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International Journal of Speleology

Official Journal of Union Internationale de Spéléologie



Diagenesis of a drapery speleothem from Castañar Cave: from dissolution to dolomitization

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Abstract:

Martín-Pérez A., Martín-García R. and Alonso-Zarza A.M. 2012. Diagenesis of a drapery speleothem from Castañar Cave: from dissolution to dolomitization. *International Journal of Speleology*, 41(2), 251-266. Tampa, FL (USA). ISSN 0392-6672. <http://dx.doi.org/10.5038/1827-806X.41.2.11>

A drapery speleothem (DRA-1) from Castañar Cave in Spain was subjected to a detailed petrographical study in order to identify its primary and diagenetic features. The drapery's present day characteristics are the result of the combined effects of the primary and diagenetic processes that DRA-1 underwent. Its primary minerals are calcite, aragonite and huntite. Calcite is the main constituent of the speleothem, whereas aragonite forms as frostwork over the calcite. Huntite is the main mineral of moonmilk which covers the tips of aragonite. These primary minerals have undergone a set of diagenetic processes, which include: 1) partial dissolution or corrosion that produces the formation of powdery matt-white coatings on the surface of the speleothem. These are seen under the microscope as dark and highly porous microcrystalline aggregates; 2) total dissolution produces pores of few cm² in size; 3) calcitization and dolomitization of aragonite result in the thickening and loss of shine of the aragonite fibres. Microscopically, calcitization is seen as rhombohedral crystals which cover and replace aragonite forming mosaics that preserve relics of aragonite precursor. Dolomitization results in the formation of microcrystalline rounded aggregates over aragonite fibres. These aggregates are formed by dolomite crystals of around 1 µm size. The sequence of diagenetic processes follows two main pathways. Pathway 1 is driven by the increase of saturation degree and Mg/Ca ratio of the karstic waters and is visible in the NW side of the drapery. This sequence of processes includes: 1) aragonite and huntite primary precipitation and 2) dolomitization. Pathway 2 is driven by a decrease in the degree of saturation of calcite and aragonite and Mg/Ca ratio of the cave waters, and it is observed in the SE side of the drapery. The diagenetic processes of the second pathway include: 1) calcitization of aragonite; 2) incomplete dissolution (micritization) of both aragonite and calcite; 3) total dissolution. This study highlights the importance of diagenetic processes on speleothems and their complexity. The correct interpretation of these processes is crucial for the understanding of possible changes in the chemistry of waters, temperature, or pCO₂ and so is critical to the correct interpretation of the paleoenvironmental significance of speleothems.

Keywords: diagenesis; speleothems; corrosion; aragonite-calcite; dolomitization

Received 8 February 2012; Revised 8 March 2012; Accepted 14 May 2012

INTRODUCTION

Speleothems can potentially yield environmental and climate proxies for paleoclimatology studies, and have been the objective of numerous research studies for the last twenty or thirty years (McDermott, 2004; Fairchild et al., 2007; Frisia & Borsato, 2010). They are attractive to paleoclimatologists because: i) they can grow continuously and be precisely dated through a series of techniques (Frisia & Borsato, 2010); ii) they capture the cave response to the external environment during their formation (cave temperature is around the mean annual external temperature and

dripwater discharge reflects the amount of infiltration) (McDermott, 2004); and iii) they generally show little secondary alteration (Fairchild et al., 2006). However, diagenetic processes affecting speleothems have been recognised in a certain number of caves around the world (Cabrol, 1978; Frisia et al., 2002; Woo & Choi, 2006; Woo et al., 2008; Hopley et al., 2009; Martín-García et al., 2009; Aramburu Artano et al., 2010; Pagliara et al., 2010). Diagenetic processes can potentially modify the original features of speleothems, including their geochemical signatures (Frisia et al., 2002; Woo & Choi, 2006), so their use in paleoclimate studies can be problematic. In addition, all these studies on speleothem diagenesis were strongly focused on the calcitization of aragonite, while other diagenetic processes have not been described in the same detail. Dissolution processes which alter the aspect of speleothems have also been widely analysed (Hill & Forti, 1997; Sánchez-Moral et al., 1999; de Freitas & Schmekel, 2006), and commonly described as

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“corrosion” due to condensation (Dublyansky & Dublyansky, 1998; Tarhule-Lips & Ford, 1998; Auler & Smart, 2004; Dreybrodt et al., 2005). Despite the fact that dolomite has been found in several caves forming part of speleothems (see Jones 2010 and references therein), very few studies have described in depth the features of this karstic dolomite (Thraikill, 1968; Bar-Matthews et al., 1991; Jones, 2010) and only a few have discussed the dolomitization process of a previous carbonate phase (Moore, 1961; Thraikill, 1968; Fishbeck & Müller, 1971).

Castañar Cave is a relatively small cave hosted in shales, greywackes and dolostones which display an interesting array of speleothems of different morphologies and mineralogies. Many of the speleothems have been affected by a variety of diagenetic processes, driven by the modification of the chemistry of the waters and the unstable nature of some of the primary minerals such as aragonite or huntite (Alonso-Zarza & Martín-Pérez, 2008; Martín-García et al., 2009). Our study focuses on one drapery of the “Banderas Hall” within Castañar Cave. This drapery contains most of the minerals and textures found within the cave. The aim of this study is to perform a detailed petrographical study of the different parts of this speleothem, in order to identify the primary characteristics and the diagenetic transformation of the various minerals and textures. In doing so, we aim: a) to explain the causes of the different diagenetic processes and b) to propose a model of the diagenetic paths that can affect speleothems.

GEOLOGICAL SETTING

Castañar Cave is located in Cáceres province, Spain (Fig. 1). Geologically, this area belongs to the Centroiberian Zone of the Iberian Massif, to a sector named Domain of Vertical Folds. In this domain,

broad antiforms of N30°W direction contain Neoproterozoic-Early Cambrian rocks, while Ordovician-Silurian materials crop out in narrow synclines (Fig. 1a) (Díez-Balda et al., 1990). The cave is hosted in the upper part of the Neoproterozoic-Early Cambrian rocks which crops out in the Ibor Anticline (Fig. 1b). These rocks are shales and sandstones with intercalation of carbonate levels. The carbonates are dolostones which are partially replaced by magnesite of hydrothermal origin (Herrero et al., 2011).

CASTAÑAR CAVE

Castañar Cave is a maze cave consisting of a network of sub-horizontal galleries a few metres wide and about 2 m high. The cave passages follow the N30°W orientation of the main folds in the area (Fig. 1c) and the morphology of the rooms also reproduces the geometry of the decametre-scale folds (Alonso-Zarza et al., 2011). These passages were formed by dissolution of the carbonate levels and subsequently enlarged by collapses of the overlying siliciclastic beds. Bedding, fractures and cleavage planes are the main paths for water circulation, promoting weathering of the host rock and areas of preferential growth of speleothems. All this indicate the structural and lithological control of the formation of the cave and the distribution of speleothems (Alonso-Zarza et al., 2011).

Castañar Cave used to be a touristic cave, but it had limited visits (i.e. 1508 persons during the year 2004, distributed among 189 groups (Fernández-Cortés et al., 2009). The cave has only one natural entrance closed with a quasi-hermetic trap door which is only opened during the visits. The environmental parameters inside the cave are very constant throughout the year (Fernández-Cortés et al., 2009). The mean temperature of the cave is 16.94 °C and shows a year-ly variation of 0.09 °C. Mean CO₂ concentration in the

