

Loss of primary texture and geochemical signatures in speleothems due to diagenesis: Evidences from Castañar Cave, Spain

Rebeca Martín-García*, Ana M. Alonso-Zarza, Andrea Martín-Pérez

Departamento de Petrología y Geoquímica-Instituto de Geología Económica, Universidad Complutense de Madrid-CSIC, Madrid, 28040, Spain

ARTICLE INFO

Article history:

Received 29 May 2009

Received in revised form 14 August 2009

Accepted 1 September 2009

Keywords:

Meteoric diagenesis

Speleothems

Isotope geochemistry

Palaeoclimate

Castañar cave

ABSTRACT

Geochemical signals from speleothems are commonly used in the investigation of palaeoenvironments. In most cases, however, little attention is paid to whether or not these signals are primary or altered by diagenesis. The speleothems of the Castañar Cave (Cáceres, Spain), which are initially formed of calcite or aragonite, have undergone a variety of meteoric diagenetic processes such as micritization and neomorphism (inversion), that collectively modify their primary features (textures, mineralogy, geochemical signals). The mean $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the aragonites in the cave are -8.66 and -4.64 respectively, whereas the primary calcites have mean $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of -9.99 and -5.77 , respectively. Following the diagenetic process of micritization, the aragonite isotopic signals averaged -7.63 $\delta^{13}\text{C}$ and -4.74 $\delta^{18}\text{O}$ and the calcite micrite signals -9.53 $\delta^{13}\text{C}$ and -5.21 $\delta^{18}\text{O}$. Where inversion took place, some secondary calcites after the aragonite show preserved aragonite, whereas others do not. The secondary calcites without aragonite relics show isotopic values slightly higher than those of the primary calcite due to the inheritance of the aragonite signal. Where aragonite relics are preserved, the isotopic signatures are very similar to those of the aragonite micrite.

In addition, the stable isotopic values and Sr and Mg contents of the speleothems became also modified by micritization and/or inversion. These diagenetic processes were driven by the changes in composition of the cave waters over time and space, but also, in the case of aragonite, by its initial unstable mineralogy.

The present results highlight how important diagenesis is in caves and how the initial features of cave minerals may be lost. These changes alter the geochemical signals shown by speleothems, which may have an impact on the interpretation of the results obtained in palaeoenvironmental studies.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The stable isotope values and trace element contents of speleothems are commonly used to infer the conditions of Quaternary palaeoclimate (McDermott, 2004; Fairchild et al., 2006) under the assumption that their constituent minerals have undergone no diagenetic modification. There is the potential, however, that various meteoric diagenetic processes can significantly modify the original precipitates. For example, Hill and Forti (1997) and Rowling (2004) indicated that aragonite, which is common in caves, may change its crystal structure to that of calcite. Only a few studies, however, have taken such diagenetic processes into account, even though Frisia et al. (2002) and Woo and Choi (2006) pointed out the importance of determining if the signals being recorded are primary or if they have

been modified by diagenetic processes such as micritization and inversion.

In marine sedimentary environments, micritization has usually been related to the action of microorganisms that affect allochems in the shallow marine realm (Alexanderson, 1972; Brand, 1989; Reid and Macintyre, 1998; Reid and Macintyre, 2000). This process, however, has also been ascribed to diagenetic dissolution with no organic implications as described by Neugebauer (1978) in crinoids from the Upper Cretaceous of Kansas. Abiotic micritization has also been studied in cave substrates (Jones and Kahle, 1995); in cave pool deposits (Jones, 1988), and in speleothems associated to condensation corrosion over the surface (Auler and Smart, 2004).

Studies of aragonite-to-calcite transformations have been usually carried out on marine shells; for example, Maliva (1998) studied this process in aragonitic molluscs from the Purbeck Group of southern England and Maliva et al. (2000) examined skeletal fragments of Plio-Pleistocene limestones and sandstones from Hollywood, Florida. Little attention, however, has been paid to neomorphism of speleothems apart from Frisia et al. (2002), Bar-Matthews et al. (1991), and Woo and Choi (2006). These studies

* Corresponding author. Tel.: +34 91 394 4903.

E-mail address: rmartingarcia@geo.ucm.es (R. Martín-García).

stressed the importance of neomorphism in caves and the need to undertake detailed petrographic and geochemical studies before using speleothems as palaeoambiental archives.

The present study characterises the diagenesis of aragonite and calcite under meteoric vadose conditions in Castañar Cave, Spain (Fig. 1). This study shows that these diagenetic processes occur in relatively stable caves, provide criteria for their recognition, and discuss their driving mechanisms. In doing so we provide a better understanding of the study of early diagenesis in caves.

2. Terminology

The meaning and uses of the term micrite are controversial. Friedman (1985), for example, gave genetic and descriptive connotations to the term micrite whereas Milliman et al. (1985) used it as a descriptive term with no genetic implications. In this paper micrite is used as a descriptive term that is independent of interpretation or

mineralogy. Thus, it follows the criteria of Milliman et al. (1985) and Jones et al. (1995) who used micrite to describe carbonate particles less than 4 µm long.

Even though the term *micrite* comes from the contraction of “microcrystalline calcite” (Folk, 1959), the term *aragonite micrite* (aragonite with micritic crystal size) has been widely used (e.g. Friedman, 1964; Alexanderson, 1972; Pedone and Ddickson, 2000; Dix et al., 2005) to refer to aragonite particles less than 4 µm long.

Residual micrite refers to micrite formed by the biogenic or abiogenic breakdown of a calcite substrate (Kobluk and Risk, 1977; Jones, 1995 et al.). If this residue stays close to its place of origin it is called *endogenetic micrite* (Jones and Kahle, 1995), whereas *exogenetic micrite* is used to describe micrite founded far from the place it was formed.

Neomorphism is an inclusive term to define isocompositional and replacive processes such as recrystallization and inversion (transformation of one polymorph into another) (Folk, 1965).

3. Geological setting

Castañar Cave is located in the southern part of the Iberian Massif. The cave is hosted in the Neoproterozoic rocks that form the core of the Ibor anticline (Fig. 1). These rocks are shales and greywackes with interbedded dolostones and magnesites (Alonso-Zarza et al., 2005). Dissolution of the dolomitic and magnesitic beds and the extensive weathering of the shales and greywackes promoted collapse that created and enlarged the cave. The dissolution of dolomite and magnesite also determines the composition of the cave waters, which are rich in Mg with Ca/Mg ratios of 0.5 to 1.0. These waters are usually saturated with respect to calcite, dolomite, and aragonite (Sánchez-Moral et al., 2006). The mean temperature of the cave is 17 °C (constant year round) and the relative humidity of the air is close to 100% (Sánchez-Moral et al., 2006).

The speleothems of the cave vary in their mineralogy and morphology. The dominant minerals are aragonite and calcite, but Mg-rich carbonates such as dolomite, huntite, magnesite and hydromagnesite are found locally, forming moon-milk deposits and crusts (Alonso-Zarza and Martín-Pérez, 2008). Aragonite fans coalesce to form the most common morphologies, which are frostworks, helictites, anthodites, stalactites, stalagmites, draperies, and flowstones.

