Linking mineral deposits to speleogenetic processes in Cova des Pas de Vallgornera (Mallorca, Spain)

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Abstract: Cova des Pas de Vallgornera (CPV) is the premier cave of the Balearic Archipelago. Over 74 km of passages develop within two carbonate lithofacies (reef front and back reef), which ultimately control the patterns of the cave and to some degree its mineral infilling. The diversity of speleothem-forming minerals is four times greater around or within hypogene-related features (vents, rims, cupolas), compared to any other vadose passages in the cave. The mineralogy of speleothems (crusts, nodules, crystals, earthy masses) associated with hypogene features in the seaward upper maze of Sector F is characterized by the presence of aragonite, ankerite, huntite, clay minerals, and quartz. In the Tragus and Nord sectors, however, the dominant mineral is dolomite, along with aragonite, celestine, huntite, clay minerals, and quartz. Calcite is by far the most ubiquitous mineral throughout the cave. Detailed macroscopic and scanning electron microanalysis and imaging have permitted the investigation of textural relationships between the minerals associated with vents, rims, and vent's roof and walls. These studies along with morphological and stable isotope analyses confirm that not all minerals are connected with a hypogene stage in the cave evolution, and furthermore, none of them appears to be sulfuric acid by-products. Instead, the mineral assemblages documented in speleothems from CPV clearly support at least three speleogenetic pathways, namely seacoast mixing, ascending of warm groundwaters, and meteoric recharge (vadose). Thus, cave minerals in Cova des Pas de Vallgornera hold the keys to reconstruction and understanding of processes and conditions under which they precipitated, allowing to establish their relationship with various speleogenetic pathways.

Keywords: cave minerals; speleogenesis; littoral caves; stable isotope; Mallorca

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INTRODUCTION

Distinguishing **hypogenic** (source of aggressiveness stem beneath surface; groundwater recharge mainly follows ascending paths) from **epigenic** (dissolution caused by acids originating from surface or near-surface processes; meteoric recharge by diffuse or floodwater flow) caves is not always straightforward. This is mainly because the hydrologic settings under which they form are responsible, sometimes, for rather similar cave patterns (maze) and morphological features (solution pockets, cupolas, spongework; Ford & Williams, 2007; Palmer, 2007, 2011; Klimchouk, 2009). The most common cave patterns displayed by hypogenic caves (i.e., sulfuric acid or thermal) includes spongework and network mazes, irregular chambers, and vertical to sub-vertical rising conduits. A suite of morphologies

generated by rising flow (i.e., feeders, wall and ceiling features, etc.) appears to be indicative for hypogenic basal recharge (Klimchouk, 2009). Throughout this paper, a feeder represents a connecting karst conduit (between two or more levels of the cave) viewed in the direction of ascending flow. Instead, when using the term vent we refer to the aperture of feeders in floor passages (i.e., the outlet where the water and/or hot air was/is emerging), around which a mineral rim commonly occur.

Apart from these very peculiar large- and small-scale cave morphologies attributed to rising flow, a growing body of mineralogical studies indicates the existence of a clear relationship between various hypogene speleogenetic pathways and the minerals hosted within those respective caves (Hill & Forti, 1997 and references therein; Onac & Forti, 2011a, b). By far, the most

complex, although expected, mineral assemblages were described from sulfuric acid caves (Hill, 1987; Polyak & Provencio, 2001; Onac et al., 2007, 2009, 2011, 2013; Plan et al., 2012; Audra et al., 2013; Puşcaş et al., 2013; Sauro et al., 2014). The reason for this situation is the presence of sulfuric acid produced by oxidation/hydrolysis of H_2S -rich solutions that react with cave sediments and bedrock to form primary or secondary speleogenetic by-products (Polyak & Provencio, 2011).

The leading speleogenetic processes responsible for producing the so-called thermal caves are mixing (thermal and meteoric water), cooling (thermal water becomes more aggressive as it cools while rising to surface), and condensation corrosion (Dublyansky, 2000, 2012). Although less abundant and diverse when compared to the sulfuric acid caves, the mineralogy of thermal cavities has certain characteristics; among them, the presence of tabular barite and celestine crystals, as well as quartz, opal, or chalcedony that coat or even replace cave bedrock walls (Takácsné Bolner, 1989; Leél-Óssy et al., 2011).

Cave development in the coastal zone is complex and often occurs during multiple sea-level changes (Myroie, 2013; van Hengstum et al., 2014). The primary mechanism in control of forming these caves is the dissolution caused by mixing of two water bodies (fresh and salt) with contrasting temperature, chemistry, salinity, or CO_2 content (Herman et al., 1985; Myroie & Carew, 1990). This particular type of caves form in shallow or deep coastal mixing zones and are characterized by spongework or crude ramifying passages. The littoral caves of Mallorca also features breakdown chambers and rectilinear karst conduits (Ginés et al., 2013, 2014). In general, the sea coast mixing caves have a narrow range of minerals composing their speleothems. Although the bedrock composition is monotonous, there are a few exceptional littoral caves that host very interesting and unusual mineral assemblages (Onac et al., 2001, 2008, 2014; Merino et al., 2009; Fornós et al., 2011). What ultimately controls the mineral diversity in these caves, is the particular geochemical environment of the mixing zone, where the carbonate bedrock is exposed to brackish groundwater.

Most of the studies investigating cave minerals rely on traditional X-ray diffraction (XRD), scanning electron imaging, X-ray fluorescence (XRF), and chemical composition inspection using microprobe, energy-dispersive X-ray spectroscopy (EDS), or inductively coupled plasma mass spectrometry (ICP-MS) techniques. The use of $\delta^{34}S$ in tracing the source of S in cave minerals was pioneered by Hill (1981) and Kirkland (1982), whereas van Everdingen et al. (1985) first investigated the $\delta^{18}O$ in sulfates to show the origin of O (meteoric H_2O or atmospheric O_2). Over the last decade, stable isotope analyses (mainly $\delta^{13}C$, $\delta^{18}O$, $\delta^{34}S$) on cave minerals come to be a routine investigation in distinguishing between different speleogenetic pathways (Dublyansky, 1997; Onac et al., 2007, 2009, 2011; Palmer & Palmer, 2012; Temovski et al., 2013; Sauro et al., 2014a, b).