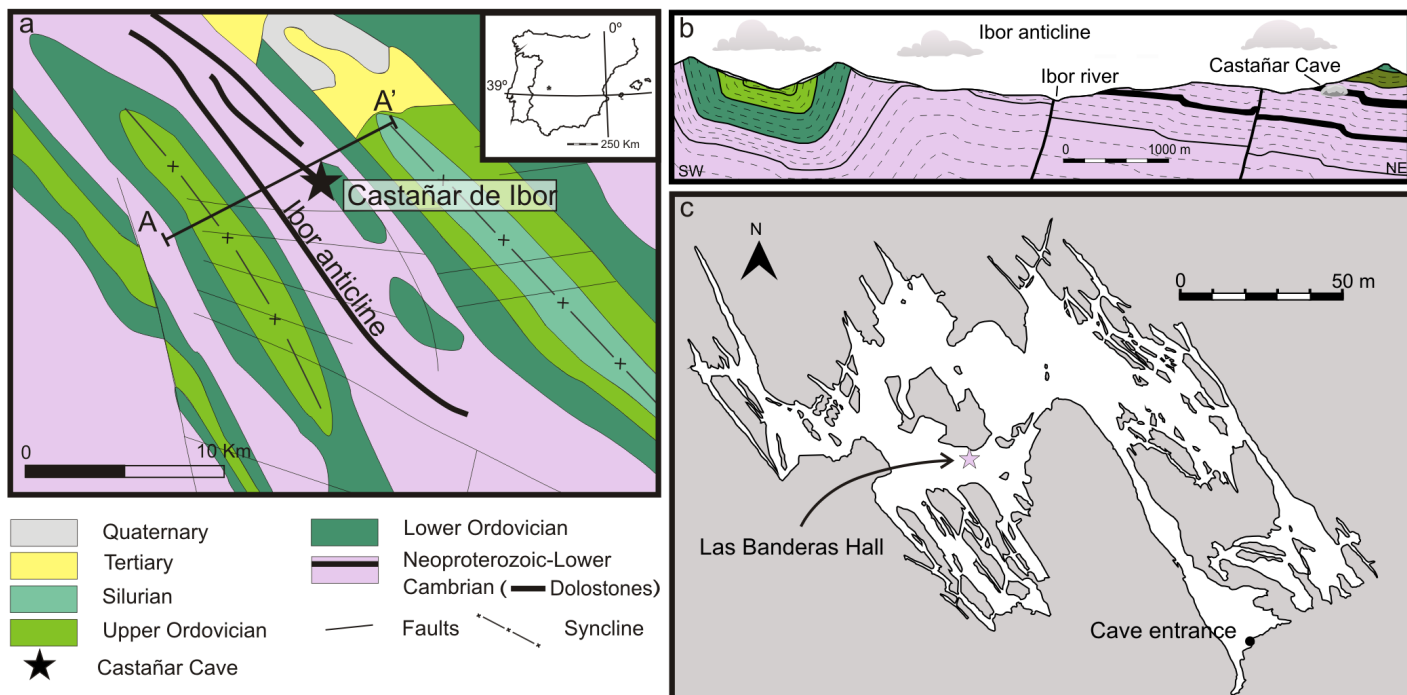


Fig. 1. a) Simplified geological map of the studied area; b) Geological cross-section through the Ibor Antiform. The location of the cave within the carbonates of the Ibor Group is indicated; c) Map of Castañar Cave. The star marks the location of the drapery DRA-1.

cave atmosphere is 3680 ppm, with an annual oscillation of 1120 ppm (Sánchez-Moral et al., 2006). Relative humidity is close to saturation (>99.5%) (Fernández-Cortés et al., 2010). At present there is no flowing water in the cave, although there are three small pools. Drip and capillary seepage water is sparsely distributed throughout the cave. Chemical composition of the water is stable throughout the year, being rich in Mg^{+2} , Ca^{2+} and HCO_3^- (Sánchez-Moral et al., 2006). Monitoring of cave waters of lakes and drips during 2004 (Sánchez-Moral et al., 2006) showed that they are close to saturation (± 0.25) in aragonite, or oversaturated (>0.25) with respect to calcite and dolomite (Fernández-Cortés et al., 2010). Waters were near to equilibrium or slightly undersaturated in magnesite, and generally undersaturated in huntite, nesquehonite and hydromagnesite. The composition of the water of a pool was monitored by Sánchez-Moral et al., (2006) from December 2003 to August 2005 obtaining values of Mg^{2+}/Ca^{2+} ranging from 1.1 to 1.8.

Cave deposits

Speleothems are very abundant in Castañar Cave and show a wide array of morphologies and different mineralogies. They appear in all the rooms on the floor, walls and ceiling. In general they can be grouped into massive and branched types (Alonso-Zarza et al., 2011). The branched morphologies are usually formed by aragonite and include frostwork, anthodites and helictites. The massive ones are usually composed of calcite and include stalactites, stalagmites, draperies and flowstones. Other speleothems are coralloids, crusts, gourds, rafts and moonmilk. Aragonite and calcite are the most abundant minerals, but there are also other minerals such as huntite, magnesite and dolomite, mostly forming part of moonmilk and crusts (Alonso-Zarza & Martín-Pérez, 2008). Many speleothems are considerably altered by diagenetic processes that have overprinted their primary features. U-Th dating on primary aragonite speleothems gives ages that range from 352.9 (8.3) to 71.2 (1.0) ka (Alonso-Zarza et al. 2011). The floor of many rooms of the cave is covered by blocks of shales, greywackes and dolostones while coatings of red clays cover large areas of ceilings and walls (Martín-Pérez et al., 2010).

SAMPLING AND METHODS

Sampling was performed in a drapery named DRA-1. Small fragments of the different textures and minerals recognised were carefully collected. The primary calcite crystals can be observed only in the internal and upper part of the drapery. This area is difficult to access, and its sampling would involve considerable damage to the speleothem. For this reason, the micro morphology and sizes of the crystals were inferred from the study carried out on the altered part of the drapery. Conventional optical petrography studies were performed on thin sections of samples of the drapery showing different textures. Due to their fragility, the samples were embedded in a resin containing Epofer EX 401 and Epofer E 432 in a vacuum system before cutting and polishing. Scanning electron microscopy (SEM) observations were performed on gold-coated samples using a JEOL JSM-820 6400

electron microscope working at 20 kV. An EDX system yielded semi-quantitative compositions. Mineralogical characterization was done by X-ray diffraction (XRD) using a Bruker D8 diffractometer operating at 40 kV and 30 mA, at $2^\circ/\text{min}$, with monochromated $CuK\alpha$ radiation. XRD spectra were obtained from 2 to $65^\circ 2\theta$.

LOCATION AND MORPHOLOGY OF DRAPERY DRA-1

The speleothem studied is a drapery situated in a hall known as “Las Banderas” (The draperies) (Alonso-Zarza et al., 2011). Draperies are curtain-like speleothems which hang down from inclined cave ceilings where the crystals grow with their long axes perpendicular to the lower edge of the drapery (Hill & Forti, 1997). “Las Banderas” Hall is characterised by the presence of a group of draperies of centrimetric to metric size, one of them (DRA-1) is the aim of our study (Fig. 2). This group of draperies is located in the topographically higher area of the hall and in the nearby of flowstone deposits, a small lake and other speleothems such as stalactites, stalagmites and aragonite frostwork. To the southwest of the group of draperies there are no large speleothems. The floor of cave is covered by blocks and crusts and the ceiling is coated with red clays (Fig. 2).

Around 1 m long and 0.70 m wide, DRA-1, oriented $N30^\circ E$, appears surrounded by four more draperies of smaller size and with similar orientation ($N30^\circ E - N035^\circ E$). Directly below these draperies there are no stalagmites, just a slope covered with flowstone that is dipping towards the lower lake. The drapery appears dry, not showing any dripping.

The white drapery studied displays various textures, and presents a central hole of around 20 cm of diameter (Fig. 3). One important feature of this drapery is that each of its sides shows differing textures and mineral composition. The side pointing towards SE is flat and striated (Fig. 3a). Striation defines the growth bands of the speleothem and display a very fragile and porous texture. In some spots, layers of crystals parallel to the surface of the drapery are

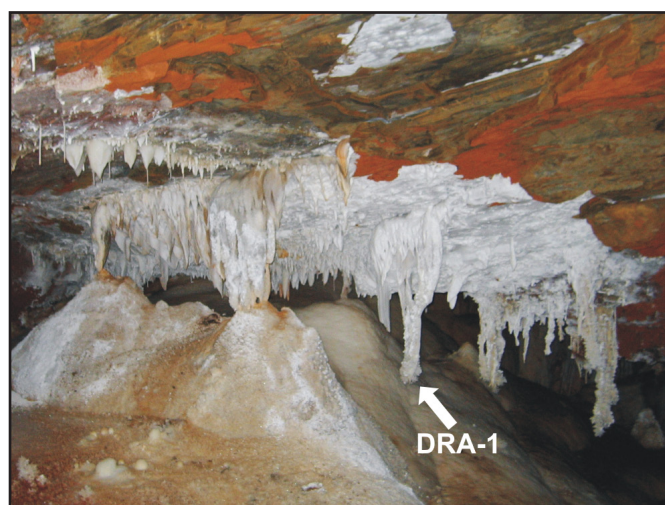


Fig. 2. General view of the higher part of “Las Banderas” Hall. The studied drapery is arrowed.

