rock of the cave is slightly dolomitic (POMAR, 1991), both theories for dolomite deposition, i.e., direct precipitation from Mg-rich solutions or alteration of bedrock (reviewed by HILL & FORTI, 1997) are applicable. Since the amount of percolating water is little and taking into consideration the high values for temperature (+22°C) and humidity (100%) (MIR, 1974), we suspect the second pathway to be responsible for the formation of dolomite crusts in this cave.

In Cova de ses Rates Pinyades, directly overlying the carbonate bedrock, a millimeter-size white-ochre crust formed under a guano-rich layer. The XRD patterns indicated the material to be composed of brushite and monohydrocalcite. To date, monohydrocalcite has been documented from only a few localities worldwide. In most of these localities, monohydrocalcite was precipitated from aerosols (HILL & FORTI, 1997, and the reference cited therein). Given the cave setting under which our sample formed, such a genetic scenario is not probable. Monohydrocalcite deposition could have been favored by the presence of organic matter that acted as nucleation centers as proposed by POLYAK *et al.* (1994).

## SULFATES

Gypsum is the only sulfate mineral identified in four caves from Mallorca (Table 1). In two of the caves, gypsum is intimately associated with guano deposits. The gypsum forms unspectacular friable nodules or ochre moonmilk paste (within the guano accumulation) in Cova de sa Guitarreta and white efflorescences on the upper surface of a dry, highly decomposed bat guano deposit in Cova de ses Rates Pinyades. At both locations, gypsum seem to be a by-product of bat guano leaching.

In Cova des Drac (Es Rafal des Porcs, Santanyi) gypsum occurs on the floor and walls as delicate white cotton balls (a few millimeters in diameter) (Figure 6). Using a binocular microscope, one can see tiny acicular to fibrous crystals making up these balls. Since this speleothem form is found in the middle part of a big hall that has a natural opening in the ceiling, a sea-spray origin for the sulfate anion is suggested. Grey-bluish crusts (approximately 0.6 cm in thick) cover the floor and limestone blocks in Cova de Cala Falcó (Figure 7), a marine-karstic cave located in Manacor (GINÉS, 1995b)



Figure 6: Gypsum balls in Cova des Drac (Es Rafal des Porcs, Santanyi).

Figura 6: Nuclis esferoïdals de guix en la Cova des Drac (Es Rafal des Porcs, Santanyi).



Figure 7: Gypsum crusts on the floor of Cova de Cala Falcó (Manacor).

Figura 7: Crostes de guix en el trespol de la Cova de Cala Falcó (Manacor).

(Figure 8). Compact crusts made up of transparent gypsum crystals were collected from the inner part of the cave as well. The origin of gypsum in this cave is attributed to the reaction of limestone with sulfate anion provided by a mixture of seawater/freshwater.

All gypsum XRD spectra were well-resolved; therefore its presence was cross-checked through a series of thermal analyses. Without exception, the differential thermal analysis (DTA) curves show two endothermic effects at ~180° and 200°C, followed by an exothermic signal at ~345°C. These are all typical for gypsum.



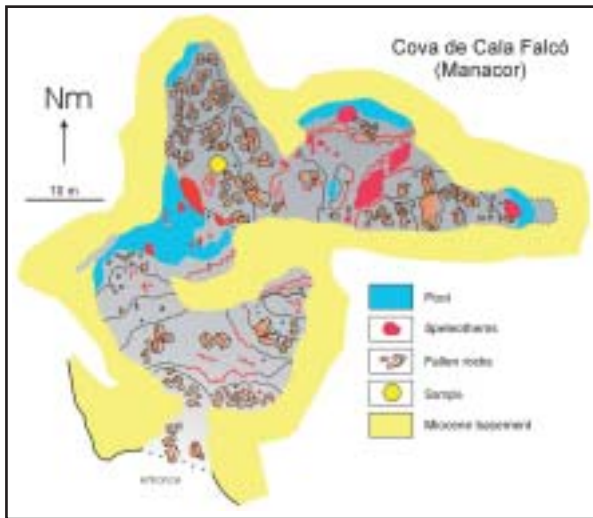


Figure 8: Map of Cova de Cala Falcó.

Figura 8: Topografia de la Cova de Cala Falcó.