4. Materials and methods

Conventional optical petrography studies were performed on 70 thin sections taken from 60 speleothems, including stalactites, stalagmites, soda straws, draperies, flowstones, and pool floors. Due to their fragility, these samples were submerged in a resin containing Epor EX 401 and Epor E 432 in a vacuum system.

Scanning electron microscopy was performed on 13 gold-coated samples. Observations were made using a JEOL 6400 electron microscope working at 20 kV and with a resolution of 35 Å. Secondary electron and backscattering detectors were used together with an X-ray detector system to obtain semiquantitative compositions.

The Mg, Sr, Fe, and Mn contents of the different minerals in selected polished samples were obtained using an electronic microprobe (JEOL JXA 8900M) operating at 15 kV and 20 nA and employing an electron beam diameter of 5 µm. The standards used are described by Jarosewich et al. (1980) and were provided by the Smithsonian Institute, Washington, USA. 50 powdered samples from 18 speleothems (selected from the zones in which the diagenetic processes were best preserved) were mineralogically characterised using a Philips PW-1710 X-ray diffraction (XRD) system operating at 40 kV and 30 mA, and employing monochromated CuKα radiation. XRD spectra were obtained from 2 to 66° 2θ. Crystals <2 mm in diameter could not be isolated.

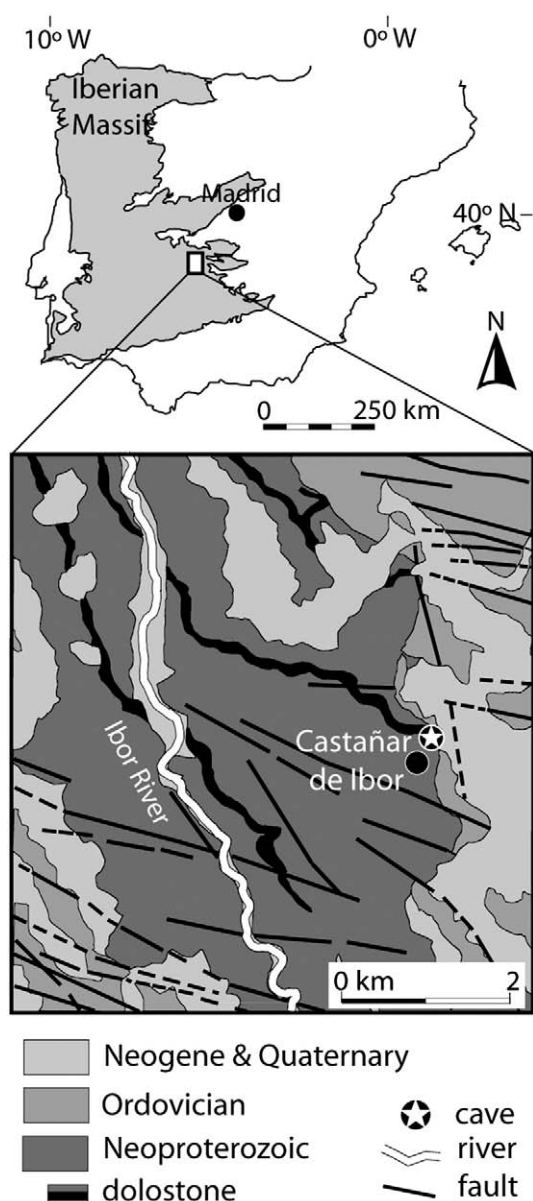


Fig. 1. Location of Castañar Cave. General situation within the Iberian Massif and geologic map of the study area showing the location of the cave.

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of these 50 powdered samples were later analysed at the Stable Isotope Laboratory, Salamanca University (following reaction with 100% phosphoric acid), using a SIRA series II spectrometer from VG Isotech. The experimental error for carbonates ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) was 0.1 ‰. A small-drill (0.5 mm in diameter) was used to avoid mixtures of the different minerals and layers of the speleothems.

5. Petrography and geochemistry of the speleothems

5.1. Primary speleothems

The aragonite speleothems of the Castañar Cave are shiny and consist of acicular and transparent crystals with length-to-width ratio $\geq 6:1$. These crystals have smooth surfaces and flat faces on the flanks (Fig. 2A). Both macro- and microscopically, the aragonite crystals are arranged in fans that cross and superimpose one another to form the speleothems. The aragonite contains little or no magnesium and the Sr content varies from 0.00 and 0.20 mol%, with a mean value of 0.108 mol% SrCO_3 . The primary aragonite crystals have mean isotopic values of -8.66 $\delta^{13}\text{C}$ and -4.84 $\delta^{18}\text{O}$ (Table 1).

The calcite speleothems, which range in appearance from transparent to beige-transparent, are less shiny than their aragonite counterparts. They consist of palisade calcite crystals, 5 mm to 1 cm long, and 0.5 mm wide (Fig. 2B). Equant mosaics, with small crystals (0.1–1 mm wide), are also very common. Irrespective of the crystal

Table 1

Isotopic and compositional mean values for the 50 analysed samples selected from stalactites, stalagmites and pool substrates at Castañar Cave on the basis of the different diagenetic processes taking place on them.

	Calcite				Aragonite	
	Primary	Micritized	Secondary		Primary	Micritized
			Without aragonite relics	With aragonite relics		
$\delta^{13}\text{C}_{\text{PDB}}$	−9.99	−9.53	−9.55	−8.51	−8.66	−7.63
$\delta^{18}\text{O}_{\text{PDB}}$	−5.77	−5.21	−5.13	−5.18	−4.84	−4.74

type, the calcite speleothems show well defined banding. In all cases the calcite speleothems have a low Mg content (up to 1.73 mol% MgCO_3) – but higher than that in the aragonite. Sr contents are very low, averaging 0.08 mol% SrCO_3 . The primary calcites have a mean $\delta^{13}\text{C}$ value of -9.99 and a mean $\delta^{18}\text{O}$ value of -5.77 (Table 1).

5.2. Micritization of the speleothems

Polished hand samples of the micritized calcite and aragonite speleothems show a 1 cm-thick, matt white, opaque external coating.

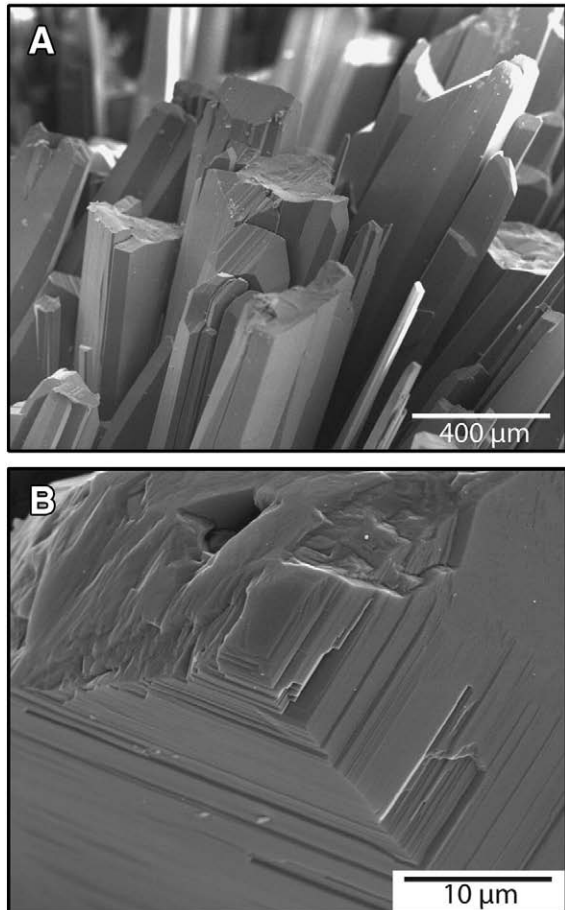


Fig. 2. SEM images of original crystals. (A) Aragonite fibres. The crystals show characteristic smooth surfaces. (B) Calcite crystal showing growing steps and flat faces.