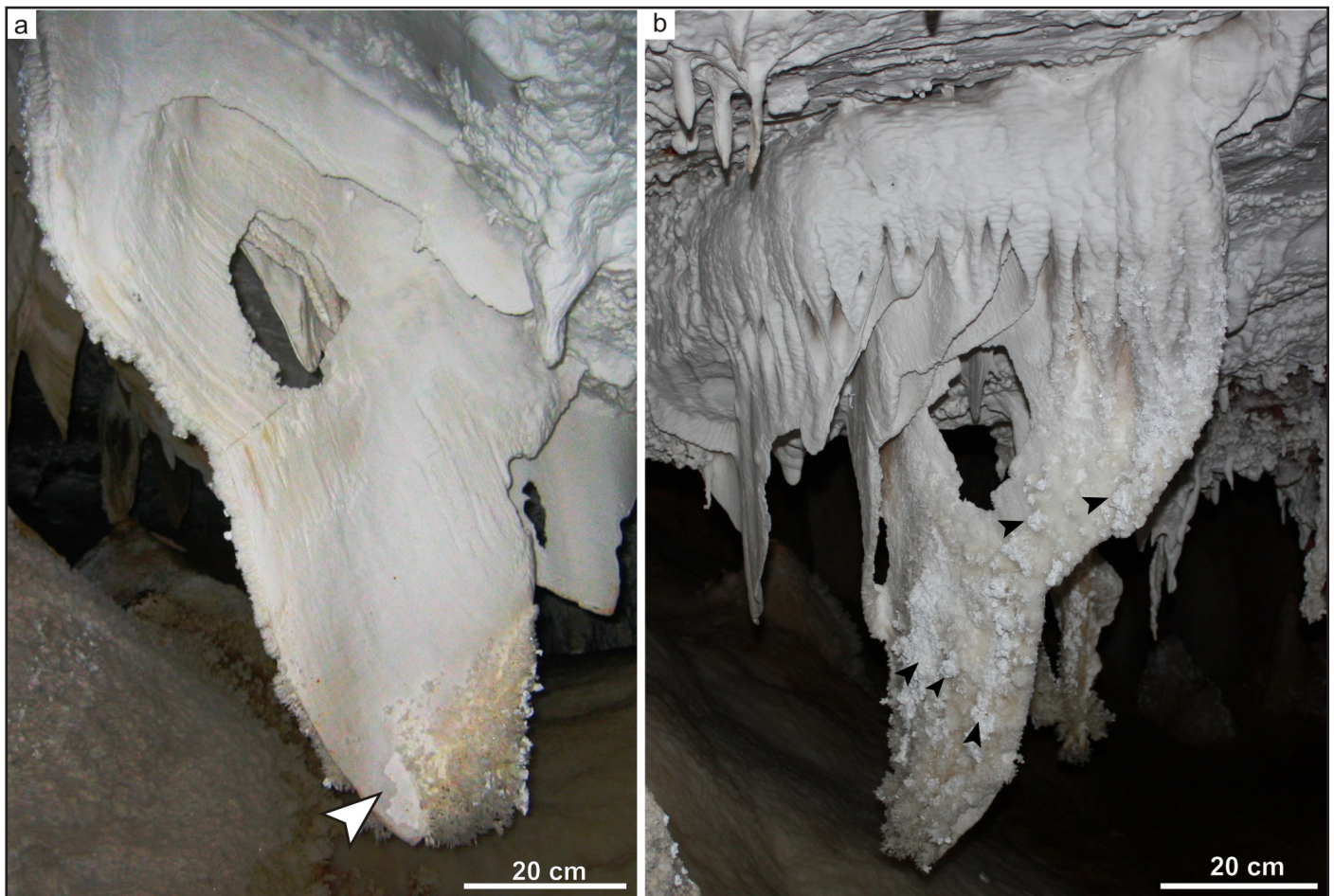


Fig. 3. Macroscopic features of the studied drapery. a) Southeast face shows a powdery striated surface. In the area pointed by arrow the upper layer of powdery crystals is getting detached and chipping off; b) The northwest face of the drapery is covered by aragonite frostwork with irregular patches of moonmilk over them (arrowed).

spalling, forming flakes and chipping off (Fig. 3a, arrow). The side pointing NW, more complex (Fig. 3b), is covered by aragonite frostwork tipped with moonmilk globules (Fig. 3b).

PETROGRAPHY

Primary features

The body of the drapery studied, formed by calcite, is of a transparent to beige-translucent appearance. This calcite, of a palisade or columnar fabric (Frisia & Borsato, 2010), presents crystals elongated perpendicularly to the growing surface, with length to width ratios $\geq 6:1$ and undulated extinction. The crystals are between 500 μm to 2 mm long and from 50 to 300 μm in width.

Aragonite occurs as frostwork in the lower part of the drapery and over the NW surface. Aragonite crystals are transparent and shiny. They present arrays of acicular fabric (Frisia & Borsato, 2010) with length to width ratio $\gg 6:1$, while the faces of the crystals are flat and smooth. Crystals grow radiating from a common point forming fans and branched morphologies. Huntite ($\text{CaMg}_3(\text{CO}_3)_4$) (Fig. 4a) is the main mineral forming moonmilk, a white, pasty and wet deposit forming globules of around 0.5-3 cm diameter and irregular powdery patches over the aragonite fans (Fig. 4b). Huntite is seen under the microscope as brownish masses of crystals of micrite size. SEM observa-

tions show that the huntite occurs as flake-like crystals, of $< 5 \mu\text{m}$ size and a few nm thick (Fig. 4c). These flakes or platelets are randomly distributed, forming aggregates of high porosity.

Diagenetic features

Powdery carbonate coatings

Powdery carbonate coatings are present over extensive areas of the drapery, especially in the SE side. The aspect of this area is dull in comparison with the translucent, brilliant non-altered areas (Fig. 5a), due to the presence of above-mentioned white, powdery and matt material. This powdery material can appear: 1) covering the surface of the drapery and other speleothems forming coatings from 1 to several mm thick; 2) forming internal powdery lines between crystalline layers or 3) constituting the whole body of the speleothem, as occurs in some areas of the drapery studied. Powdery areas are seen in the microscope as dark dirty aggregates of calcite crystals (Fig. 5b-e). These aggregates show pores of different sizes which give the crystals a high heterogeneity in thickness and shape. In aggregates displaying less porosity, the outline and the extinction pattern of the original crystals are preserved (Fig. 5b). The most porous aggregates consist of an opaque structureless mass of anhedral crystals (Fig. 5c) ranging in size from less than 1 μm to 100 μm . Large areas of the drapery show this texture, especially in the central part where there are no relics

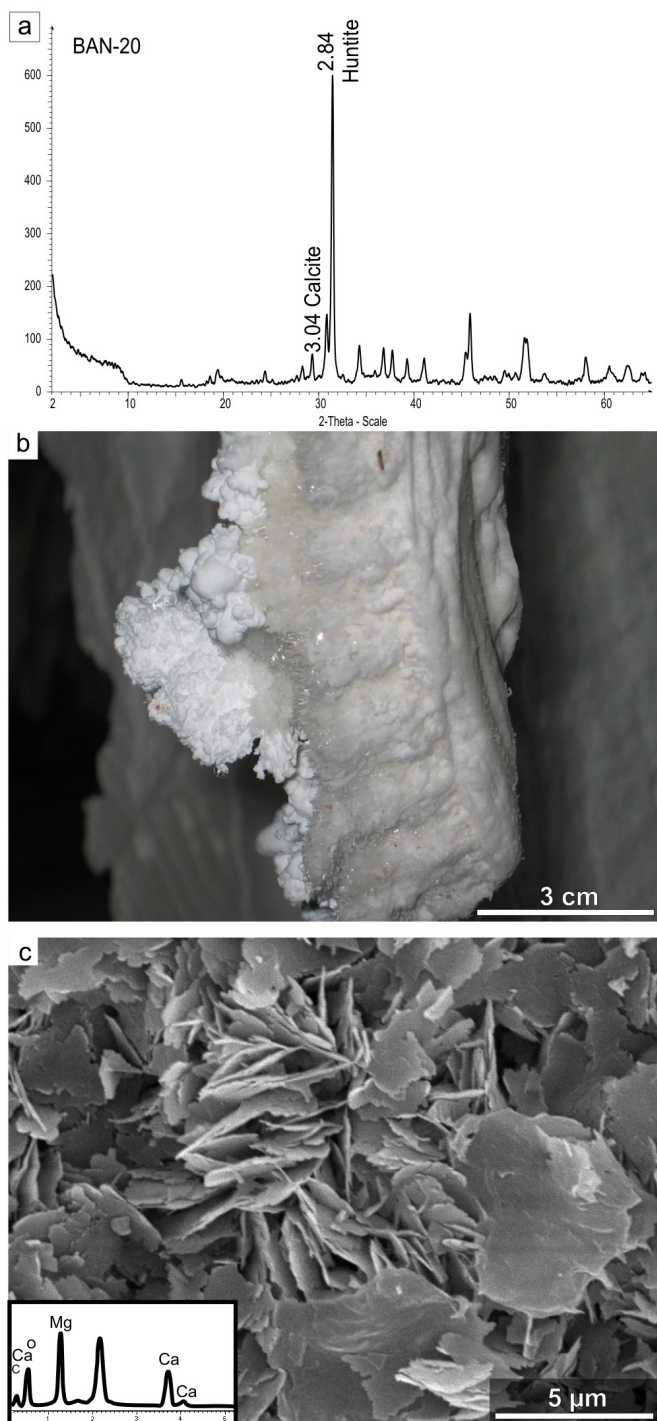


Fig. 4. a) XRD pattern showing mineralogy of moonmilk. All the peaks correspond to huntite except the $2\theta=3.04$ that corresponds to calcite; b) Huntite moonmilk globules in the NW face of the drapery; c) SEM image of an aggregate of flake-like huntite crystals. EDS scan indicate the composition of the crystals.

of the primary texture. In cases where powdery lines are located between layers of clean crystals (Fig. 5d) the contact between them can be sharp or gradual. In the last case, the dark masses are mostly situated on the boundaries between the crystals (Fig. 5e), or along growing surfaces. SEM images of this porous calcite show that the pores range in size from less than $1\ \mu\text{m}$ to $200\ \mu\text{m}$, they display rhombohedral shapes and are distributed following crystallographic directions (Fig. 5f). They are so abundant that the remaining crystals form a fragile structure that in some parts can be as

thin as $1\text{--}5\ \mu\text{m}$. Larger-scale porosity can result in the total loss of material, leaving pores of few cm^2 , as those seen in the central part of DRA-1 and the nearby speleothems.