## PHOSPHATES

The phosphates are best represented in Majorcan's caves in terms of number of species, although, only two caves hold the majority of these species. Except for collinsite, which is a rare phosphate, all the others (i.e., brushite, hydroxylapatite, carbonate hydroxylapatite, taranakite, and ardealite) are rather abundant, mirroring the overall situation from other karst regions (HILL & FORTI, 1997; ONAC, 2004). The availability of  $PO_4$  radical is essential for the precipitation of various phosphates. In caves, this anion is derived from bat guano. Whenever the  $PO_4$  reacts with carbonate host rock or clay minerals a number of phosphates will form.

From a thermodynamically point of view the most stable phosphate minerals are hydroxylapatite and carbonate hydroxylapatite. These species were identified in four and three caves, respectively (Table 1). In most of the occurrences, the two minerals are intimately associated (Figure 9a) in the form of ochre, reddish brown to dark brown crusts or earthy masses that cover the walls or limestone blocks that are located under a bat guano

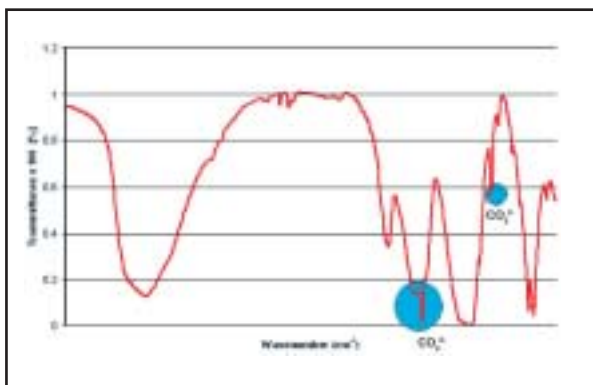


Figure 10: Infrared spectra of carbonate hydroxylapatite.

Figura 10: Espectre d'infraroigs d'hidroxilapatita carbonatada.



a



b

Figure 9: a: Crusts and earthy masses of hydroxylapatite and carbonate hydroxylapatite in Cova de ses Rates Pinyades (Inca); b: Hydroxylapatite in Coves del Pirata (Manacor).

Figura 9: a: Crostes i masses terroses d'hidroxilapatita i hidroxilapatita carbonatada a la Cova de ses Rates Pinyades (Inca); b: Hidroxilapatita a les Coves del Pirata (Manacor).

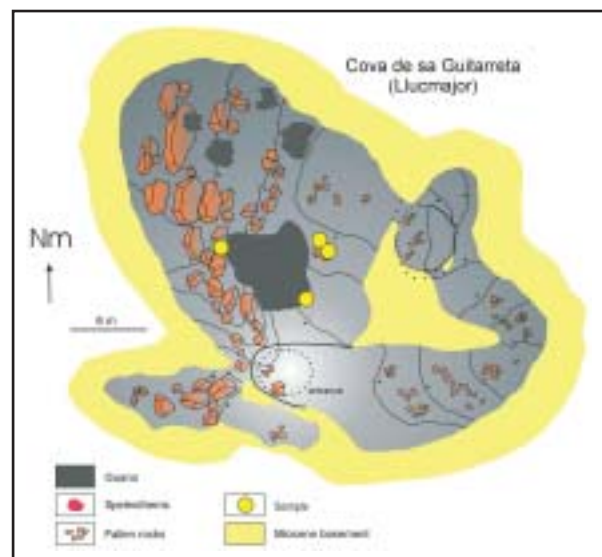


Figure 11: Map of Cova de sa Guitarreta showing the sampling points.

Figura 11: Topografia de la Cova de sa Guitarreta amb la localització dels punts de mostreig.



Figure 12: Efflorescences of ardealite in Cova de sa Guitarreta (Llucmajor).

Figura 12: Eflorescències d'ardealita a la Cova de sa Guitarreta (Llucmajor).

blanket (Figure 9b). The thickness of these coatings may vary from less than a 1mm to more than 3-4 cm.

Given their XRD patterns are similar, the distinction between the two phosphates relies on IR analyses. The samples that showed weak bands at  $\sim 876\text{ cm}^{-1}$  (out-of-plane bending),  $1385\text{ cm}^{-1}$ , and  $1420\text{ cm}^{-1}$  (antisymmetric stretching) indicate the presence of carbonate groups and therefore were ascribed to carbonate hydroxylapatite (Figure 10); the samples missing those absorption bands are typical spectra for hydroxylapatite.