The present paper reports on the CPV mineral inventory, discusses the origin of the unusual species with respect to their occurrence within the cave (i.e., Sector F, Tragus and Nord sectors), and makes an

attempt to link the mineral assemblages to various speleogenetic pathways identified and discussed by Ginés et al. (2014).

GEOLOGIC AND KARST SETTINGS

Cova de Pas de Vallgornera is the most significant (morphologically, scientifically, and length-wise) karst feature of Mallorca (Merino et al., 2011, 2014a, b; Ginés et al., 2014). Its artificial entrance opens on the southern coast of the island and gives access to an extensive 2-D spongework maze and fracture-controlled angular passages, currently exceeding 74 km of development (for cave location see Fig. 1 in Merino et al., 2014a). There is a clear relationship between geologic setting and cave patterns in that the 2-D spongework passages and collapse chambers develop in the more porous reef front facies of Upper Miocene age, whereas the angular galleries are typical for the outer lagoon facies (calcarenites and calcisiltites; Fig. 1) (Ginés et al., 2014). As highlighted in this paper, a similar relationship holds true for the mineral assemblages. For additional information on the geologic and karst settings of this cave, readers are directed to the publications of Ginés & Ginés (2007), Ginés et al. (2009), Fornós et al. (2011), Merino et al. (2011), as well as those included in this special issue of the *International Journal of Speleology*.

The geothermal studies conducted over the last decade in Mallorca pointed out the existence of at least two aquifers with anomalous temperatures in the vicinity of CPV (Mateos et al., 2005). The major thermal aquifer is hosted at depth in limestone and breccia of Lower Jurassic age (López, 2008; Fig. 1). Pools with thermal waters (23 to 27°C) are presently known in the lowermost parts of Cova de sa Guitarreta and Pou de Can Carro, two vertical caves located just few km NE of CPV (Merino et al., 2011). The water pooling in these caves is related to the shallow unconfined aquifer hosted within the Reef

Fig. 1. Lithostratigraphical column showing the position of Cova des Pas de Vallgornera in the Upper Miocene unit and the Lower Jurassic thermal aquifer (modified Fornós & Gelabert, 1995; Mateos et al., 2005).

Complex, in which hot water from the deep thermal aquifer migrates along a NE-SW fracture (Mateos et al., 2005).

SAMPLES AND METHODS

More than 100 mineral samples were collected over the last six years during exploration and survey expeditions or at times of dedicated mineralogical cave trips. Samples were acquired mainly from the landward passages of Tragus and Nord sectors (71), but also from the seaward upper maze of Sector F (37) (Fig. 2), both developed within back reef facies limestone. The sampling activities focused on speleothems associated with hypogene-related features, such as vents and rims (Fig. 3a, b) or within feeders (Fig. 3c) located along the above mentioned sections of the cave.

All investigated samples (108) on which this paper relies, received a thorough macroscopic characterization at the time of collection in the cave and were later examined under the binocular microscope. The identification of minerals is primarily based on X-ray diffraction (XRD). The samples were all air-dried in the laboratory, and clay and other detritus was then removed. An agate mortar was employed for grinding the handpicked subsamples down to a fine powder (less than 38 μm in size particles) before running them on a Siemens D5000 diffractometer (Serveis Científicotècnics, University of Balearic Islands in Palma de Mallorca, Spain) equipped with a diffracted-beam graphite monochromator and operated at 40 kV and 30 mA. Digitally recorded patterns were collected between 3 and 80° 2 θ (step size of 0.04° 2 θ and count rate of 2 to 4 second/step) and analyzed using EVA software (version 8.0). Silicon (NBS 640b) was used as the internal standard. Additional mineralogical analyses were performed in the Department of Chemistry,

Fig. 2. Location of the mineral samples on the map of CPV. The two orange lines across Tragus Gallery define the cross-section in Fig. 3.

University of South Florida using a Bruker Analytical X-Ray System, Inc. D8 Endeavor XRD. Samples were scanned from 5° to 75° 2 θ with a step increment of 0.02°, a scan speed of 0.5 sec/step (analytical conditions: 50 kV, 40 mA, CuK α radiation, line source filtered with a Ni foil). Mineral identification and abundance was evaluated quantitatively (in few samples) by measuring the integrated intensity of the strongest peak in each phase and then, using the reference intensity ratio (RIR) these intensity values were converted into weight percent (Hubbard & Snyder, 1998). The overall results based on XRD identification are tabulated in Table 1.

For scanning electron microscope (SEM) observations, freshly fractured speleothem fragments or hand-picked aggregates were gold-coated for better results while performing the semi-quantitative chemical analyses. SEM investigations were made at the University of Balearic Islands on a Hitachi

Fig. 3. Cross-section along Tragus Gallery showing the position of floor feeders (vents); a-b) vents (holes in the floor connecting different cave levels; scale bar = 10 cm) and rims (the projecting white mineral fringe); c) multicolored ceiling deposit above a complex vent.

Table 1. List of minerals identified in speleothems from Cova des Pas de Vallgornera and their possible origin. Minerals are divided by their location in two major areas of the cave and further sorted based on the number of occurrences around or within hypogene features or vadose settings.