Secondary minerals

Secondary minerals, either calcite or dolomite, occur over the aragonite frostwork of the lower and NW part of the drapery. The presence of these minerals results in the thickening and loss of shine and transparency of the aragonite crystals (Fig. 6a, b). It is possible to recognise the existence of a previous precursor since the calcite/dolomite crystals are aligned following the direction of the aragonite needle crystals. In the aragonite fans a transition from totally-replaced to unaltered crystals can be seen. The external part of the fans is composed of transparent needle aragonite while in the inner part the aragonite needles are totally replaced and thickened (Fig. 6c).

Calcite thickenings (Fig. 7) consist of rhombohedral crystals of $100\ \mu\text{m}$ to $1\ \text{mm}$ in length, which are arranged following the direction of the aragonite fibres in the fans (Fig. 8a). They usually contain prismatic or needle-shaped relics of aragonite (Fig. 8b). The secondary calcite crystals can also show microcrystalline coatings or lines similar to those of powdery coatings (Fig. 8a, b). Calcite crystals as seen in the SEM images are very euhedral and very precisely reproduce the shape of the previous aragonite fibres (Fig. 8c and d).

Dolomite thickenings (Fig. 9a) occur as globular-spheroidal microcrystalline aggregates which cover (Fig. 9b) and replace aragonite (Fig. 9c, d). Rounded to spheroidal dolomite in the SEM images is seen to coat the surface of aragonite needles totally (Fig. 9e) or partially (Fig. 9f). Each spheroid is composed of dolomite crystals of around $1\ \mu\text{m}$ size (Fig. 9g).

DISCUSSION

Controls on primary mineralogy of speleothems

The main body of the drapery DRA-1 is formed by elongated columnar calcite, a fabric sub-type defined by crystals with length to width ratios $\gg 6:1$ and undulate extinction (Frisia & Borsato, 2010). Columnar fabrics are indicative of near-equilibrium conditions and constant flow, and elongated sub-type has been observed to develop when the Mg/Ca ratio (molar) in the feeding water exceeds 0.3 (Frisia et al., 2000). Relatively Mg enriched waters, as those found in Castañar Cave, can explain the formation of this type of calcite, and they would also be responsible for the presence of aragonite in the studied drapery, since it is commonly accepted that aragonite forms in the speleothems when Mg/Ca ratios in the waters are high (Cabrol & Coudray, 1982; González & Lohmann, 1988; Frisia et al., 2002; Rowling, 2004) due to the inhibiting role of Mg^{2+} in calcite growth (Berner, 1975; Lippmann, 1973; Fernández-Díaz et al., 1996). Commonly, the high Mg/Ca necessary for aragonite formation has been related to evaporation that may accompany seasonal dryness (Railsback et al., 1994) and warmer and dryer climatic conditions (Pagliara et al., 2010), although aragonite precipitation has also been reported in comparatively wet climatic conditions due to the effect of Zn^{2+} or Pb^{2+} in inhibiting precipitation of calcite (Caddeo et al., 2011).

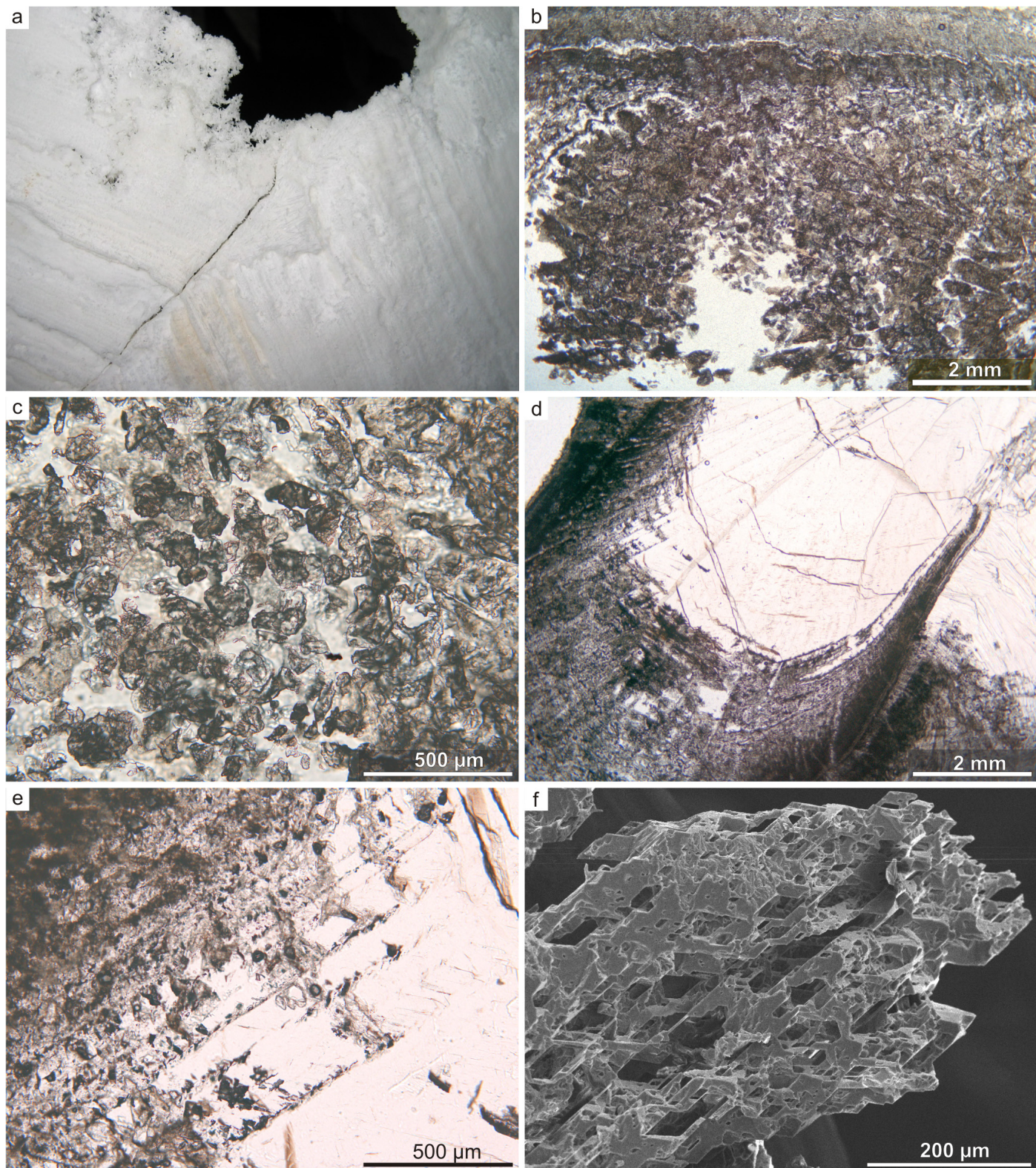


Fig. 5. a) Powdery carbonate coatings on the SE face of the drapery; b) Microphotograph of a fragment of the powdery coating. Note that the columnar fabric of primary calcite can be outlined, plane-polarized light; c) Microphotograph showing the internal texture of powdery coatings, composed of an aggregate of anhedral crystals of different sizes. Plane-polarized light; d) Microcrystalline envelope coating clean primary calcite crystals, plane-polarized light; e) Detail of d. The advance of the coating to the interior of crystals preferentially follows crystal boundaries. Plane-polarized light; f) SEM image showing the distribution of pores of the crystals constituting the powdery coatings.