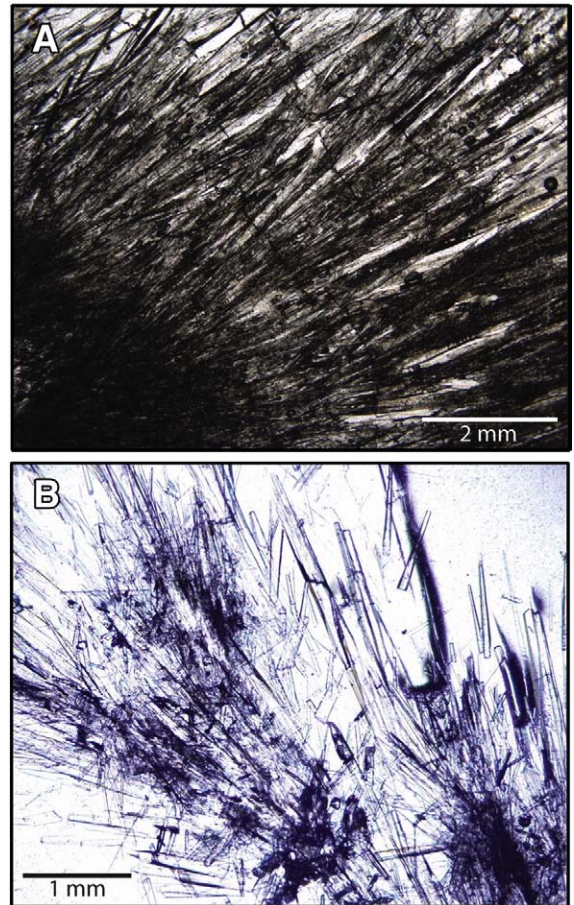


Fig. 3. Thin-section microphotographs with plain-polarized light. (A) Aragonite speleothem almost completely micritized. Micrite has a dark opaque colour whereas the primary crystals are transparent and clean. (B) Branching speleothem. Micrite appears especially in the nucleus of the fans forming dark opaque areas. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

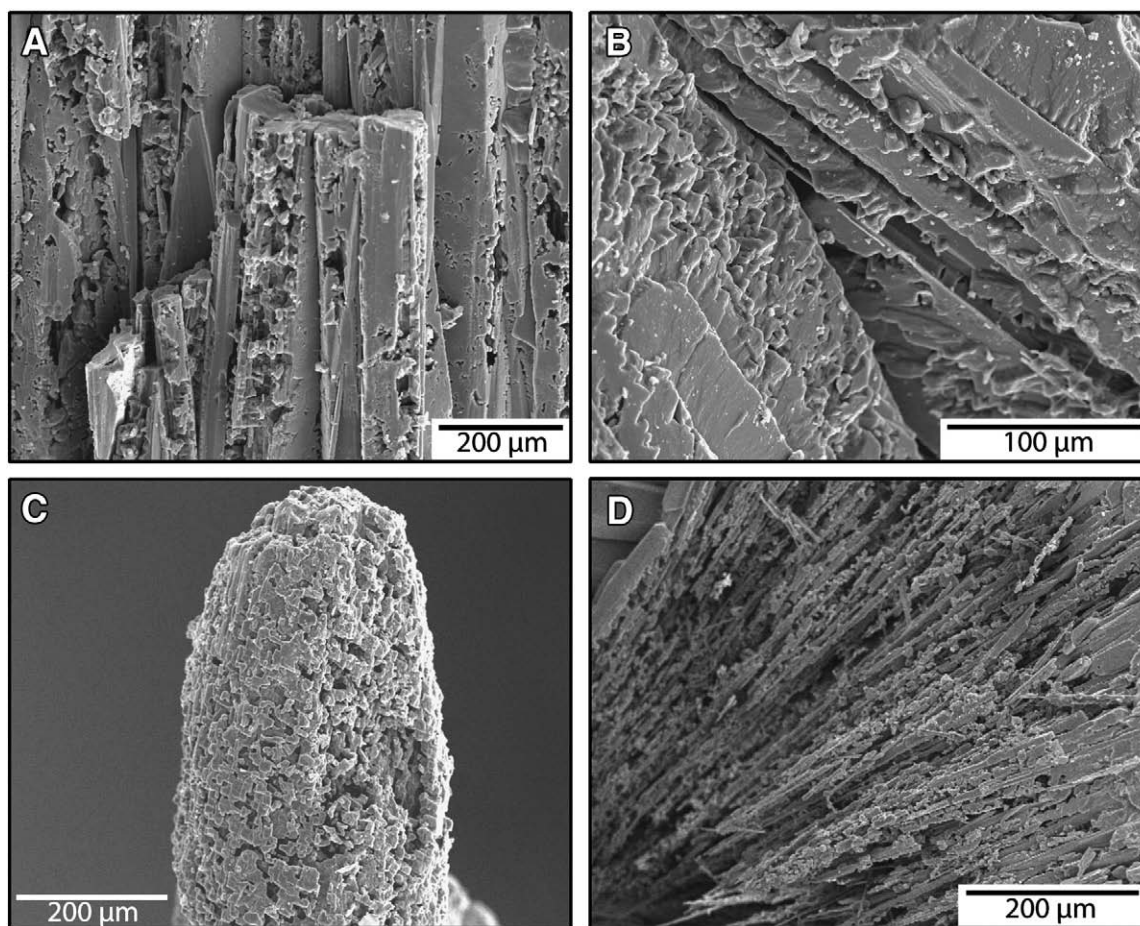


Fig. 4. SEM microphotographs of micrite aragonite. (A) Dissolution features over an aragonite crystal. Micron-sized pores appear and detach parts of the crystal surfaces. (B) Detailed view of the formation of monticules over an aragonite fibre. (C) Aragonite speleothem tip completely covered by monticules that in some parts are separated from the substrate. (D) Fan formed by aragonite needles that are partially dissolved and covered by a mass of residual micrite.

In the inner zone, micritization occurs as thin (mm) concentric lines of similar characteristics to the surface coating.

In the case of aragonite, micrite appears as dark opaque structureless masses around the original crystals that are transparent and clean (Fig. 3A and B). At an advanced stage, none of the original crystals are left and the speleothems are formed entirely of micrite. The micritization process starts when the surfaces of the crystals are etched forming small pores ~2 µm long, that coalesce to form larger ones (Fig. 4A and B). This process releases micron-sized parts of the crystals that stay on the surface and thereby start to form a mat of residual micrite (cf., Jones and Kahle, 1995) (Fig. 4C and D).