As in most of the other known occurrences, both hydroxylapatite and carbonate hydroxylapatite are derived from guano leached phosphate solutions reacting with the limestone bedrock in a neutral to slightly alkaline pH environment (HILL & FORTI, 1997).

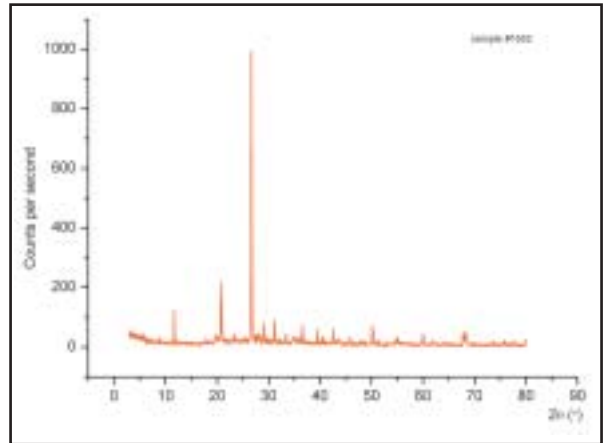


Figure 13: XRD patterns of ardealite collected from Cova de sa Guitarreta (Llucmajor).

Figura 13: Difractograma de raigs-X d'ardealita recollida a la Cova de sa Guitarreta (Llucmajor).

Some locations on the floor in the main hall of Cova de sa Guitarreta are covered by a thick layer of bat guano (Figure 11). About  $3\text{ m}^2$  of the largest guano patch is interspersed with a pale white to yellowish finely powdered material forming unspectacular efflorescences (Figure 12). The XRD analyses of hand-picked minute crystals showed the typical spectra of ardealite, another common phosphate cave mineral (Figure 13).

In Cova de ses Rates Pinyades (Figure 14), slabs of guano (up to  $50\text{-}60\text{ cm}^2$ ) can easily be lifted-up revealing the weathered outward part of the limestone blocks. At the surface of the downside part of these slabs, very fine grained crystals of ardealite overgrow brushite. Ardealite crystals were also documented from the weathered layer on the limestone blocks. The XRD patterns are almost identical to those illustrated in Figure 13. Under the SEM, ardealite occurs as aggregates composed of tiny tabular, subhedral to anhedral crystals (almost always fractured). The image of a single subhedral ardealite crystal is shown in Figure 15.

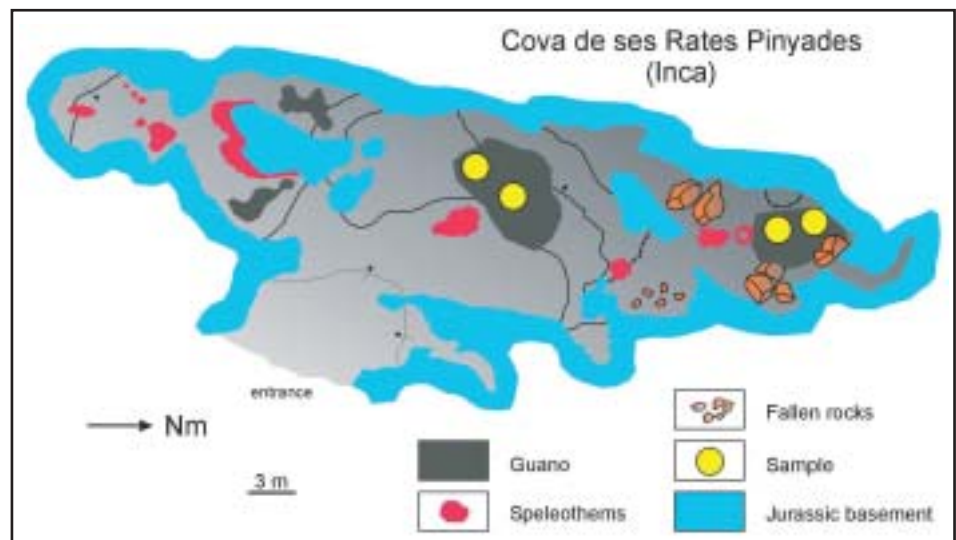


Figure 14: The sampling points in the upper chambers of Cova de ses Rates Pinyades (Inca).