In Castañar Cave dissolution of dolostones and magnesites provides initially Mg-enriched solutions in which the Mg/Ca ratio can be increased in a several ways, as for instance, by removal of Ca from the waters by processes of “prior calcite precipitation” occurring in the epikarst before the waters reach the cave atmosphere, during relatively dry periods (Fairchild

& McMillan, 2007). Similar mechanism of increasing Mg/Ca ratios, by removal of Ca^{2+} ions from solution, can explain the formation of hydromagnesite or huntite, which requires even higher Mg/Ca ratios and higher alkalinity than aragonite formation (Müller et al., 1972; Lippmann, 1973; Davies et al., 1977). The evaporative concentration of cave waters and the CO_2

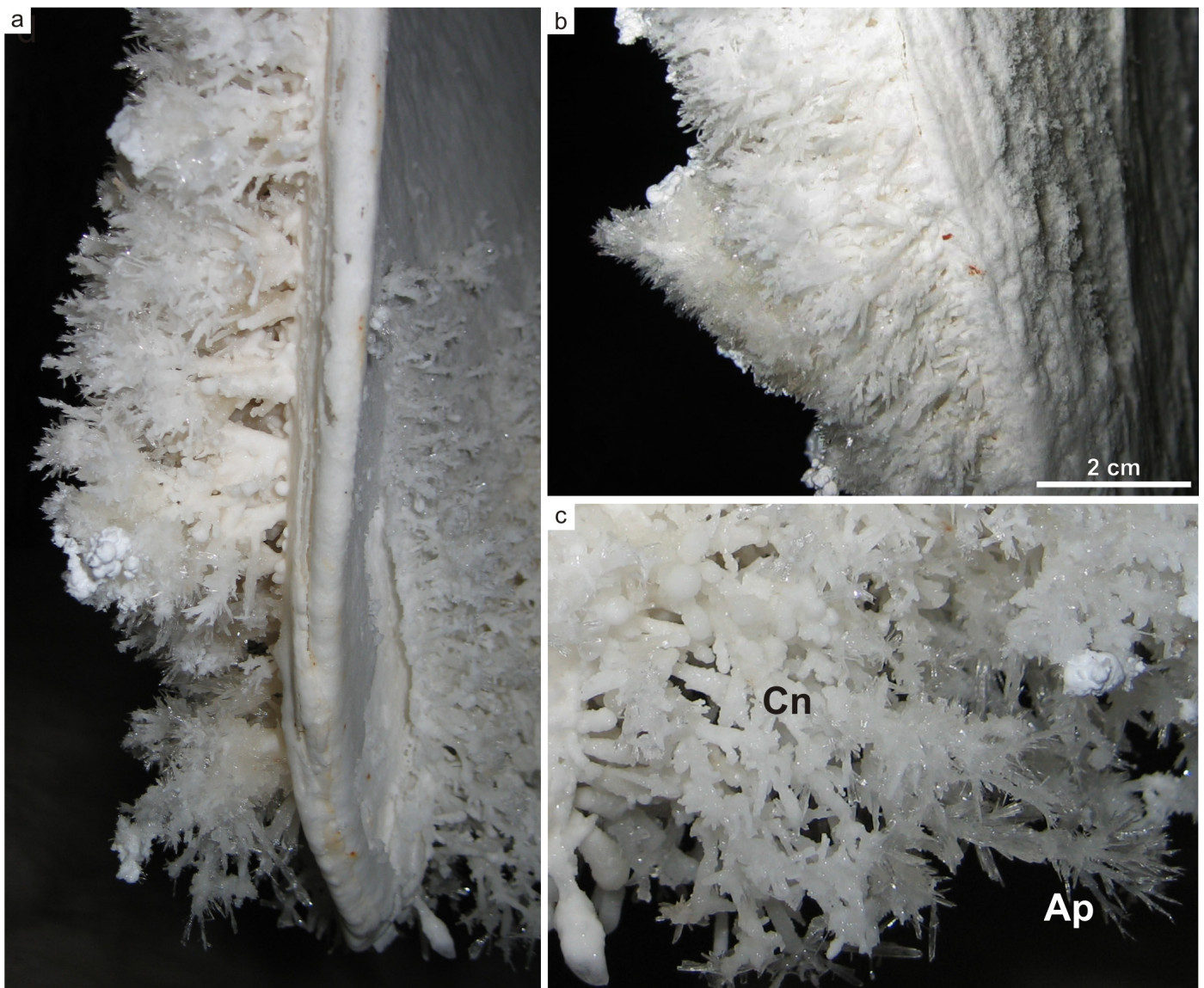


Fig. 6. Thickening of crystals due to formation of secondary minerals. a) In the lower part of the NW face of the drapery the base of the aragonite fans is thickened and shows a cream colour; b) In other areas of the drapery the aragonite fans are totally replaced and show a matt white surface; c) Transition from shiny transparent primary aragonite crystals (Ap) to aragonite crystals totally replaced by neomorphic calcite (Cn).

loss results in the sequential precipitation of calcite, aragonite, huntite and hydromagnesite (Fishbeck & Müller, 1971; González & Lohmann, 1988; Hill & Forti, 1997; Casas et al., 2001). Progressive degassing increases the CO_3^{2-} concentration of fluids and results in calcite precipitation that depletes the thin cave water film on the speleothems of Ca ions, increasing the Mg/Ca ratio. This increase promotes aragonite precipitation, which further depletes the water film of Ca^{2+} and further increases the Mg/Ca ratio, allowing precipitation of huntite and/or hydromagnesite (Hill & Forti, 1997) and, if silica is available, smectites (Pol-yak & Güven, 2000).

Summarizing, in Castañar Cave dissolution of the host rock control the initial Mg-rich composition of the cave waters, which will also be determined by the hydrological regime. These variations in the chemistry of the waters together with the microclimatic conditions prevailing in the cave in each moment will control which mineral will precipitate in the cave: 1) elongated columnar calcite would have formed in con-

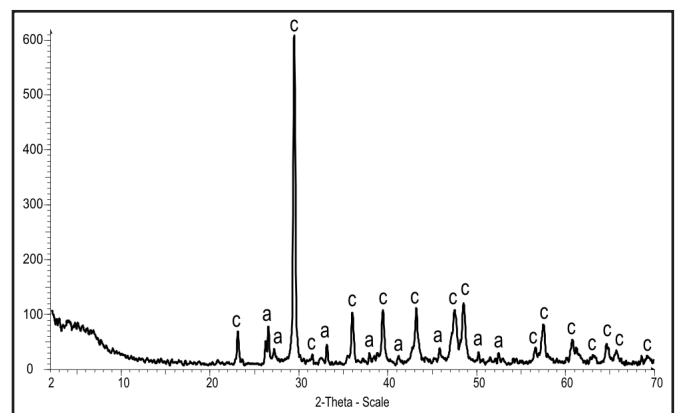


Fig. 7. XRD pattern of the calcitized aragonite. Sample is composed of 76% of calcite (c) and 24% of aragonite (a).

ditions of low and constant degree of calcite supersaturation in environments of constant drip rate and Mg/Ca ratios ≥ 0.3 (Frisia & Borsato, 2010), probably in relatively humid periods; 2) acicular aragonite pre-