The isotopic signals of this aragonite micrite (recognised by DRX) are different to those obtained in the original crystals, especially for $\delta^{13}\text{C}$ which shows a mean value of -7.63 . The mean value for $\delta^{18}\text{O}$ is -4.74 . In the aragonite micrite the Sr content averages 0.13 mol% SrCO_3 , higher than in the primary aragonite (Table 1).

The micrite associated with the calcite speleothems is similar to the micrite found on the aragonite speleothems. It appears as a disordered opaque mass over the original crystals that are usually corroded (Fig. 5A). In some cases, the calcite crystals present micritic lines following the growth bands inside the crystals (Fig. 5B). Under SEM, it is apparent that the primary crystal surfaces are smooth with no dissolution features such as those described by Jones (1987). On the other hand, the surface of the micritized crystals show small protuberances caused by the etching of the surface (Fig. 6A). This etching is followed by the formation of flakes (Fig. 6B) or monticules

(Fig. 6C). The flakes are about 10 µm long and conserve the embossed surfaces of the crystals. Individual monticules in calcite surfaces consist on rounded to euhedral calcite particles detached from the background from which they are formed (Fig. 6C) that are left upstanding after the surrounding material has been dissolved. These small structures form the residual micrite (Fig. 6D).

Geochemical analysis revealed that in the same crystal, the micritized bands contain 1.2 times more Mg (1.05 mol% MgCO_3) than the non-micritized bands. The Sr contents are as low as in the primary calcites. No differences are evident between the isotope values of the original calcite crystals (-9.99 $\delta^{13}\text{C}$ and -5.77 $\delta^{18}\text{O}$) and the calcite micrite (-9.53 $\delta^{13}\text{C}$ and -5.21 $\delta^{18}\text{O}$) (Table 1).

Dissolution and formation of residual micrite, formed of calcite or aragonite, is usually found on the surfaces of the speleothems that stay in contact with waters for the longest time, such as on the tips of the elongated speleothems where water drops accumulate before dripping, or in the surfaces of the larger ones (draperies, flowstones, etc.). In addition, the inner parts of the crystals can also be altered, especially in those crystals that have defects or show compositional zoning (Fig. 7A and B). In the case of calcite, which is commonly zoned, dissolution and micritization preferentially affect those bands with the highest Mg content. Morse and Arvidson (2002) also showed that the dissolution rate of calcites is controlled by the Mg content. All the micrite in this paper is considered as endogenetic, as demonstrated by its distribution, closely controlled by the dissolution of previous crystals.

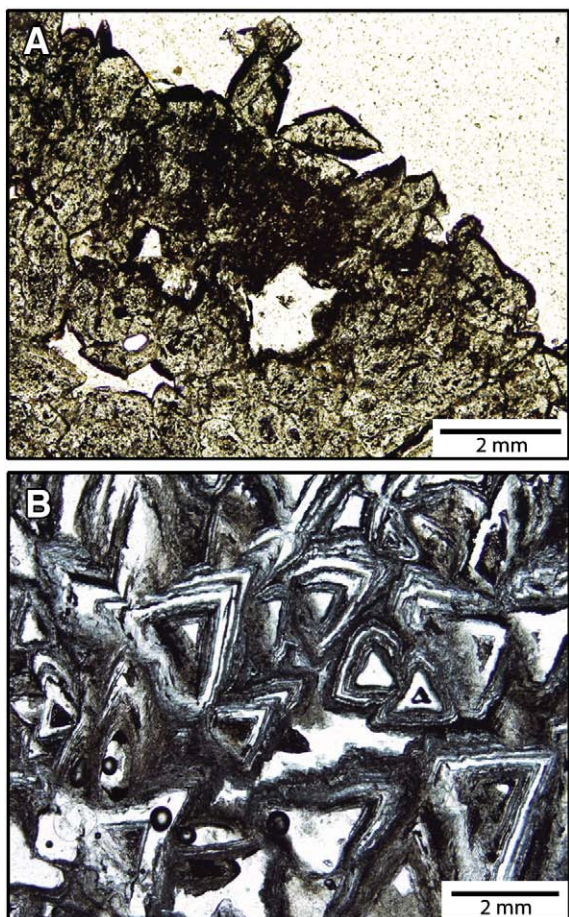


Fig. 5. Thin-section microphotographs with plain-polarized light. (A) Formation of micrite on calcite crystals. Dissolution disaggregates the crystals. (B) Micritization also occurs inside the crystals following their discontinuities.

5.3. Inversion

In hand sample, initially, aragonite speleothems show a shiny translucent white fibrous aspect that contrasts with the speleothems that have undergone inversion which are matt, brownish, and grainy due to the appearance of calcite mosaics.

Under the microscope, the aragonite speleothems that underwent inversion show a mosaic of equigranular calcite crystals that preserved either relic fibres of original aragonite or their textural ghosts (Fig. 8A to C). These fibres or ghosts can be followed from one calcite crystal to the next (Fig. 8A and B). Some inversion also took place in the micritized aragonite, as shown by the presence of darker lines (ghosts of micrite) in the calcite mosaics (Fig. 8B). Elsewhere, the secondary calcite after the aragonite crystals inherited the morphologies of the acicular aragonite crystals, being elongate and usually lacking relics (Fig. 8C).

SEM images show that small euhedral calcite crystals, ~15 μm long, grow on the surfaces of the acicular aragonite crystals (Fig. 9A). If these crystals continue to grow, they would eventually encase the aragonite fibres (Fig. 9B) and in some cases transform them into calcite (Fig. 9C). In other cases the fibres are not completely transformed and aragonite is preserved as relics inside the calcite crystals.

Isotope analyses show that the values of the secondary calcites with aragonite relic fibres are close to those of aragonite micrite. The mean $\delta^{13}\text{C}$ value is -8.51 and the mean $\delta^{18}\text{O}$ value is -5.18 . In secondary calcites lacking aragonite relics but containing ghosts (100% calcite), the values are close to those of primary calcite at -9.55

$\delta^{13}\text{C}$ and -5.13 $\delta^{18}\text{O}$, but with a slight shift towards the aragonite values. The Mg and Sr contents of the secondary calcites are similar to those of primary calcite (Table 1).

6. Interpretation and discussion

The diagenesis of the speleothems in the Castañar Cave is driven by the composition of its waters – which are temporally and spatially variable. Studies performed in recent years have shown that the cave's waters are always saturated with respect to calcite, but vary from saturated to undersaturated with respect to aragonite (Sánchez-Moral et al., 2006). Although calcite is the most common and stable polymorph of CaCO_3 , aragonite formation is favoured when the solutions present a high Mg/Ca ratio and low supersaturations with respect to CaCO_3 (De Choudens-Sánchez and González, 2009). Partially dehydrated Mg attaches to the surface on incipient calcite nuclei, inhibiting their growth (Bernier, 1975) but favouring the precipitation of aragonite (Lippmann, 1973; Gutjahr et al., 1996a). The dissolution of the dolostones and magnesites of the host rock in Castañar Cave, provides Mg-enriched solutions that favour the precipitation of aragonite.