Figura 14: Localització dels punts de mostreig a les sales superiors de la Cova de ses Rates Pinyades (Inca).



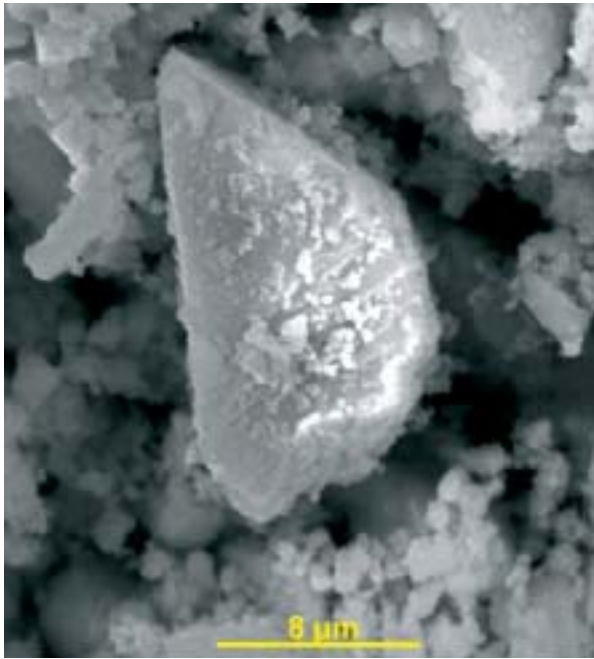


Figure 15: SEM image of a subhedral ardealite crystal.

Figura 15: Imatge SEM d'un cristall subhedral d'ardealita.

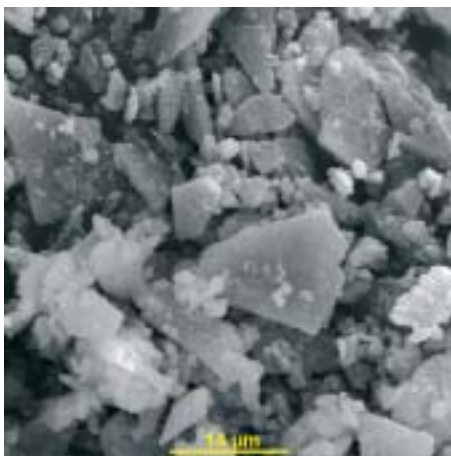


Figure 16: a: Brushite deposit in Cova de sa Guitarreta (Llucmajor); b: SEM image of fractured brushite crystals.

Figura 16: a: Dipòsit de brushita a la Cova de sa Guitarreta (Llucmajor); b: Imatges SEM de cristalls de brushita fracturats.

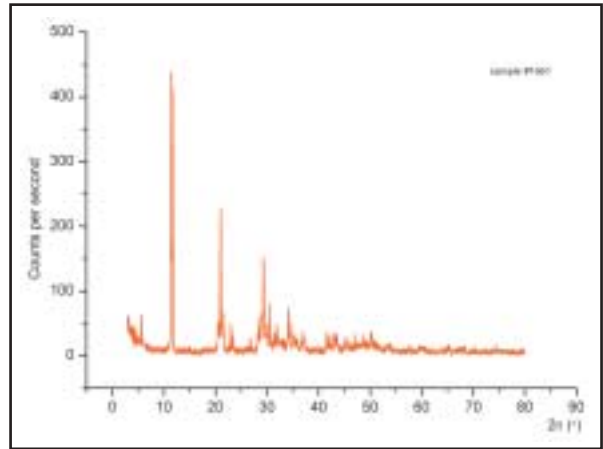


Figure 17: X-ray diffraction patterns of brushite.

Figura 17: Difractograma de raigs-X de brushita.