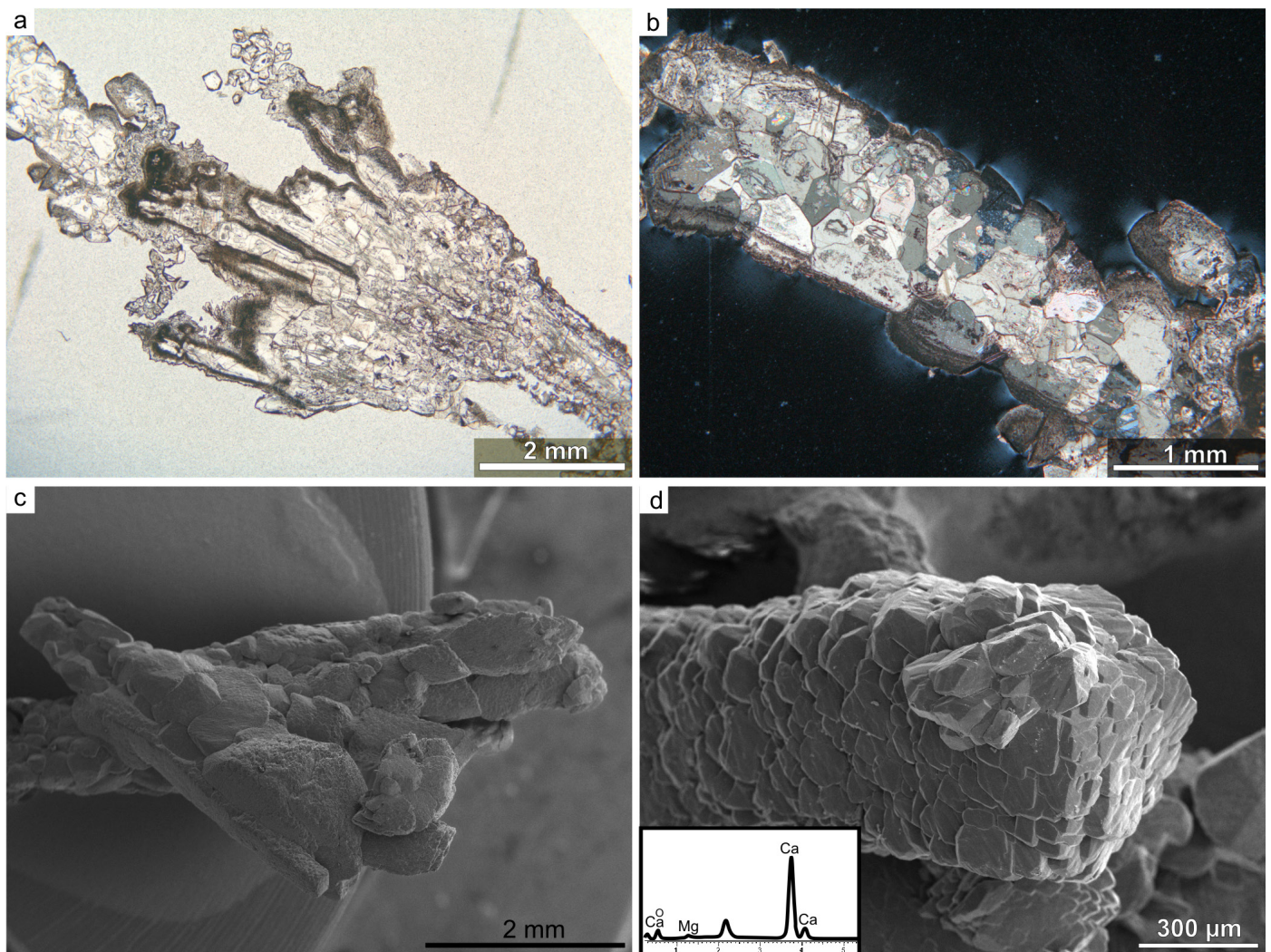


Fig. 8. Petrography of calcitization. a) Mosaic of calcite crystals arranged following the orientation of previous aragonite fans of fibres. Plane-polarized light; b) The calcite equant crystals show prismatic and needle-like relics of aragonite precursor. Cross-polarized light; c) and d) SEM image of rhombohedral calcite crystals aligned in the direction of previous aragonite fibres. EDS scan indicate the composition of the crystals.

precipitation should occur through prolonged degassing and evaporation at very low drip rates and high Mg/Ca ratios (Gonzalez & Lohmann, 1988; Frisia et al., 2002) and 3) huntite probably formed by evaporative concentration of waters and elevated Mg/Ca ratios and alkalinity in the fluids (Fishbeck & Müller, 1971; Hill & Forti, 1997). Both aragonite and huntite precipitation would have required relatively high Mg/Ca ratios which were probably achieved by seasonal and global drier conditions outside the cave or by evaporation processes taking place inside the cave.

Origin of the diagenetic features

Powdery carbonate coatings

The presence of pores at all scales in the powdery coatings of speleothem leads us to interpret them as a product of partial dissolution. This process implies the transformation of massive crystalline parts of speleothems into porous, disaggregated masses of smaller crystals. If the smaller crystals are washed away, the porosity becomes the main feature and the result is a fragile network of etched crystals, while if the water flow is slow enough, the smaller crystals remain attached to the surface of speleothem. More intense

dissolution causes the formation of macroscopic pores such as the one seen in the centre of the drapery.

These alteration features produced by dissolution have usually been termed “corrosion” (Tarhule-Lips & Ford, 1998; Sánchez-Moral et al., 1999; Auler & Smart, 2004; Martín-García et al., 2011) or “partial dissolution” (Zupan-Hajna, 2003). Since the smaller crystals observed are of less than 4 µm, and due to the dark structureless microcrystalline textures of the corroded areas observed under the microscope, we have also designated this alteration process as “micritization” (Martín-García et al., 2009). The term micrite in this case describes carbonate particles less than 4 µm long, without genetic implication (Milliman et al., 1985; Jones & Kahle, 1995). The process of micritization has mostly been used to describe a shallow marine diagenetic process that results in a loss of the original internal structure of carbonates via alteration to cryptocrystalline textures (Reid & Macintyre, 1998) often related to the activity of microorganisms (Perry, 1999). In Castañar Cave, no evidence of the activity of microorganisms has been found, and micritization/corrosion is considered to be inorganic, due to dissolution. This inorganic mechanism has also been

addressed in marine settings where partial dissolution can cause micritization of crinoids (Neugebauer, 1978). Micritized or corroded bands interlayered with bands of clean crystals represent antique weathered surfaces of the speleothem and they indicate interruptions of growth and subsequent corrosion (Martín-García et al., 2011).

The fluid causing corrosion can be liquid water, but it can also be water vapour. Corrosion of the minerals in speleothems and host rocks occurs if the fluid is dilute and/or acidic (Hill & Forti, 1997) and can be caused by two main processes:

1) Condensation of moisture on cave walls and speleothems (Dublyansky & Dublyansky, 1998) can cause corrosion because moisture is undersaturated and can be acidic due to the presence of H_2S (Forti et al., 2002) or CO_2 (Sarbu & Lascu, 1997; Audra et al., 2007) in the cave atmosphere. Condensation will occur when the temperature of the cave walls is below the dew point of air, creating water film in equilibrium with the partial pressure pCO_2 of the cave atmosphere. This solution is therefore corrosive to limestone and such a dissolution process has been termed “condensation-corrosion” (Dreybrodt et al., 2005; Gabrovšek et al., 2010). Condensation processes are governed by the type and amount of heat transfers in the cave (Dreybrodt et al., 2005). They can be quite intense above thermal lakes where the thermal gradient is high (Audra et al., 2007; Cigna & Forti, 1986) or close to cave entrances, where diurnal or seasonal variations of the air temperature are active (Tarhule-Lips & Ford, 1998). In other situations, cave air temperature and condensation is mainly determined by outside air temperature and cave ventilation rate, which is itself a function of outside air temperature (de Freitas & Schmekal, 2006). The entrance of visitors in a cave can contribute to condensation-corrosion (Sánchez-Moral et al. 1999; Cuevas-González et al., 2010), since visitors breathe out warm air saturated with water vapour together with over 4% by volume of carbon dioxide at a temperature usually much higher than the cave air (de Freitas & Schmekal, 2006).

Up to now, the extent of present day condensation in Castañar Cave has not been evaluated. However, numerous studies have investigated the microclimatic conditions of the cave (Sánchez-Moral et al., 2006; Lario et al., 2006; Fernández-Cortés et al., 2009, 2010, 2011) describing it as a system with very high microenvironmental stability under natural conditions and low energy exchange with the outside. The temporal evolution of CO_2 and ^{222}Rn concentrations has shown that during the summer there is an air exchange between the cave and the exterior atmosphere which mainly takes place through the network of fissures and pores of the soil and host-rock. During the cold and wet season, the porosity is saturated with water and the cave atmosphere remains isolated (Fernández-Cortés et al., 2011). Short term fluctuations of CO_2 and ^{222}Rn are due to forced ventilation by door opening during visits (Fernández-Cortés et al., 2009). According to this, condensation processes can be taking place in the present to maintain the thermal equilibrium in the cave. However, existence and extent of condensation in the cave in past times could

have been much more important, when microclimatic variations were different. Particularly, different conditions of the natural cave entrance, or existence of other connexions with the outer atmosphere, could have determined a different behaviour of air exchange inside the cave, allowing much higher temperature gradients than those observed nowadays, and/or the presence of air flows. Those conditions could have been produced more intense processes of condensation which would produce the corrosion features observed in drapery DRA-1.

2) Undersaturated waters entering the cave.

The chemistry of karstic waters can be modified by changes in the use of soils above the cave (Broers & van der Grift, 2004; Petelet-Giraud et al., 2009) or variations in the hydrological regime inundating certain cave areas (Hill & Forti, 1997), but variability of climate in the area (McDonald et al., 2007) at different scales (Fairchild & McMillan, 2007) should be the main modifier. In the case of a Holocene stalagmite with interlayered aragonite-calcite mineralogy, Railsback et al. (1994) found that the dissolution of aragonite layers could be produced in years of high rainfall. At the beginning of intense rainfalls cave waters do not reach equilibrium with carbonate host rock due to the speed of flow, so the carbonic acid from soil is not buffered. In addition, the rapid water flow limits residence time of waters on the speleothem surface, not long enough for the degassing of CO_2 necessary to increase the saturation state of $CaCO_3$, so the result is the dissolution of aragonite.

Dissolution due to infiltration of undersaturated waters in Castañar Cave is shown by the common presence of red clays in the corroded areas of the draperies in the nearby of DRA-1. Clays and/or iron oxides were washed away by entrance of rain water and deposited over the speleothems.

Calcitization

The formation of secondary calcite in the speleothem studied occurs in two steps: 1) The first step is the nucleation of small crystals of calcite over the aragonite surface. These crystals grow over aragonite and start to cement the previously-existing porosity between aragonite fibres. 2) The calcite crystals grow further and enclose and replace the aragonite, so the final result is an equant mosaic of calcite crystals containing aragonite relics. To describe this transformation we could use the term neomorphism, as a term that describes texture transformations in a mineral (recrystallization) or its transformation into its polymorph (inversion) (Folk, 1965). However, in Castañar Cave there is a calcite cementation process previous to the inversion, so we prefer to use calcitization more broadly.