Micritization has frequently been reported as a shallow marine diagenetic process involving the obliteration of the internal structure of carbonates via the formation of cryptocrystalline textures (Reid and Macintyre, 1998). Traditionally, the formation of micritic wraps over different skeletal components has been attributed to the action of microorganisms that bore and fill these components (Bathurst, 1966; Calvet, 1982). In contrast, dissolution has been considered the driving mechanism for micritization that takes place in the absence of organic influences (Neugebauer, 1978). This may be the case in the Castañar Cave, where the surfaces of the large crystals began to dissolve partially to form a mass of micron-sized crystals that partially or totally replaced the original components. In the case of aragonite, this micritization continued inwards randomly, following no preferred crystalline discontinuity. In the case of calcite, however, micritization preferentially advances along growth bands that have a high Mg content. Dissolution leading to micritization may be controlled by differences in the amount of Mg and Sr in the primary minerals. The fact that the micritized aragonite contains more Sr, and the calcite more Mg than their corresponding original minerals, suggests that differences with respect to stoichiometric composition may favour the preferential dissolution of these crystals (or zones within these crystals). Experiments on calcite and aragonite containing different amounts of Mg, Sr, and other trace elements have confirmed that the dissolution rates of both polymorphs increase with increasing quantities of these elements (Gutjahr et al., 1996b; Morse and Arvidson, 2002). The heavier $\delta^{13}\text{C}$ values of the micritized aragonites compared to their primary counterparts are owed to the fact that $\text{Ca}^{12}\text{CO}_3$ is preferentially dissolved because of its greater mobility (Skidmore et al., 2004). In the Castañar Cave, micritization driven by dissolution occurs when the cave waters are close to undersaturation in either calcite or aragonite. Water with such properties can be found in different areas of the cave (Sánchez-Moral et al., 2006).

Most of the studied speleothems formed by inverted aragonite show a mosaic of calcite crystals with aragonite relics preserved within them. The inversion process appears to take place in two stages. In the first stage the initial porosity of the aragonite fans propitiates the nucleation of small crystals of calcite (10 μm) along the aragonite fibres, which act as nuclei for the growth of larger calcite crystals. Large calcite crystals may grow to incorporate smaller calcite crystals and the aragonite fibres.

The transformation of one polymorph to another in the presence of a fluid takes place by the dissolution of the metastable one, in this case aragonite, and the precipitation of the stable phase, calcite (Perdikouri et al., 2008). A thin film of solution (from 100 Å to 1 μm

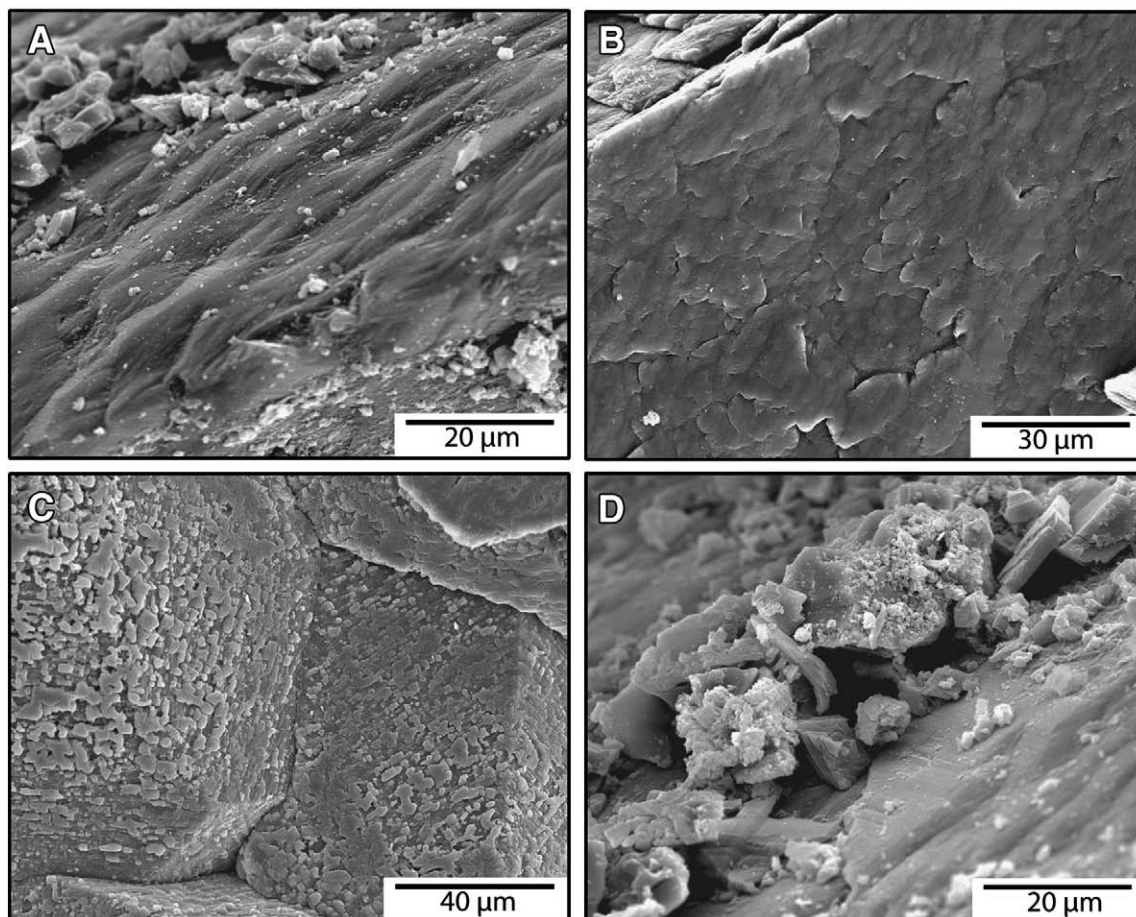


Fig. 6. SEM microphotographs. (A) Etched surface of a calcite crystal. (B) Formation of flakes over a face of a calcite crystal. The flakes conserve the etching of the surface. (C) Small protuberances over a crystal which can lead to the formation of micrite by the detachment of the monticully. (D) Detail of the formation of micrite by the breakage of a flake.

thick) propitiates the dissolution of aragonite, as the solution dissolves aragonite and precipitates calcite it becomes locally saturated in aragonite, leaving relics (Pingitore, 1976; Frisia et al., 2002). The incomplete inversion of the aragonite results in the preservation of aragonite crystals as solid inclusions within the calcite crystals. If the inversion is complete the relics are texturally but not mineralogically preserved (ghosts).

The overall inversion, which occurs at the microscale, takes place when waters are undersaturated in aragonite and oversaturated in calcite (Maliva et al., 2000; Frisia et al., 2002).

In this work it is seen that, as the aragonite relic content increases, the isotopic signals of the relic-bearing calcites become more similar to those of the aragonite micrite, averaging -8.51 $\delta^{13}\text{C}$ and -5.18 $\delta^{18}\text{O}$. This may indicate that inversion progresses easily on previously micritized aragonites, as indicated by Morse and Mackenzie (1990) and Perdikouri et al. (2008). Similarly, in aragonite shells of different ages, Maliva (1998) observed areas of small crystals of dissolved aragonite (which this author called the 'chalky zone') but with a simultaneous precipitation of calcite. In the present work secondary calcites without aragonite relics show isotopic values similar to those of the primary calcite, with a small trend towards those of aragonite. This indicates that these values are the consequence of the composition of the cave waters, with the precursor mineral having only a small influence.