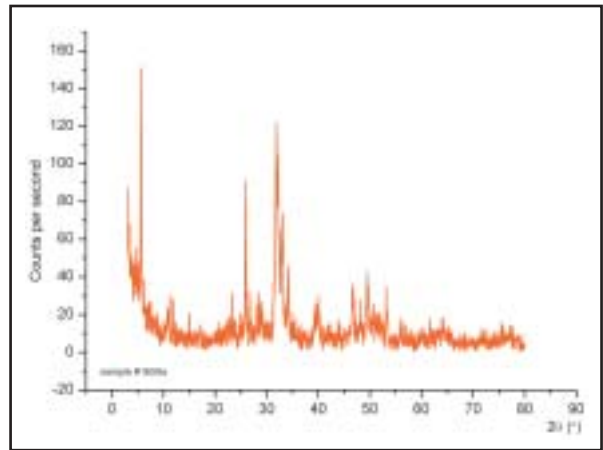


Figure 18: XRD patterns of taranakite from Cova de ses Rates Pinyades (Inca).

Figura 18: Difractograma de raigs-X de taranakita procedent de la Cova de ses Rates Pinyades (Inca).

**a**

Ardealite is an indicator of an acid environment. The pH of the ardealite-rich zone from Cova de sa Guitarreta must have been below 5.5 since brushite and hydroxylapatite are completely missing. A different situation, however, occurs in Cova de ses Rates Pinyades. In Cova de ses Rates Pinyades, ardealite and brushite are in close association. The close occurrence of these two minerals indicates pH values situated above 5.5 but below 8 which is the upper limit for brushite nucleation (FERREIRA *et al.*, 2003; ARIFUZZAMAN & ROHANI, 2004).

Brushite, another common cave mineral phosphate was identified in three caves (Table 1, Figure 16a). At all these locations it was found to be closely associated with its isostructural mineral: gypsum. Brushite was positively identified by means of XRD and thermal analyses. Since all the XRD spectra are very similar and well-resolved, the brushite spectrum from the Cova de ses Rates Pinyades is shown in Figure 17. Two endothermic and one exothermic peak are readily observed



on the DTG curve. The first endothermic peak located at  $\sim 196^{\circ}\text{C}$  was assigned to the removal of molecular water. The peak centered around  $\sim 435^{\circ}\text{C}$  was attributed to a new dehydration when the earlier formed  $\text{CaHPO}_4$  (monetite) is transformed into  $\text{Ca}_2\text{P}_2\text{O}_7$  (amorphous) +  $\text{H}_2\text{O}$ . The exothermic peak recorded around  $500^{\circ}\text{C}$  marks the crystallization of the amorphous  $\text{Ca}_2\text{P}_2\text{O}_7$ . The thermal behaviors of our samples are in good agreement with those reported by MURRAY & DIETRICH (1956) and FIORE & LAVIANO (1991).

SEM images of brushite aggregates show them to be composed of fractured euhedral crystals, tabular on (010), up to  $20\ \mu\text{m}$  in length, and 4 to  $6\ \mu\text{m}$  in width. The thickness of any individual crystals never exceeds  $2\ \mu\text{m}$  (Figure 16b).

The formation of brushite within these three caves was interpreted as being the final product of the reaction between acidic phosphate solutions and limestone bedrock or blocks buried by guano in damp conditions.

A light ochre, cream-like material was collected from within the guano deposit in Cova de sa Guitarreta. Most of the XRD patterns of the material indicate it to be gypsum. However, the spectrum contains at least 15 additional reflections that best fit those of collinsite. This mineral has been precipitated in a damp microenvironment from Mg-rich solutions passing through the guano blanket and reacting with the  $\text{CaCO}_3$  at the upper part of the limestone blocks. An atmospheric source (dust) is tentatively ascribed for Fe, although its presence in the guano should not be neglected.

Taranakite is the last mineral to be presented under the phosphate group. It was discovered in some bowl-shaped features at the surface of highly weathered limestone blocks in Cova de ses Rates Pinyades. The succession from the top to bottom is as follows: guano (3 to 7 cm), 1 cm of clay layer (mainly illite), a layer of soft taranakite (2 to 8 mm), a crumbly crust of carbonate hydroxylapatite (2 mm to 1 cm), and weathered limestone.

The presence of taranakite was unequivocally confirmed by a set of XRD (Figure 18) and SEM-EDX analyses. Microphotographs taken with a SEM show the taranakite aggregates to be composed of hundreds of almost hexagonal thin, platy crystals flattened on (0001) like those illustrated in Figure 19. The precipitation of taranakite in this occurrence is due to the fixation of K and Al into a phosphate structure under a less acidic environment. Both K and Al are derived from illite, whereas ammonium and  $\text{PO}_4$  radical comes from the decomposition of guano.