Calcitization has been recognised in a certain number of caves (Folk & Assereto, 1976; Cabrol & Coudray, 1982; Frisia et al., 2002; Woo & Choi, 2006; Pagliara et al., 2010). This process takes place by dissolution at the microscale of metastable aragonite and precipitation of the stable phase, calcite (Perdikouri et al., 2008), when waters are undersaturated in aragonite and oversaturated in calcite (Maliva et al., 2000; Frisia et al., 2002). The process can be fabric destruc-

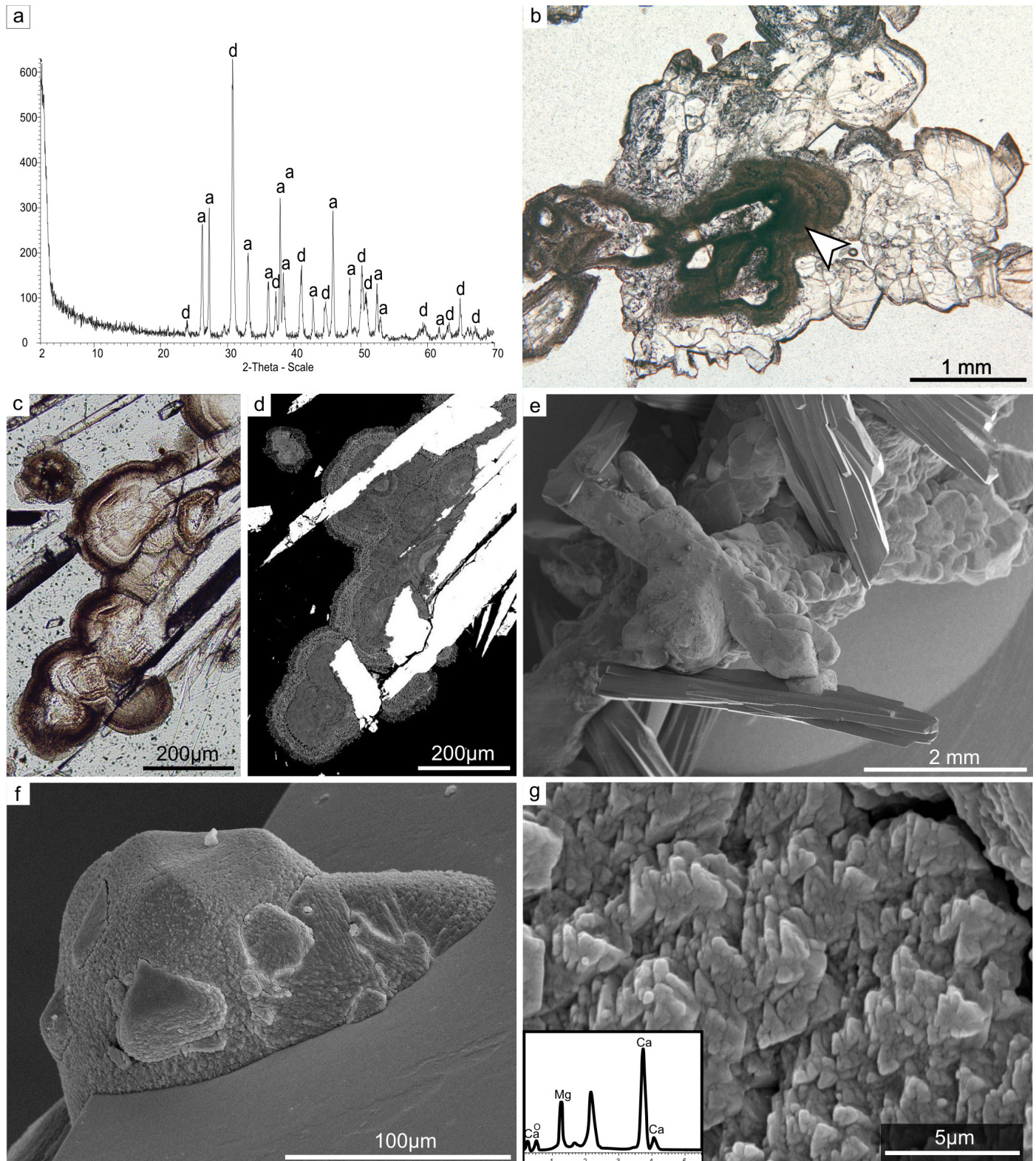


Fig. 9. Petrography of secondary dolomite. a) XRD pattern of the dolomitized aragonite. Sample is composed of 55% of dolomite (d) and 45% of aragonite (a); b) Dolomite is seen in thin section as a microcrystalline brown masses with globular shapes (arrow). Plane-polarized light; c) Spheroidal dolomite growing over aragonite crystals, PPL; d) Same sample observed in SEM under backscattered mode. It is possible to see how dolomite (grey) coats and replaces the aragonite (white); e) SEM image of rounded dolomite aggregates coating an aragonite fibre; f) Detail of globular dolomite masses over an aragonite crystal; g) The globules of dolomite are formed by dolomite crystals of around 1 μm size. EDS scan indicate the composition of the crystals.

tive, but a common feature of neomorphism, as occurs in Castañar, is the preservation of fabrics and the presence of relics (Folk, 1965; Mazzullo, 1980). Relics are preserved due to the incomplete replacement of aragonite by neomorphic calcite (Woo & Choi, 2006). Microscale dissolution of aragonite and precipitation

of calcite occurs through a thin film of fluid (100Å-1 μm) (Pingitore, 1976) and, as calcite precipitates, the solution becomes locally supersaturated with respect to aragonite, leaving undissolved aragonite relics. Calcification of aragonite is favoured by the presence of previously precipitated calcite cements which act as

nucleation sites (Maliva et al., 2000). In the calcitization process, neomorphic calcite inherits the chemical characteristics of previous aragonite (Frisia et al., 2002; Woo & Choi, 2006) as has been observed in Castañar Cave, where the neomorphic calcite show isotopic values slightly higher than those of the primary calcite due to the inheritance of the aragonite signal (Martín-García et al., 2009).

Dolomitization

The features of dolomite found in the studied drapery in Castañar Cave indicate a secondary origin by replacement of aragonite, as shown by the interpenetrated contacts between the crystals (Fig. 9d) and the alignment of crystals following aragonite fibres (Fig. 9e). Dolomitization processes most commonly take place in marine and burial environments (Machel, 2004) with less examples of dolomite formation in vadose settings (Müller & Irion, 1969). Nevertheless, the presence of dolomite has been reported in several caves around the world (see Jones 2010 and references therein). Its origin has been considered primary (González & Lohmann, 1988; Bar-Matthews et al., 1991; Polyak & Güven, 2000) or secondary, as a transformation of a carbonate precursor such as aragonite or huntite (Moore, 1961; Thrailkill, 1968). A huntite to dolomite transformation has been inferred in other speleothems of Castañar Cave based on textural relationships (Alonso-Zarza & Martín-Pérez, 2008; Martín Pérez, 2012). Such replacement was previously reported (Moore, 1961; Kinsman, 1967; Lippmann, 1973) because both minerals present strong structural and chemical similarities (Graf & Bradley, 1962; Lippmann, 1973; Dollase & Reeder, 1986). In spite of its higher solubility, huntite could form more eas-

ily due to the kinetics related to its more open structure, acting as a reservoir of Mg and Ca for the further transformation into the stable mineral dolomite (Lippmann, 1973; Davies et al., 1977). A primary precipitation of dolomite as cement on aragonite which would initiate the dolomitization, similar to what happens in calcitization could also be possible. Nevertheless, this possibility has to be considered carefully since precipitation of dolomite under sedimentary conditions without involving microorganisms has been proved to be difficult due to kinetic inhibition (Land, 1998; Arvidson & Mackenzie, 1999; Wright & Wacey, 2004). Activity of microorganisms can contribute to overcome kinetic barriers (Jones, 2010), but up to now very little evidence of the presence of microbes has been found in Castañar speleothems (Alonso-Zarza & Martín-Pérez, 2008).