Mineral and Chemical formula ¹	Sector F		Tragus and Nord sectors		Origin ²
	Hypogene	Vadose	Hypogene	Vadose	
Ankerite, $\text{Ca}(\text{Fe}^{2+}, \text{Mg})(\text{CO}_3)_2$	6	1	3	3	bb, v
Aragonite, CaCO_3	12	-	12	3	hw, v, bb
Barite, $\text{Ba}(\text{SO}_4)$	4	-	1	1	hw
Braunite, $\text{Mn}^{2+}\text{Mn}^{3+}_6\text{SiO}_{12}$	-	-	1	1	hw, bw?
Brushite, $\text{Ca}(\text{PO}_3\text{OH}) \cdot 2\text{H}_2\text{O}$	-	-	-	1	v
Calcite, CaCO_3	24	1	26	4	v, bb
Celestine, SrSO_4	-	1	8	1	hw
Chamosite, $(\text{Fe}^{2+}, \text{Mg}, \text{Al}, \text{Fe}^{3+})_6(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH}, \text{O})_8$	-	-	1	-	hw? bw ($\pm$ m)
Cristobalite, SiO_2	-	-	1	-	hw, bw
Dolomite, $\text{CaMg}(\text{CO}_3)_2$	3	1	15	4	v, bb ($\pm$ m)
Epsomite, $\text{Mg}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$	-	-	-	1	v, bb?
Gibbsite, $\text{Al}(\text{OH})_3$	-	-	1	-	hw
Goethite, $\text{FeO}(\text{OH})$	2	-	-	2	v
Gypsum, $\text{Ca}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$	-	3	3	4	hw, v, bb
Jacobsite, $\text{Mn}^{2+}\text{Fe}^{3+}_2\text{O}_4$	1	-	1	1	hw, bw?
Hematite, Fe_2O_3	-	-	5	1	v
Huntite, $\text{CaMg}_3(\text{CO}_3)_4$	5	-	6	-	v
Illite (series) ³ , $\text{K}_{0.65}\text{Al}_{2.0}\square\text{Al}_{0.65}\text{Si}_{3.35}\text{O}_{10}(\text{OH})_2$	5	-	2	-	bw ($\pm$ m)
Kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	4	1	9	3	bw ($\pm$ m)
Konyaite, $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$	-	-	-	1	v
Montmorillonite, $(\text{Na}, \text{Ca})_{0.3}(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$	3	1	3	1	bw ($\pm$ m)
Nordstrandite, $\text{Al}(\text{OH})_3$	-	-	1	-	hw
Quartz (low), SiO_2	6	1	11	4	hw, bw
Roman��chite, $(\text{Ba}, \text{H}_2\text{O})_2(\text{Mn}^{4+}, \text{Mn}^{3+})_5\text{O}_{10}$	-	-	-	1	bw ($\pm$ m)
Strontianite, $\text{Sr}(\text{CO}_3)$	-	-	1	-	hw
Todorokite, $(\text{Na}, \text{Ca}, \text{K}, \text{Ba}, \text{Sr})_{1-x}(\text{Mn}, \text{Mg}, \text{Al})_6\text{O}_{12} \cdot 3-4\text{H}_2\text{O}$	1	-	1	2	hw ($\pm$ m)

¹According to the official IMA-CNMNC list of minerals (<http://pubs.ics.uzh.ch/ima-cnmnc/imalist.htm>).

²hw: hot water; v: vadose; bw: bedrock weathering; bb: bedrock/brackish water interface; $\pm$ m: microbial

³According to Rieder et al. (1998).

S-3400N using a backscattered electron detector (BSE) for atomic-number contrast imaging. The operation parameters were high-vacuum, 15 kV, 5 to 10 nA, and a defocused electron-beam diameter of 30 μm . Further chemical analyses on bedrock samples were conducted in the Center for Geochemical Research (School of Geosciences, University of South Florida) using a Perkin-Elmer Elan DRC II Quadrupole Inductively Coupled Plasma Mass Spectrometer.

The $\delta^{34}\text{S}$ ratios of 11 samples representing S-bearing minerals (barite, celestine, and epsomite) were measured on a Delta V Isotope Ratio Mass Spectrometer (IRMS) coupled with an Elemental Analyzer Costech ECS 4100 at the School of Geosciences Stable Isotope Lab (University of South Florida) following the method described in Grassineau et al. (2001). The results reported in standard δ -notation were normalized to CDT (Can Diablo Troilite) using $\delta^{34}\text{S}$ values of four IAEA standards (IAEA, International Atomic Energy Agency, S-2 and S-3 for sulfides and SO-5 and SO-6 for sulfates). The reproducibility between replicate standards in each run was better than $\pm 0.1\text{‰}$ (1 σ). Selected speleothems collected from vents and rims and around these features and three bedrock samples (two from reef front and one from back reef limestone) were analyzed for oxygen and carbon isotopic ratio in CO_2 expelled after reacting the samples for 24 hours (or 5 days for ankerite) with 103% H_3PO_4 at

25C. The isotopic ratios were measured on the same IRMS instrument, but the values are reported in $\delta\text{‰}$ relative to the PDB (Pee Dee Belemnite) standard. For accuracy control, NBS-18 and NBS-19 were used as internal laboratory standards. Reproducibility was better than $\pm 0.12\text{‰}$.

RESULTS AND DISCUSSION

Twenty-six minerals were identified throughout the cave (Table 1); the highest diversity (20 species) is around or inside typical hypogene features (although not all minerals are necessarily related to a hypogene speleogenetic phase) occurring within back reef limestone in the Tragus and Nord sectors (see Fig. 3). In the upper maze of Sector F (seaward part) which also develops on back reef facies only 13 minerals occur. At all these locations they form either monomineral speleothems (spar, crusts, coatings, powder, moonmilk) or multi-mineral associations (especially in the abundant corrosion residues overlying the walls and ceilings). We note an even larger mineralogical contrast in the composition of speleothems that are unrelated to hypogene features; nineteen are deposited in galleries and chambers developed in Tragus and Nord sectors whereas only eight in Sector F. Examining the occurrences of all minerals identified, their crystal morphology, and the

relationship between various species at each location, we distinguish three groups: 1) minerals related to hypogene speleogenetic processes, 2) minerals precipitated at the bedrock/brackish water interface, and 3) minerals of vadose/epiphreatic origin, typical for low-temperature epigenetic caves. A few species (e.g., aragonite, celestine, barite, gypsum, todorokite, etc.) belong to either group 1 and 3 or 2 and 3, but only aragonite and gypsum precipitate under all three minerogenic settings. The most abundant or peculiar minerals of these groups are characterized below; those having multiple origins are presented only under one of the genetic categories.