## SILICATES

None of the silicates identified in our investigated samples are true cave minerals. Illite, montmorillonite (grey-greenish clay-like material in Figure 20), and part of the quartz were probably washed into the cave by percolating and running waters. The micron-size flakes of muscovite and majority of the low quartz grains observed in the cave environment were derived from wind-blown sediments. All these minerals were identified in either phosphate- or carbonate-bearing samples and are allogenic in origin.

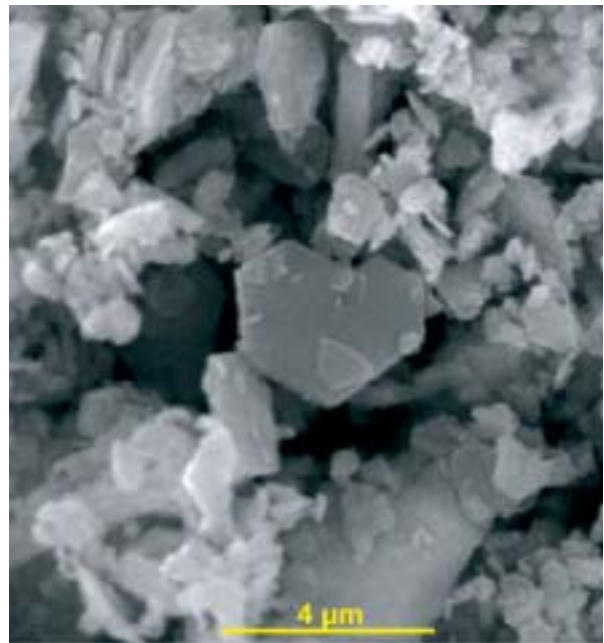


Figure 19: SEM microphotograph of platy-like hexagonal crystal of taranakite.

Figura 19: Microfotografia SEM de cristalls laminars hexagonals de taranakita.



Figure 20: Residual accumulation of montmorillonite in Cova des Drac (Es Rafal des Porcs, Santanyi).

Figura 20: Acumulació residual de montmorillonita a la Cova des Drac (Es Rafal des Porcs, Santanyi).

## Conclusions

Carefully evaluating the information in Table 1, one can observe that 16 minerals assigned to 4 chemical classes were discovered in 18 caves (10 of them carved in Upper Miocene limestone and 8 in Mesozoic limestone). Phosphates (6) and carbonates (5) are the best

represented groups. The only mineral present throughout all investigated caves is calcite. Four other minerals share the second position. Each of these minerals was found in four different caves, but only aragonite, gypsum, and hydroxylapatite are considered to be true cave minerals, as quartz is more likely detrital (allogenic) in origin. In fact, the group of silicates is represented by 4 species, but probably, none of them qualify as cave minerals according to the definition of HILL & FORTI (1997).

This first mineralogically-dedicated work reveals the existence of two outstanding caves: Cova de sa Guitarreta and Cova de ses Rates Pinyades. Both these caves display the most diverse mineralogy on the island. This is due to presence of massive deposits of bat guano (fresh and fossil) that cover bedrock, clay sediments, and speleothems to the extent that they barely protruded through it. A forthcoming paper deals with some specific mineralogical issues related to these two caves.

Based on the mineral inventory derived from our investigations, the following mechanisms are ultimately responsible for the precipitation of minerals in Majorcan's caves: (i) precipitation from percolating water (calcite, aragonite, hydromagnesite, monohydrocalcite, dolomite, and gypsum), (ii) precipitation related to the freshwater/sea-water mixing zone (calcite, aragonite, and gypsum), (iii) reaction between the phosphate-rich leachates derived from bat guano and the underlying bedrock and clay sediments (ardealite, brushite, carbonate-hydroxylapatite, collinsite, hydroxylapatite, taranakite, and gypsum), and (iv) phase transitions (aragonite to calcite inversion).

The present investigation was intended as a mineralogy reconnaissance in selected caves from Mallorca Island in order to reveal the scientific potential of this field. Further work on these and additional samples is required to answer more specific questions of origin and depositional mechanisms.

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