Although microorganisms could play an important role in small-scale diagenetic processes in caves (Jones and Kahle, 1995; Boston et al., 2008), no evidence has been found in Castañar to prove their influence in both micritization and inversion.

7. Implications for the interpretation of the geochemical signatures

The main changes to be expected in the speleothems geochemical signatures result from the interaction of the primary minerals with the cave waters. These waters can be different depending mostly on the climatic conditions and on the time of interaction with the host rock. Thus the reaction of the primary minerals with heavier cave water inputs in more arid periods will result in a heavier isotope values than the initial ones. However, the problem is more complex because of the preference of the different minerals to incorporate heavier or lighter isotopes. In general any transformation of aragonite to calcite will result in lighter isotope values independently of the composition of the cave waters.

Therefore, before starting a palaeoclimate study, detailed petrographical studies must be done to reject the speleothem areas which have undergone any diagenetic process and to focus the study into the primary minerals. This is important specially in caves where metastable minerals as aragonite, high magnesium calcite, etc., can be found. In addition, by the moment, the prediction of the exact pathways of the geochemical signatures through diagenesis is difficult because many factors interplay to vary the initial geochemical signals, such as: climate, initial mineralogy or time interacting with the host rock.

8. Conclusions

The diagenetic processes taking place in the Castañar Cave lead to important changes in the mineralogy, texture and geochemistry of its

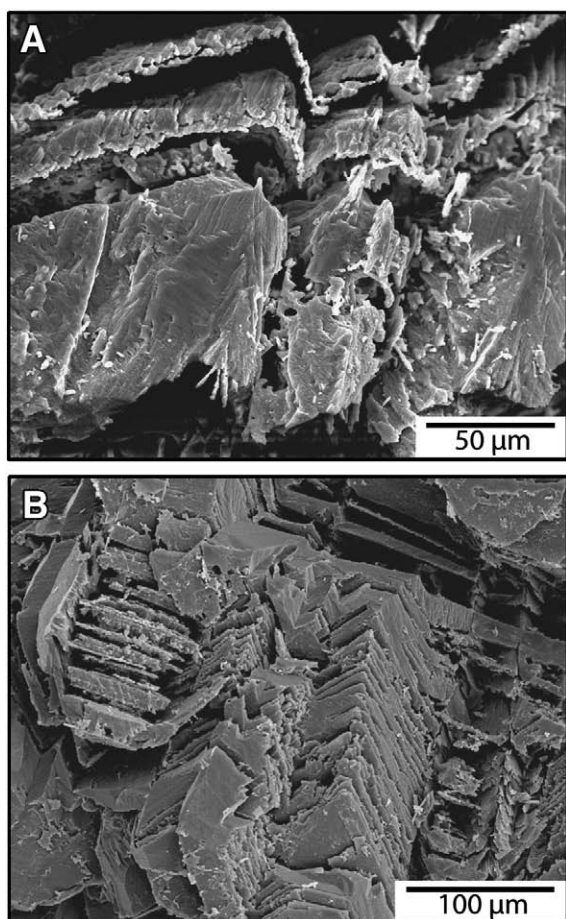


Fig. 7. SEM microphotographs. (A) Appearance of calcite crystals dissolved following crystalline discontinuities or differences in the composition of the growing bands of the crystals. (B) Detailed view of A.

speleothems. Changes in the mineralogy of primary speleothems are due to the stabilization of aragonite, which transforms into calcite. This stabilization also results in the loss of the initial fibrous texture of the aragonite and the appearance of coarse and equant mosaics of calcite, with or without aragonite relics. The secondary calcites show no difference in the Sr and Mg contents comparing to the original calcites, but isotopically the secondary calcites are heavier in $\delta^{13}\text{C}$ than their primary counterparts, especially those containing aragonite relics. The micritization of both aragonite and calcite appears to be driven by partial dissolution without the activity of organisms. The resultant texture consists of mosaics of micron-sized crystals. The isotopic and Sr contents of the micritized calcites are similar to the primary calcites, although their Mg contents are higher. Micritized aragonites show an increase in $\delta^{13}\text{C}$ and Sr.

These results highlight how important diagenesis is in caves, and how the initial features of primary cave minerals can be lost. Some of these diagenetic processes show striking similarities to those that occur in marine deposits, such as micritization and the stabilization of aragonite sediments, although with the differences discussed above. These changes may alter the palaeoenvironmental signals extracted from the analysis of speleothems – and therefore the way in which they should be interpreted. Certainly: 1) secondary calcites have $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values different to those of their primary minerals; care must therefore be taken when identifying materials as primary; 2) the interpretation of palaeofluid characteristics should take into account that diagenesis also resets the major and trace element contents. In agreement with Frisia et al. (2000), the present results also suggests

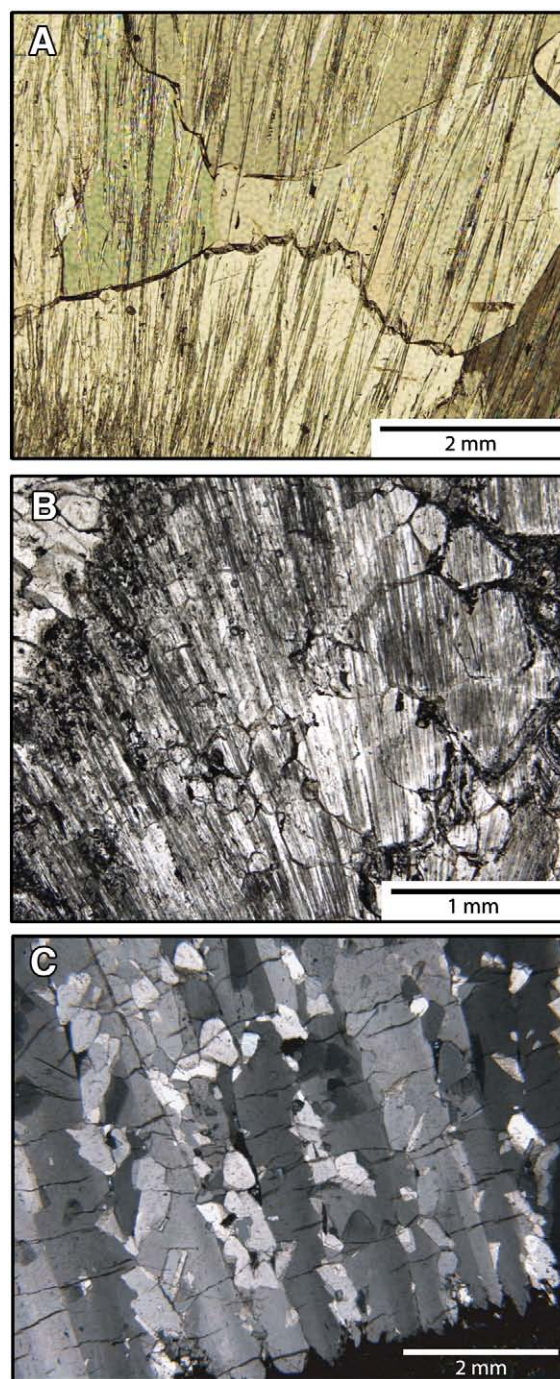


Fig. 8. Thin-section microphotographs. (A and C) Cross-polarized light. (B) Plain-polarized light. (A) Calcite mosaic with aragonite relics preserved. Note how the fibres can be followed from one calcite crystal to another. (B) Calcite mosaic with micritized aragonite relics inside. (C) Calcite crystals with acicular morphology inherited from the aragonite. Small calcite crystals are found between the larger ones.

that if the analysis of calcite is used to extract physical and chemical data for palaeoenvironmental reconstructions or the calculation of growth rates, detailed microtextural (conventional petrography and SEM) studies must necessarily be performed.