Minerals related to hypogene speleogenetic processes

In CPV, the minerals framed within this category are related to: i) either direct subaerial precipitation of dissolved species transported *per ascensum* by warm solutions (hw in Table 1) or ii) replacement/weathering of the bedrock (bw) due to corrosion when warm, humid air originating from these warm waters condensed onto the cold cave walls. This latter process might be enhanced/controlled by microbial activity [bw ($\pm$ m)]. Although there are no documented thermal water pools *per se* in CPV, the abundance of vents (characterized by rich mineral assemblages) suggests hypogene (thermal water-related) basal recharge was common in many parts of the cave at various times during its evolution (Ginés et al., 2009; Fornós et al., 2011; Ginés et al., 2014).

Barite & Celestine

Barite occurs as patchy crusts (few centimeters across) covering either bedrock or other coatings in and around hypogene features located in Sector F. At these locations barite appears as tabular after {001} closely associated with dolomite (Fig. 4a) and prismatic (after [010] and [100]) or bladed crystals (sometimes massive aggregates) along with acicular aragonite (Fig. 4b). It was also found precipitated on top of calcite and/or ankerite aggregates (see discussion under ankerite entry).

Celestine appears as bouquets of sub-centimeter long colorless to light blue shaded crystals (Fig. 4c) in eight occurrences, all related to hypogene features hosted within cave passages developed in Tragus and Nord sectors. SEM investigation reveals euhedral to subhedral equant prismatic crystals formed by the development of {011}, {001}, and {210}; another crystal habit observed is pyramidal with {122}, {011}, or {102} (Fig. 4d, e).

There is only one location in the Tragus Gallery (Aragonite Tub section) where the two minerals are closely associated and were precipitated over and in between ~1 million year old (Polyak, pers. comm.) aragonite needles (Fig. 4f). Based on the relationship between the two sulfates and their host mineral (aragonite) and considering that barite and celestine form a solid solution, we believe they precipitated from *per ascensum* migrating strontium- and barite-bearing hot groundwater after the thick aragonite crust covered the cave passage at this particular location. Considering the average $\delta^{34}\text{S}$ values obtained on these

Fig. 4. BSE and hand specimen microphotographs. a) Tabular crystals of barite precipitated over dolomite; b) Granular aggregates of barite covered by long prismatic crystals of aragonite; c) Light blue bouquets of celestine crystals over either dolomite or gypsum crusts; d-e) Crystals of celestine displaying subhedral and pyramidal morphologies; f) Tabular, prismatic, and granular aggregates of barite and celestine precipitated in a late-stage over prismatic crystals of aragonite.

two sulfates (+21.6‰ for barite ($n = 3$) and +21.7‰ for celestine ($n = 5$), respectively) it is obvious that it derived from dissolution of primary marine sulfate (average $\delta^{34}\text{S}$ values of Miocene seawater sulfate is ~22‰; Paytan et al., 1998) interbedded or existing within limestones and is not a by-product of sulfuric acid speleogenesis.

Chamosite

Chamosite is a monoclinic mineral of the chlorite group first time identified in a cave environment. It occurs within the red fluffy ceiling deposit above a vent on Tragus Gallery. It is closely associated with quartz, hematite, braunite, kaolinite, and montmorillonite. It was identified by means of XRD (peak at 7.05Å that vanished after digesting the sample in concentrated HCl) and subsequently confirmed by SEM-EDS microchemical analyses. The crystals are tabular {001} arranged in the shape of sheafs (Fig. 5), < 100 μm across and are flattened on (001).

Vallgornera is an unusual occurrence of chamosite and the following two scenarios seem plausible to explain its presence: i) authigenically formed under slightly acidic to slightly alkaline conditions (pH 5 to 8). Under this model, hot air-condensing above feeders liberate (by corrosion) Fe^{2+} , Fe^{3+} , Al^{3+} , and silica from the carbonate rock, which then co-precipitate with the subsequent formation of chamosite. Hence it is “secondary” in origin, thus a true cave mineral; ii) chamosite might have been a primary mineral in the carbonate rock (Akande & Mücke, 1993) and became exposed by various weathering processes (including bacterial activity) that affected the bedrock. If so, chamosite would not be a true cave mineral.

Fig. 5. Foliated and radiating crystals of chamosite.

However, crystal faces look fresh and unaffected by dissolution, suggesting an authigenic mineral. Further investigations are planned to confirm the exact origin of chamosite.

Jacobsite

This spinel-group mineral has been identified in three locations (two of them related to hypogene features) on both seaward (Sector F) and inner part (Tragus Gallery) of the cave. The samples we investigated occur as dark (brown to black), centimeter-thick deposits on a tube that is genetically related to a large floor feeder. Under SEM, jacobsonite appears as coarse granular (Fig. 6a) to massive (Fig. 6b) crystals, 20 to >100 μm in length, showing no cleavage. It is closely associated with either quartz and calcite or clay minerals and calcite (Fig. 6).

Without having explored in greater detail the presence of this mineral in CPV, we assume it is a condensation-corrosion product of Mn-bearing minerals such as braunite and romanèchite. The ICP-MS analyses showed the manganese is present in both bedrock and water in concentrations in the order of up to 120 ppm. To our knowledge these are the first confirmed occurrences of jacobsonite in a cave worldwide.

Nordstrandite

Nordstrandite was first described by Polyak & Provencio (2001) from Lechuguilla Cave, interpreting its origin as the alteration product of alunite and halloysite-10Å. They assumed nordstrandite was possibly a speleogenetic by-product and subsequently,

Fig. 6. Granular (a) and massive (b) aggregates of jacobsonite.

other authors considered its occurrence in caves as diagnostic for hypogene speleogenesis (Merino et al., 2009; Fornós et al., 2011).

The sample in which nordstrandite was positively identified consists of a millimeter-size thick brown film, collected from the ceiling of Tragus Gallery, above a feeder. The SEM observations reveal clay mineral aggregates and radiating clusters of tabular to prismatic crystals of nordstrandite, terminated by sharp, clear pyramidal faces (Fig. 7). The size of the crystals does not exceed 50-60 μm and they show perfect cleavage after {110}.