DIAGENETIC EVOLUTION

In the DRA-1 drapery of Castañar Cave, the succession of diagenetic processes may reveal cave air CO₂ oscillations and changes of composition of karstic waters, both controlling the saturation index of the different minerals. Even though the sequence of primary and diagenetic processes is complex, possibly involving several repetitions with time, it is possible to infer two main diagenetic pathways (Fig. 10) which approximately correspond with what is seen on each side of the drapery: Pathway 1) **Progressive increase in the saturation and Mg/Ca ratio of waters** results in the precipitation of calcite, aragonite and, if the Mg/Ca ratio is high enough, oversaturation in huntite and dolomite causing dolomitization of aragonite. These minerals and processes have been observed in

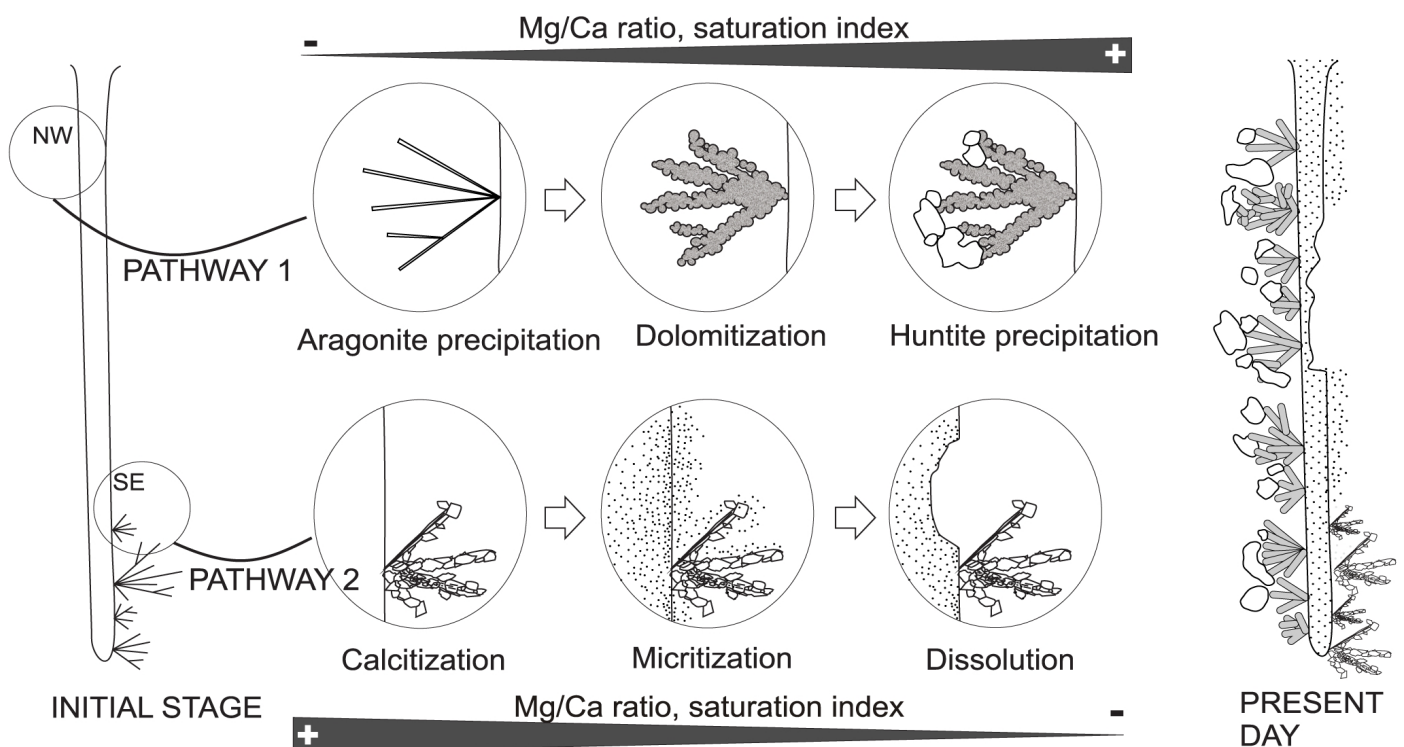


Fig. 10. Sketch of the diagenetic evolution of drapery DRA-1 showing the different pathways observed in each side of the drapery.

the NW side of the drapery. Pathway 2) **Progressive dilution of the waters and decrease in Mg/Ca ratio.** Once primary calcite and aragonite have formed, a decrease in Mg/Ca ratio in combination with more diluted waters would cause oversaturation in calcite and undersaturation in aragonite, leading to calcitization. If the waters are undersaturated in both minerals, due either to the infiltration of undersaturated waters or to the condensation of cave air moisture, dissolution processes begin. Slow and incomplete dissolution leads to the formation of powdery coatings or micritization. Rapid flow leads to more rapid dissolution and produces a loss of material with the final result being the formation of macroscopic porosity. This sequence is represented in the SE side of the drapery.

The necessary increase in Mg/Ca ratio and oversaturation to produce the diagenetic pathway 1 could be expected in conditions of prolonged CO₂ degassing (Frisia et al., 2002) and evaporation (González & Lohman, 1988; Hill & Forti, 1997). Such processes can occur in the cave, in certain conditions of low water flow in capillarity waters or during drier cave conditions, but high Mg/Ca ratios can also be achieved by longer water-rock interactions (Musgrove & Banner, 2004) or processes of prior calcite precipitation (Fairchild & Treble, 2009), usually associated to climatic arid conditions (Railsback et al., 1994; Denniston et al., 2000; McMillan et al., 2005). It is important to point out the role of cave air ventilation in drip water compositions. Very low values of pCO₂ due to ventilation can be responsible of forced degassing (Spötl et al., 2005) and seasonal ventilation can influence the extent of prior calcite precipitation and consequently Mg/Ca ratios of the water (Wong et al., 2011).

Conditions leading to calcitization and eventually dissolution in pathway 2 can be related with more humid climatic conditions (Denniston et al., 2000; Woo & Choi, 2006; Pagliara et al., 2010) or with seasonal events of high rainfall (Railsback et al., 1994). Another source of fluids undersaturated in calcite and aragonite can be the condensation of water from cave air (de Freitas, 2010) which can be especially aggressive if the CO₂ contents in the cave are high (Sarbu & Lascau, 1997; Sánchez-Moral et al., 1999).

It is not clear by the moment which mechanisms and processes controlled the differential diagenetic paths in the two sides of the drapery. However, the following possibilities should be considered:

1) The two diagenetic paths could have formed in different geological periods under different climatic conditions. The trend in the SE side leading to dissolution could correspond to the more humid periods, whereas the formation of huntite and/or dolomite could represent the more arids. However, this case does not seem very probable, since it is difficult to explain why the two trends formed in specific sites of the drapery. In addition, in that situation during wetter periods aragonite and huntite would also have been dissolved.

2) Differential condensation rates in each side. In this case an air current is needed in order to achieve condensation in one side and drier conditions in the other one (Hill & Forti, 1997). This scenario is not

supported by the present day conditions of Castañar Cave, where no air currents have been detected, but it may have occurred during past times.

3) Differences in amount and velocity of the water feeding the drapery. A preferable feeding of water along the SE side would favour that these areas were preferably dissolved. Slower flow circulation in the NW area, together with the morphology of the drapery (curved to the NW) may enable the increase of Mg in that side and so huntite and dolomite formation.

CONCLUSIONS

Detailed petrographic study of a drapery of Castañar Cave reveals the complexity of the mechanisms of mineral precipitation in caves as well of the diagenetic processes affecting speleothems. Calcite, aragonite and huntite are primary minerals forming DRA-1, whereas dolomite is found replacing aragonite. The main diagenetic processes identified are partial dissolution (also named corrosion and micritization) and formation of secondary calcite and dolomite. These processes are governed by the temporal evolution of composition of the waters, -initially rich in Mg due to the dissolution of dolostones and magnesites-, the velocity and type of flow path and the microclimate of the cave. Two main diagenetic pathways have been observed, each of them taking place in one side of the drapery: In the first pathway, progressive increase of Mg/Ca ratio and oversaturation, and degasification of CO₂ favour aragonite precipitation over calcite, and enable the dolomitization of aragonite and huntite precipitation. In the second pathway, the progressive dilution and decrease of Mg/Ca relationships produces calcitization when waters are under-saturated in aragonite and saturated in calcite, and partial or total dissolution when waters are undersaturated in all the minerals. The fact that each pathway is taking place in different side of the drapery is not easy to explain. One possibility is that the formation of each side took place in different periods under different hydrological regimes. Another explanation would be the differential condensation-corrosion produced in each side due to air currents, but the most probable causes are related to the morphology of speleothem and differential amount and movement of water along the two sides.

ACKNOWLEDGEMENTS

This work received financial support from the Junta de Extremadura through FEOGA-ORIENTACION-FEDER funds, Projects CGL-2008-05584-C02-02 and CGL-2011-27826-C02-01 from the MCINN and UCM-910404 from UCMCAM. Inma Gil and Ana Blázquez are thanked for helpful discussion during field work. R. M-G was supported by a JAEPredoc-CSIC grant and A. M-P by an I3P-CSIC grant. J. Cerne carefully reviewed the text style. We greatly acknowledge the editorial handling by J. de Waele and the thorough and constructive comments of G. A. Caddeo, L. B. Railsback, P. Forti and an anonymous reviewer, which helped us to significantly improve this manuscript.

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