Acknowledgments

This work received financial support from the *Junta de Extremadura* through FEOGA-ORIENTACION-FEDER funds, Project CGL-2008-

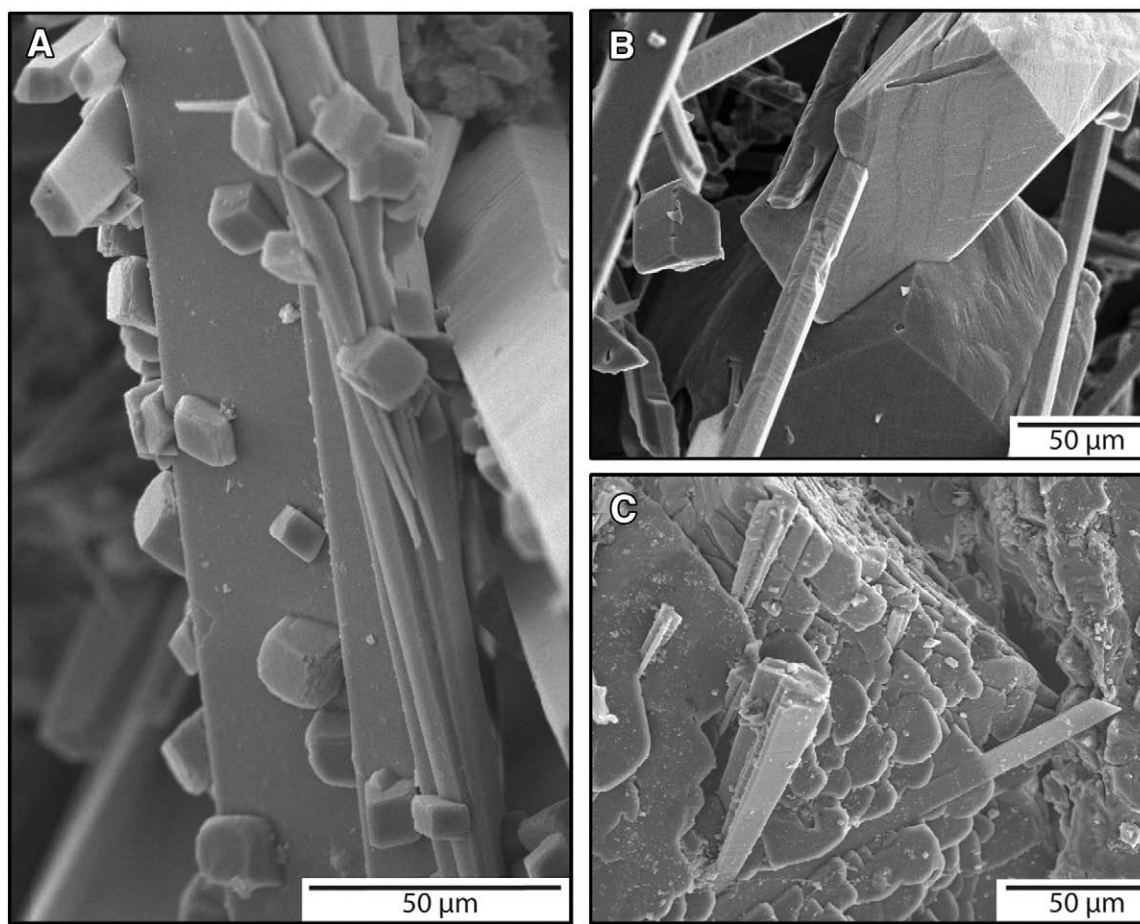


Fig. 9. SEM microphotographs. (A) Aragonite fan with small calcite crystals over the surfaces. (B) Calcite crystals grow surrounding the aragonite fibres including them to its structure. (C) Relic fibres of aragonite included within a calcite mosaic.

05584-C02-02 from the MCINN and UCM-910404. B. Jones is gratefully acknowledged for the critical and constructive comments on the manuscript. I. Gil, P. Muñoz-Barco, E. Martínez and A. 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.