Given the environmental conditions from which nordstrandite was previously reported (outside the cave; Wall et al., 1962; Hathaway et al., 1965; Milton et al., 1975), its precipitation in CPV is a matter of conjecture. Based on the relationship between nordstrandite and the other minerals/deposits at the sampled location in the Tragus Gallery, it appears to be a late-stage precipitate. The exact chain of reactions that led to its deposition is still unclear. A carbonization mechanism, similar to the one proposed by Lipin (2001) seems reasonable, although it is difficult to imagine a limestone cave environment with pH above 13. However, nordstrandite was also obtained experimentally at lower pH (7.5 to 9) but under specific ionic concentrations and temperatures (Van Nordstrand et al., 1956). Not having such information for the CPV nordstrandite, we assume a combination of the two models cited above, with aluminous solutions transported into the cave by the hypogene hot waters or with Al^{3+} sourced from either limestone bedrock or clay minerals already present in the cave.

Strontianite

During one of the visits in CPV, a fragment of bedrock (within a rim around a vent) on which two distinct, transparent and translucent minerals occurred as tiny crystals was sampled. The XRD investigation clearly identified dolomite as well as the presence of celestine and gypsum (by their characteristic peaks). The BSE imaging and micro-chemical analysis confirmed these three minerals, but in addition, we noticed spiky, radiating clusters of long (60 to 80 μm) prismatic crystals [001] growing on top of botryoidal aggregates of dolomite (Fig. 8). The EDS micro-analyses revealed the presence of only three elements: Sr, C, and O that make up strontianite.

Due to some geochemical constraints (e.g., temperature- and CO_2 partial pressure-dependent solubility, ion activity, Sr/Ca ratios, and pH; Helz & Holland, 1965; Busenberg et al., 1984) in the $SrCO_3$ - CO_2 - H_2O system, strontianite is an uncommon mineral in nature. There are only three reported cave occurrences from Sima de las Fumarolas, Spain (Fernández-Rubio et al., 1975), a small, nameless cave in the Terrace

Fig. 7. BSE image of radiating clusters of tabular to prismatic crystals of nordstrandite. Note the pyramidal faces on some of the crystals.

Fig. 8. Radiating clusters of short prismatic strontianite crystals developed over dolomite aggregates (BSE image).

Mountains, USA (Hill & Forti, 1997), and Serizjan, Iran (Calaforra et al., 2013).

The mineral association that includes strontianite in CPV suggests a precipitation of this rare carbonate by cooling of Sr^{2+} -rich ascending hot waters as they entered the cave. Strontium is likely derived from the leaching of nearby carbonate and evaporite beds. In order to precipitate strontianite, two other requirements need to be met: small concentrations or absence of sulfate anion and a high Sr/Ca ratio (Calaforra et al., 2013). Having celestine and gypsum precipitated out of the solution in an early stage of minerogenesis consumes the majority of the available sulfate. Combining this sulfate deficit with an increase of the Sr/Ca ratio due to cooling of the solution and precipitation of dolomite, may be responsible for localized deposition of strontianite. Microbial-influenced accumulation of strontianite, following the mechanism proposed by Bonny and Jones (2003) cannot be ruled out.

Minerals precipitated in the vicinity of bedrock/brackish water interface

A limited number of minerals (ankerite, aragonite, calcite, dolomite, epsomite, and gypsum) form speleothems near the contact between limestone and brackish water in CPV (bb in Table 1). The

geochemical conditions under which aragonite, calcite, and gypsum speleothems are deposited in littoral caves at or a few centimeters below and above the present brackish water table are well documented and will not be discussed here (Bottrell et al., 1991; Onac et al., 2001, 2005; Csoma et al., 2006; Ginés et al., 2012). The phreatic overgrowths on speleothems (POS) used to reconstruct past sea-level positions (Vesica et al., 2000; Dorale et al., 2010; Tuccimei et al., 2010; Ginés et al., 2012) fall into this category as calcite and/or aragonite encrustations are precipitated over preexisting vadose speleothems from brackish waters. Dolomite is discussed along with the vadose minerals, thus ankerite and epsomite are the highlights of this group.

Ankerite

Ankerite was positively identified (XRD and SEM-EDS) in millimeter-size microcrystalline crusts of various colors, from white to yellowish-brown or dark brown. Eight of the samples come from cave passages rich in hypogene features, whereas the other 4 samples were collected at vadose sites. Similar to dolomite, ankerite forms rhombohedral crystals {1011} (Fig. 9a) or pseudo-octahedral (Fig. 9b). Dissolution features (pits) are frequent on many crystal faces; another characteristic of the rhombohedral ankerite crystals is the stepped morphology along their edges and at corners (Fig. 9a). In sample VL-M101, ankerite is intergrown with calcite and closely associates with aragonite crystals elongated in the direction of [001] and flattened on (110) (Fig. 9b). Bright white prismatic barite crystals were observed under SEM (Fig. 9b). Given their relationship with the other mineral phases, it certainly precipitated in a late stage after calcite/ankerite were already deposited.

Apart from XRD, staining techniques, and chemical analysis, ankerite in sedimentary environments is commonly investigated using stable isotope geochemistry. However, oxygen isotope fractionation between water and ankerite at low-temperatures is poorly constrained (Zheng, 1999). Multiple oxygen and carbon isotopic analyses were performed on nine samples of both hypogene- and vadose-related speleothems collected above vents in Sector F and Tragus Gallery and along other vadose passages. The isotopic composition ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) of these samples is listed in Table 2. Plotted in Fig. 10 the data show two distinct populations with significantly different $\delta^{13}\text{C}$ values ($\sim 10\text{‰}$), whereas the $\delta^{18}\text{O}$ values are within 2‰. The ankerite crusts precipitated in conjunction with known hypogenic features group as Population 1, which is characterized by relatively high $\delta^{13}\text{C}$ (1.97 to 2.04‰) and $\delta^{18}\text{O}$ values between -4.71 and -4.65‰ (Fig. 10). The bedrock samples plot very close to this population. Population 2 includes ankerite crusts sampled along vadose passages, and has low $\delta^{13}\text{C}$ (-7.91 to -7.87‰) and $\delta^{18}\text{O}$ values (-6.47 to -6.22‰), comparable with other carbonate speleothems precipitated from low-temperature meteoric solutions in other carbonate caves worldwide.

The oxygen isotopic composition of meteoric and sea water nearby the cave is -5.6‰ (Araguas-

Fig. 9. BSE images of rhombohedral ankerite showing stepped morphology at edges and corners (a) and close up of needle-like aragonite and tabular barite crystals growing upon intimately associated calcite and ankerite (b).

Fig. 10. Plot of carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) isotopic composition of two cave ankerite populations and limestone bedrock. Data for modern meteoric (Araguas-Araguas & Diaz Teijeiro, 2005), brackish, and Mediterranean sea waters (Boop et al., 2014) are also represented.

Araguas & Diaz-Teijeiro, 2005) and +1.5‰ (Boop et al., 2014), respectively. The average $\delta^{18}\text{O}$ value of the limestone bedrock is -3.5‰ whereas the $\delta^{13}\text{C}$ value is +2.0‰. Combining this information with our isotope data, it is reasonable to consider the ankerite within Population 1 as being deposited at the bedrock/brackish water interface. At these locations the reaction between the brackish water supplying Mg^{2+} and the carbonate bedrock is responsible for its precipitation. The iron is probably derived from ferric oxides deposited in limestones. This idea is supported by the fact that all three samples of Population 1 have almost similar $\delta^{13}\text{C}$ values with the limestone, indicating that the source of carbon is likely the carbonate bedrock. Instead, the isotopic signature of samples in Population 2 clearly suggest

Table 2. Oxygen and carbon isotope values of bedrock limestone and ankerite speleothems from CPV.

Location and Sample code	$\delta^{18}\text{O}$ (‰)	$\delta^{13}\text{C}$ (‰)
Sector F (limestone)	-2.51	2.04
Sector Antic (limestone)	-2.53	2.02
Sector F (VL-M96)	-6.22	-7.91
Sector F (VL-M101)	-6.47	-7.87
Tragus Gallery (limestone)	-2.47	2.0
Tragus Gallery (VL-M26)	-6.31	-7.88
Tragus Gallery (VL-M55)	-4.65	1.93
Tragus Gallery (VL-M57)	-4.7	1.98
Tragus Gallery (VL-M57a)	-4.71	1.97

that soil pool represents the main source of carbon. Furthermore, the observed distribution of $\delta^{18}\text{O}$ values indicates that Population 1 apparently precipitated from brackish water of which isotopic signature is likely the result of mixed seawater and warm ascending waters. The more negative $\delta^{18}\text{O}$ values of samples belonging to Population 2 plot close to the mean

value of the meteoric water, thus suggesting these ankerite samples have a vadose origin and were deposited by percolating vadose solutions. It could be precipitated directly from low-temperature solutions or it may replace calcite, providing an adequate supply of Fe^{2+} and Mg^{2+} relative to Ca^{2+} is available. Ankerite is the product of the reaction between Mg^{2+} -enriched meteoric solutions (Mg^{2+} originates from sea spray or is leached from the carbonate bedrock) percolating through the epikarst and the Upper Miocene limestone.

Epsomite

The observations presented here are based on a single occurrence of epsomite, in sample VL-M030 recovered from the Tragus Gallery, more specifically, at the Aragonite Tub. The mineral occurs as a sub-millimeter thin, dull white to slightly yellowish fibrous crust closely associated with aragonite. Calcite was also identified in this sample by means of XRD. The precipitation and preservation of epsomite is highly dependent on temperature and relative humidity (RH). Considering the stability field of epsomite provided by Hill & Forti (1997) and Posern & Kaps (2008) and the topoclimatic conditions within the Aragonite Tub ($T = 20.4^\circ\text{C}$ and $\sim 90\%$ RH), its occurrence in CPV is not surprising.

Our hypothesis regarding the presence of epsomite in CPV is as follows: according with Berner (1975), Fischbeck & Müller (1971) and De Choudens-Sánchez & González (2009), from a parent solution with Mg/Ca between 2.9 and 4.4, aragonite is the main calcium carbonate mineral (calcite may also form) that will precipitate. The only way to suppress aragonite deposition, but form epsomite, is to increase the molar ratios $\text{SO}_4^{2-}/\text{CO}_3^{2-}$ to ≥ 1 while the solution remains rich in Mg^{2+} . It has been experimentally documented that incorporation of less than 3 mole% of sulfate is energetically unfavorable to aragonite precipitation (Fernández-Díaz et al., 2010).

The source of Mg^{2+} could have been the bedrock, percolating sea spray-rich waters, or even the close proximity of cave brackish water at a time when sea-level stood higher than present. Indistinguishable, the last two sources work for SO_4^{2-} as well, knowing that the sulfur isotopic signature of the CPV epsomite ($\delta^{34}\text{S} = +21.3\text{‰}$; $n = 3$) points toward a marine source (Paytan et al., 1998). If epsomite precipitated during

one of the high sea stands and both Mg^{2+} and SO_4^{2-} come from the cave brackish water (evaporation of capillary pore waters), then it is with certainty that the mineral belongs to this genetic group.

Minerals precipitated under vadose conditions

This category includes the most common cave minerals; such are calcite, aragonite, gypsum, or huntite, precipitated throughout the cave (v in Table 1) by flowing, dripping, seeping, or pooling water (Hill & Forti, 1997). These minerals are also present in the composition of speleothems in and around hypogene features (feeders, vents, cupolas) but at such locations they were deposited from cold meteoric waters in a late minerogenic stage. The precipitation of some minerals occurring in the highly weathered bedrock skin is likely controlled by microbial activity (bw $\pm$ (m) in Table 1).

Clay minerals

Abundant colorful “corrosion” residues coat floors, walls, and ceilings in many parts of CPV (Figs. 3c and 11a, b). This “mineral skin” is several centimeters in thickness and its texture progressively changes from a very fluffy, low-density layer (mm to cm thick) in the outer-most part to a soft, but denser one represented by weathered bedrock. Similar cave deposits were described in the literature under various names, such as okher (Maltsev, 1997) or speleosol (Spilde et al., 2006). Apparently, these materials are active biological media, rich in reworked and bacteria-mediated secondary minerals (Korshunov & Semikholennykh, 1994; Northup & Lavoie, 2001; Polyak & Provencio, 2001; Spilde et al., 2005; Barton & Northup, 2007). They are home of a variety of oxides and hydroxides of iron, manganese, and aluminum, as well as certain clay minerals. Apart from kaolinite, montmorillonite, and illite (Fig. 11c), the following mineral species were identified in the multicolored deposits of CPV: romanèchite, todorokite, goethite, hematite, gibbsite, and quartz.