References

- Alexanderson, E.T., 1972. Micritization of carbonate particles: processes of precipitation and dissolution in modern shallow-marine sediments. *Universitet Uppsala, Geologiska Institut Bulletin* 7, 201–236.
- Alonso-Zarza, A.M., Martín-Pérez, A., 2008. Dolomite in caves: recent dolomite formation in oxic, non-sulfate environments. Castañar Cave, Spain. *Sedimentary Geology* 205, 160–164.
- Alonso-Zarza, A.M., Gil-Peña, I., Martínez-Flores, E., Muñoz-Barco, P., 2005. La Cueva de Castañar. In: Muñoz-Barco, P., Martínez-Flores, E. (Eds.), *Patrimonio geológico en Extremadura: geodiversidad y lugares de interés geológico*. Dirección General de Medio Ambiente, Consejería de Agricultura y Medio Ambiente, Junta de Extremadura, Mérida.
- Auler, A.S., Smart, P.L., 2004. Rates of condensation corrosion in speleothems of semi-arid northeastern Brazil. *Speleogenesis and Evolution of Karst Aquifers* 2.
- Bar-Matthews, M., Matthews, A., Ayalon, A., 1991. Environmental controls of speleothem mineralogy in a karstic dolomitic terrain (Soreq Cave, Israel). *Journal of Geology* 99, 189–207.
- Bathurst, R.G.C., 1966. Boring algae, micrite envelopes and lithification of molluscan bioparites. *Geology Journal* 5, 15–32.
- Berner, R.A., 1975. The role of magnesium in the crystal growth of calcite and aragonite from sea water. *Geochimica et Cosmochimica Acta* 39, 489–494.
- Brand, U., 1989. Aragonite–calcite transformation based on Pennsylvanian molluscs. *GSA Bulletin* 101, 377–390.
- Boston, P., Spilde, M.N., Northup, D.E., Curry, M.C., Melim, L.A., Rosales-Lagarde, L., 2008. Microorganisms as speleogenetic agents: passive and active processes. 33rd International Geological Congress. Abstracts, 33, Abstract 1340156.
- Calvet, F., 1982. Constructive micrite envelope developed in vadose continental environment in Pleistocene eolianites of Mallorca (Spain). *Acta Geologica Hispanica* 17, 169–178.
- De Choudens-Sánchez, V., González, L.A., 2009. Calcite and aragonite precipitation under controlled instantaneous supersaturation: elucidating the role of CaCO_3 saturation state and Mg/Ca ratio on calcium carbonate polymorphism. *Journal of Sedimentary Research* 79, 363–376.
- Dix, G.R., James, N.P., Kyser, T.K., Bone, Y., Collins, L.B., 2005. Genesis and dispersal of carbonate mud relative to Late Quaternary sea-level change along a distally-steepened carbonate ramp (Northwestern Shelf, Western Australia). *Journal of Sedimentary Research* 75, 665–678.
- Fairchild, I.J., Smith, C.L., Baker, A., Fuller, L., Spötl, C., Matthey, D., McDermott, F., E.I.M.F., 2006. Modification and preservation of environmental signals in speleothems. *Earth Science Reviews* 75, 105–153.
- Folk, R.L., 1959. Practical petrographic classification of limestones. *AAPG Bulletin* 43, 1–38.
- Folk, R.L., 1965. Some aspects of recrystallization in ancient limestones. In: Pray, L.C., Murray, R.C. (Eds.), *Dolomitization and limestone diagenesis – A symposium*. Society of Economic Paleontologists and Mineralogists Special Publication, pp. 14–48.
- Friedman, G.M., 1964. Early diagenesis and lithification in carbonate sediments. *Journal of Sedimentary Research* 34, 777–813.
- Friedman, G.M., 1985. The term micrite or micrite cement is a contradiction – discussion of micritic cements in microrings is not necessarily a shallow-water indicator. *Journal of Sedimentary Petrology* 55, 777.
- Frisia, S., Borsato, A., Fairchild, I.J., McDermott, F., 2000. Calcite fabrics, growth mechanisms, and environments of formation in speleothems from the Italian Alps and Southwestern Ireland. *Journal of Sedimentary Research* 70, 1183–1196.
- Frisia, S., Borsato, A., Fairchild, I.J., McDermott, F., Selmo, E.M., 2002. Aragonite–calcite relationships in speleothems (Grotte de Clamouse, France): environment, fabrics, and carbonate geochemistry. *Journal of Sedimentary Research* 72, 687–699.
- Gutjahr, A., Dabringhaus, H., Lacmann, R., 1996a. Studies of the growth and dissolution kinetics of the CaCO_3 polymorphs calcite and aragonite I. Growth and dissolution rates in water. *Journal of Crystal Growth* 158, 296–309.
- Gutjahr, A., Dabringhaus, H., Lacmann, R., 1996b. Studies of the growth and dissolution kinetics of the CaCO_3 polymorphs calcite and aragonite I. The influence of divalent cation additives on the growth and dissolution rates. *Journal of Crystal Growth* 158, 310–315.

- Hill, C.A., Forti, P., 1997. Cave minerals of the world. National Speleological Society, Huntsville.
- Jarosewich, E.J., Nelen, J.A., Norberg, J.A., 1980. Reference samples for electron microprobe analysis. *Geostandards News* 4, 43–47.
- Jones, B., 1987. The alteration of sparry calcite crystals in a vadose setting, Grand Cayman Island. *Canadian Journal of Earth Sciences* 24, 2292–2304.
- Jones, B., 1988. Calcite rafts, peloids, and micrite in cave deposits from Cayman Brac, British West Indies. *Canadian Journal of Earth Sciences* 26, 654–664.
- Jones, B., Kahle, C.F., 1995. Origin of endogenetic micrite in karst terrains: a case study from the Cayman Islands. *Journal of Sedimentary Research* A65, 283–293.
- Kobluk, D.R., Risk, M.J., 1977. Micritization and carbonate-grain binding by endolithic algae. *AAPG Bulletin* 61, 1069–1082.
- Lippmann, F., 1973. *Sedimentary Carbonate Minerals*. Springer-Verlag, Berlin.
- Maliva, R.G., 1998. Skeletal aragonite neomorphism — quantitative modelling of a two-water diagenetic system. *Sedimentary Geology* 121, 179–190.
- Maliva, R.G., Missimer, T.M., Dickson, J.A.D., 2000. Skeletal aragonite neomorphism in Plio-Pleistocene sandy limestones and sandstones, Hollywood, Florida, USA. *Sedimentary Geology* 136, 147–154.
- McDermott, F., 2004. Palaeo-climate reconstruction from stable isotope variations in speleothems: a review. *Quaternary Science Reviews* 23, 901–918.
- Milliman, J.D., Hook, J.A., Golubic, S., 1985. Meaning and usage of micrite cement and matrix — reply to discussion. *Journal of Sedimentary Petrology* 55, 777–784.
- Morse, J.W., Arvidson, R.S., 2002. The dissolution kinetics of major sedimentary carbonate minerals. *Earth Science Reviews* 58, 51–84.
- Morse, J.W., Mackenzie, F.T., 1990. *Geochemistry of sedimentary carbonates*. Elsevier, Amsterdam. 707 pp.
- Neugebauer, J., 1978. Micritization of crinoids by diagenetic dissolution. *Sedimentology* 25, 267–283.
- Pedone, V.A., Dickson, J.A.D., 2000. Replacement of aragonite by quasi-rhombohedral dolomite in a Late Pleistocene tufa mound, Great Salt Lake, Utah, U.S.A. *Journal of Sedimentary Research* 70, 1152–1159.
- Perdikouri, C., Kasioptas, A., Putnis, C.V., Putnis, A., 2008. The effect of fluid composition on the mechanism of the aragonite to calcite transition. *Mineralogical Magazine* 72, 111–114.
- Pingitore, N.E., 1976. Vadose and phreatic diagenesis; processes, products and their recognition in corals. *Journal of Sedimentary Petrology* 46, 985–1006.
- Reid, R.P., Macintyre, I.G., 1998. Carbonate recrystallization in shallow marine environments: a widespread diagenetic process forming micritized grains. *Journal of Sedimentary Research* 68, 928–946 Part A.
- Reid, R.P., Macintyre, I.G., 2000. Microboring versus recrystallization: further insight into the micritization process. *Journal of Sedimentary Research* 70, 24–28.
- Rowling, J., 2004. Studies on aragonite and its occurrence in caves, including New South Wales Caves. *Journal and Proceedings of the Royal Society of New South Wales* 137, 123–149.
- Sánchez-Moral, S., Cuezva, S., Lario, J., Taborda-Duarte, M., 2006. Hydrochemistry of Karstic Waters in a Low-energy Cave (Castañar de Ibor, Spain). In: Durán, J.J., Andreo, B., Carrasco, F. (Eds.), *Karst, cambio climático y aguas subterráneas*. IGME, Madrid.
- Skidmore, M., Sharp, M., Tranter, M., 2004. Kinetic isotopic fractionation during carbonate dissolution in laboratory experiments: implications for detection of microbial CO₂ signatures using $\delta^{13}\text{C}$ -DIC. *Geochimica et Cosmochimica Acta* 68, 4309–4317.
- Woo, K.S., Choi, D.W., 2006. Calcitization of aragonite speleothems in limestone caves in Korea: diagenetic process in a semiclosed system. In: Harmon, R.S., Wicks, C. (Eds.), *Perspectives on karst geomorphology, hydrology, and geochemistry. A tribute volume to Derek C. Ford and William B. White*. GSA Special Paper. Geological Society of America, Boulder, Colorado.