To date, there are no dedicated studies to investigate the geomicrobiology and mineralogy of these residues in CPV. The clay minerals-rich “corrosion” residues

are very common nearby vents (26 out 33 samples total) where they form abundant accumulations on both ceilings and walls. Many other passages in the cave (more or less ventilated) display rich multicolored deposits. Regardless to their location within the cave, these weathering residues appear to be the result of a combination of condensation-corrosion that is significantly enhanced by biochemical breakdown of the bedrock. The idea that microorganisms are involved in this process is supported by SEM images that show bacterial filaments and other microbial structures (Fig. 11d).

Dolomite

Although a common rock in ancient sedimentary deposits, dolomite is relatively rare in the recent ones and even rarer as mineral in low temperature environments (Tucker, 2001). The reason for this situation is attributed to a number of factors including Mg/Ca ratio, kinetics, temperature, pH, presence of sulfates, etc. (see Roberts et al., 2013 and references therein). Only a handful of cave locations are known and well documented with respect to the presence of dolomite speleothems (Thraillkill, 1968; Martini, 1987; Hill & Forti, 1997; Polyak & Güven, 2000; Alonso-Zarza & Martín-Pérez, 2008).

Macroscopically, the dolomite in CPV occurs as white to gray sub-millimeter thin crusts precipitated on either side of rims around vents. Sometimes dolomite microcrystals are deposited upon aragonite crystals or gypsum coatings. In one sample (VL-M38) dolomite and huntite are closely associated. Typically, the dolomite occurs near hypogene features (18), but it was also found in 5 locations that are characterized by exuberant vadose precipitates.

A detailed morphological investigation by SEM reveals that commonly, dolomite forms isolated or coalescing spheroidal aggregates of various sizes (30 μm to 0.5 mm across; Fig. 12a, b), which internally consist of individual rhombic crystals (Fig. 12c). Notable are the bacterial filaments (Fig. 12d) and what appears to be mucus strands (Fig. 12e) that covers or bridges dolomite crystals in many of the investigated samples.

Considering the morphology of crystals and mineral assemblages with which dolomite is associated in CPV, the following precipitation scenarios are proposed:

1. Locations where dolomite occurs with aragonite and/or huntite. After calcite and aragonite were deposited out of dissolved inorganic carbon (DIC)-rich vadose solutions, these become enriched in Mg^{2+} and will precipitate huntite and then dolomite. Huntite and dolomite have similar structures, but huntite will always precipitate before dolomite because of its open structure (low-density phase; Graf & Bradley, 1962; Dollase & Reeder, 1986) that favors enhanced magnesium dehydration (Lippmann, 1973). Another possible way in which dolomite may have formed under this scenario is considering that either aragonite or huntite acted as precursors. An argument for such a process is the presence in some samples of micro-aggregates consisting

Fig. 11. a-b) Multicolored fluff residue coating consisting of Fe and/or Mn oxides and hydroxides, clay minerals, calcite, and quartz silt; c) Feathery crystals of illite; d) SEM image reveals microbial structures within a sample of multicolored residual material.

Fig. 12. a-b) Isolated and coalescing rounded aggregates of dolomite; c) Close up of dolomite crystals shaping the spheroidal aggregates; d-e) Bacterial and mucus strands bridging or covering dolomite crystals; f) Crystals of dolomite nested in corrosion pits at the surface of gypsum crystals.

of euhedral to subhedral dolomite crystals, tentatively interpreted as representing totally replaced huntite (Fig. 12a, b). A similar dolomite occurrence was described from Castañar Cave in Spain (Alonso-Zarza & Martín-Pérez, 2008).

2. Locations where dolomite is associated with gypsum. A high-resolution SEM examination of sample VL-M22 shows dissolution pockets on the surface of gypsum that are filled with crystals of dolomite (Fig. 12f). Vadose fluids could simply cause corrosion of gypsum, but at the same time, it might be the result of microbial boring activity (Douglas & Yang, 2002). Regardless the origin of the micro-dissolution features on the gypsum crystal faces, the dolomite filling them appears to be microbially mediated. This hypothesis is supported by SEM imagery that shows the presence of organic structures, binding or coating part of the dolomite crystals. Such examples are known from modern settings in Brazil and Spain (Vasconcelos et al., 1995; Sanz-Montero et al., 2006) as well as from laboratory experiments (Warthmann et al., 2000).
3. Locations where dolomite is only associated with calcite: The presence of the dolomite along with calcite in speleothems from CPV may suggest its precipitation from DIC-rich meteoric waters mixed with Mg-rich groundwaters. The source of magnesium could be twofold: 1) the extensive bodies of brackish water in CPV or/and 2) dissolution of magnesium from the bedrock.

Knowing that abiotic precipitation of modern dolomite is limited in low-temperature environments, and because the SEM observations on dolomite samples reveal biological structures, we argue, without any dedicated microbiological investigations that precipitation of dolomite in CPV is bio-induced.

Huntite

Eleven samples collected in the close proximity of vents in all three sectors of the cave tested positive for huntite. The mineral occurs as dull white, fine-grained earthy deposits or moonmilk, as well as small spheres (Fig. 13a). SEM imaging reveals huntite is intimately associated with aragonite and dolomite (Fig. 13b, c). Inspecting at higher magnification the globular aggregates of huntite, we noticed that at their surface the platy rhomboidal crystals are visible (Fig. 13b inset).

Without exception, all huntite deposits occur near well-ventilated areas (in connection with the floor feeders), confirming its precipitation by evaporative concentration of magnesium-rich percolating solutions (mainly) and carbon dioxide loss. An interesting observation is that none of the common magnesium carbonates were identified in CPV. Because the precipitation of nesquehonite requires very high CO_2 partial pressure (P_{CO_2}) its absence is easy to explain (Lippmann, 1973). However, although the stability field of hydromagnesite overlaps the one of cave environment in terms of relative humidity, evaporation, and P_{CO_2} (Hill & Forti, 1997; White, 1997), the mineral is not forming in CPV. The reason might be twofold: the P_{CO_2} is still too high or, more likely, the Mg/Ca ratio is below the critical threshold (16) at which hydromagnesite forms (Fischbeck & Müller, 1971).

On the theoretical curve of the evolution of cave water in the CaCO_3 - MgCO_3 - H_2O system, huntite lies between aragonite and hydromagnesite. Thus, the presence of huntite and aragonite association at various locations within CPV confirms the depositional sequence of carbonate minerals proposed by Lippmann (1973). It also directly relates the two minerals with a late vadose speleogenesis phase. Diagenetic mechanisms similar to those invoked by Martínez-Pérez et al. (2012)

Fig. 13. a) Moonmilk-type fine-grained aggregates of huntite precipitated over aragonite ($\pm$ dolomite) crusts in the close vicinity of vents; b) SEM microphotograph showing the association of huntite spheres (platy rhomboidal crystals are visible in the inset image) with prismatic aragonite crystals and micro-aggregates of dolomite; c) Close up SEM photo of spheres intergrown with acicular and prismatic aragonite crystals.

in Castañar Cave (Spain) could be a viable alternative for huntite precipitation as well.

Romanèchite

Earlier known as psilomelan (now an obsolete term), romanèchite is a barium-containing manganese oxide, commonly occurring in caves in the composition of soft or hard dark brown to black ferromanganese coatings, crusts, nodules, and earthy deposits (Hill & Forti, 1997; Onac et al., 1997; White et al., 2009; Gázquez et al., 2011). The sample analyzed (VL-M05) was collected near the end of the Galeria d'en Pau, where it occurs as black earthy masses. Apart from this location, ferromanganese deposits are widespread in CPV both in sediment sequences (Fornós et al., 2014) and as wall and ceiling deposits (Fornós et al., 2011).

Romanèchite crystals observed under SEM in our sample are either thin bladed or short acicular forming fibrous crusts (Fig. 14). The SEM imaging combined with mineral specific spot EDX analysis indicates that romanèchite is intergrown with hematite (also identified by means of XRD) and various clay minerals (Fig. 14, inset). This assemblage documents an intense subaerial weathering process, relating the presence of this mineral with a vadose phase in the cave evolution. Without further investigations it is difficult to precisely infer the

the CPV romanèchite are probably a product of Mn^{2+} oxidation (a microbially mediated) in oxic, subaerial conditions. The barium is probably supplied by the carbonate bedrock in which concentrations of up to 1.5% were found (Fornós et al., 2011).

CONCLUSIONS AND IMPLICATIONS FOR SPELEOGENETIC DIAGNOSIS

The excitement about investigating the minerals of Cova des Pas de Vallgornera came from the fact that the most diverse assemblages group around typical hypogene features occurring in Tragus and Nord sectors (21 species) as well as in Sector F (13). Only after detailed studies we learned that not all these minerals were precipitated in conjunction with a hypogenic phase. Considering the textural relationship between the minerals of a given assemblage, and noticing the absence of only hypogene or non-hypogene mineral associations, we concluded that their precipitation is a result of several mineral-forming events. Given the spatial distribution of cave minerals throughout CPV, we argue that particular mineral associations are also related to different speleogenetic phases (seacoast mixing, ascending thermal groundwater, and meteoric recharge) in the cave evolution.

Fig. 14. Thin bladed and fibrous crusts of romanèchite. In inset, the EDS spectrum showing the presence of manganese and barium.

The minerogenic role of ascending thermal waters in the Mallorcan karst is somehow different from the classical one documented in caves under Budapest (Hungary). At certain locations the hot waters rising from depth are responsible for the precipitation of an abundant and diverse suite of carbonates and sulfates (gypsum, barite, and celestine), along with some exotic minerals (e.g., fluorite, quartz, etc.; Dublyansky, 1995; Leél-Össy et al., 2011). In contrast, in CPV the minerals are not deposited directly from deep-seated thermal groundwaters, but instead, they are a product of the interaction between mineralized warm brackish waters and the carbonate bedrock or preexisting minerals. Thus, most minerals (e.g., aragonite, barite, celestine, jacobsonite, todorokite, etc.) were precipitated inside feeders while the solutions moved upward and in the near vicinity of vents (floor, wall, or ceiling).

In addition, the rising hot air released by these waters is responsible for complex replacement and condensation-corrosion processes acting upon bedrock. The result is a fluffy colorful organo-mineral thick skin, rich in clay minerals, Fe and/or Mn oxides and hydroxides (goethite, hematite, romanèchite, todorokite), chamosite, and quartz silt. Traces of microbial activity observed under SEM suggest microorganisms may play a significant role in the precipitation of certain minerals in CPV.

Ankerite, aragonite, calcite, dolomite, epsomite, and gypsum are the only minerals in the composition of speleothems occurring nearby (above, at, and below) the brackish water table. Apart from sea-controlled calcite and aragonite phreatic overgrowths on speleothems (POS), which are widespread in CPV, all the other minerals occur as crusts, coatings, and minute crystals. All are precipitated from cold, Ca^{2+} , Mg^{2+} , and SO_4^{2-} -rich brackish waters.

The mineralogy of speleothems deposited from low-temperature, downward-circulating meteoric waters is dominated by calcite. Gypsum, aragonite, dolomite, and ankerite are the other important mineral species associated with a late-stage, vadose cave evolution. Some less frequent minerals were also identified in the composition of other vadose speleothems (Table 1).

Although barite, celestine, todorokite, gibbsite, and nordstrandite were earlier associated with sulfuric acid speleogenesis (Polyak & Provencio, 2001; Onac et al., 2009), none of these or any of the other investigated cave minerals in CPV are actually speleogenetic by-products. This observation is supported by our stable isotope ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $\delta^{34}\text{S}$) investigations.

Here we show that combining mineralogical mapping throughout CPV with precise mineral phase identification and textural relationship analysis is an efficient way to understand various mineral-forming events and their link to particular speleogenetic pathways. In this vein, stable isotope studies provide strong evidences that further help deciphering both the mineral origin and cave genetic history.

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