

DOLOMITE IN SPELEOTHEMS OF SNEŽNA JAMA CAVE, SLOVENIA

DOLOMIT V SPELEOTEMIH IZ SNEŽNE JAME

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Andrea Martín-Pérez, Adrijan Košir & Bojan Otoničar: Dolomite in speleothems of Snežna Jama cave

In Snežna Jama cave, Slovenia, extensive speleothems composed of dolomite, aragonite and hydromagnesite have been found, occurring as 5 cm thick globular crusts coating the host rock. Arborescent aragonite constitutes the skeleton of the crust, whereas dolomite is cementing, coating and replacing the aragonite. The dolomite displays two distinctive fabrics: coarse rounded to spheroidal crystals, frequently showing fibrous-radial and concentric patterns, and microcrystalline aggregates. Dissolution of the dolostone host rock has provided Mg, which is the main control on the precipitation of aragonite, dolomite and hydromagnesite. Dolomite precipitation could be promoted by increased Mg/Ca ratios due to the prior precipitation of calcite and aragonite and by forced degassing due to ventilation caused by the existence of shafts cutting the main cave passage and a former entrance to the cave. However, in many caves such conditions do not lead to the formation of dolomite and so we discuss other mechanisms which might promote dolomite precipitation, like the possible contribution of microbes, or the transformation of precursor phases such as amorphous Ca-Mg carbonates, or hydromagnesite.

Key words: Snežna Jama cave, Raduha, Kamnik-Savinja Alps, dolomite speleothems, aragonite, hydromagnesite, spheroidal textures.

Izvleček

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Andrea Martín-Pérez, Adrijan Košir & Bojan Otoničar: Dolomit v speleotemih iz Snežne jame

V Snežni jami so bili odkriti obsežni speleotemi iz dolomita, aragonita in magnezita v obliki globularnih skorjastih tvorb, ki prekrivajo matično kamnino. Ogradje skorij je zgrajeno iz razvejanih kristalnih skupkov aragonita, cementiranih z dolomitom, ki prekriva in deloma nadomešča aragonit. Dolomit se pojavlja v dveh teksturnih različikih: v obliki grobo zaobljenih do sferoidálnih kristalov, ki imajo pogosto fibrozno-radialno in/ali sferično notranjo zgradbo, ter v obliki mikrokristalnih agregatov. Magnezij, ki izvira iz raztopljene matične dolomitne kamnine, ima bistven vpliv na izločanje aragonita, dolomita in hidromagnezita. Izločanje dolomita je lahko spodbujeno s povišanim razmerjem Mg/Ca v raztopini, ki sledi izločanju kalcita ali aragonita, ali s povečanim izhlapevanjem zaradi cirkulacije zraka v jami v času, ko je bil jamski sistem s površjem povezan z več vertikalnimi prehodi in skozi nekdanji glavni vhod. Podobni pogoji verjetno obstajajo v mnogih jamah, vendar pa se dolomit v jamskih pogojih le redko izloča, zato v članku razpravljamo o mogočih drugačnih mehanizmi nastajanja dolomita – od izločanja pod mikrobnim vplivom do transformacije predhodnih mineralnih faz, kakršne bi lahko bile amorfne oblike Ca-Mg karbonatov ali hidromagnezita.

Ključne besede: Snežna jama, Raduha, Kamniško-Savinjske Alpe, speleotemi, dolomit, aragonit, hidromagnezit, sferoidna tekstura.

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INTRODUCTION

Dolomite is a mineral rarely present in caves. Although at least 350 different cave minerals have been described, more than 90 % of speleothems are composed of only calcite and aragonite (Onac & Forti 2011).

In other recent, low temperature sedimentary environments, dolomite is also scarce, in contrast with the abundance of dolomite in ancient rocks. This scarcity, together with the failure to inorganically precipitate dolomite in the laboratory in conditions of low temperature and pressure (Land 1998), are some of the aspects of the “dolomite problem” (Warren 2000; Machel 2004), a topic of debate for decades.

Some of the most important settings where recent dolomite has been found are sabkhas (McKenzie *et al.* 1980; Bontognali *et al.* 2010), saline or hypersaline lakes (Corzo *et al.* 2005; Last *et al.* 2012) and coastal lagoons (Vasconcelos & McKenzie 1997; Wright & Wacey 2005). In contrast, little is known about the formation of dolomite in the subaerial meteoric conditions that are preva-

lent in caves, and a study of this particular setting can reveal new insights into the formation of dolomite.

The occurrence of dolomite has been reported from different caves around the world (Fishbeck & Müller 1971; Polyak & Güven 2000; Jones 2010a and references therein). However, in most cases it appears in a very small amount, and only a few studies have given a detailed description and interpretation of its possible origin (Thraillkill 1968; Bar-Matthews *et al.* 1991; Alonso-Zarza & Martín-Pérez 2008; Jones 2010a; Onac *et al.* 2014).

In Snežna Jama cave, Slovenia, we have found centimetre-thick botryoidal crusts on the cave walls, composed of up to 60 % dolomite of different textures, aragonite, hydromagnesite and minor amounts of calcite. The aim of this work is to report this occurrence of dolomite speleothem and provide a detailed description of its characteristics, comparing them with previously reported cave dolomite.

MATERIAL AND METHODS

Samples were collected from naturally fallen blocks adjacent to the cave wall. Speleothems were carefully compared with their in-situ counterparts. Freshly broken surfaces and cut slabs were examined under a binocular microscope. Conventional optical petrography was performed on thin sections. Due to their fragility, the speleothems were embedded in Epofer EX 401 and Epofer E 432 epoxy resin in a vacuum system before cutting and polishing. Selected thin sections were stained with alizarin red S and potassium ferricyanide (Dickson 1966) to distinguish aragonite and calcite from dolomite. Mineralogical characterisation was done by X-ray diffraction (XRD) using a Bruker D8 diffractometer operating at 40 kV and 30 mA, at 1.7 °/min, with monochromated CuK α radiation at Complutense University in Madrid

and a Bruker AXS endeavour diffractometer from the Department of Advanced Materials of the Jožef Stefan Institute, Ljubljana. XRD spectra were obtained from 2 to 65° 2 θ . Scanning electron microscopy (SEM) observations were performed on gold-coated samples using a JEOL JSM 330A microscope at the Institute of Paleontology ZRC SAZU, Ljubljana and a JEOL JSM-820 6400 electron microscope at the National Electronic Microscopy Centre (CNME), Madrid. An EDX system allowed semi-quantitative compositions to be obtained. Elemental analyses were performed in polished thin sections on a JEOL JXA-8900 M WD/ED electron microprobe at CNME, operating at 15 kV and 20 nA and employing an electron beam diameter of 5 μ m.

LOCATION AND GEOLOGICAL SETTING

Snežna Jama cave is located on the south-eastern slope of the Raduha Mountain (Fig. 1) in the NE part of the Kamnik-Savinja Alps. The entrance is located at 1556 m.a.s.l., at a height of 1000 m above the level of the Savinja River (Naraglav & Ramšak 1990). The cave (Fig. 2) consists of

a nearly horizontal main passage, about 1600 m long, of phreatic-epiphreatic origin (Bosák *et al.* 2002), cut by four vertical shafts. The cave was formed in Middle and Upper Triassic massive limestone and dolomite (Mioć *et al.* 1983; Celarc 2004). According to a detailed geologi-

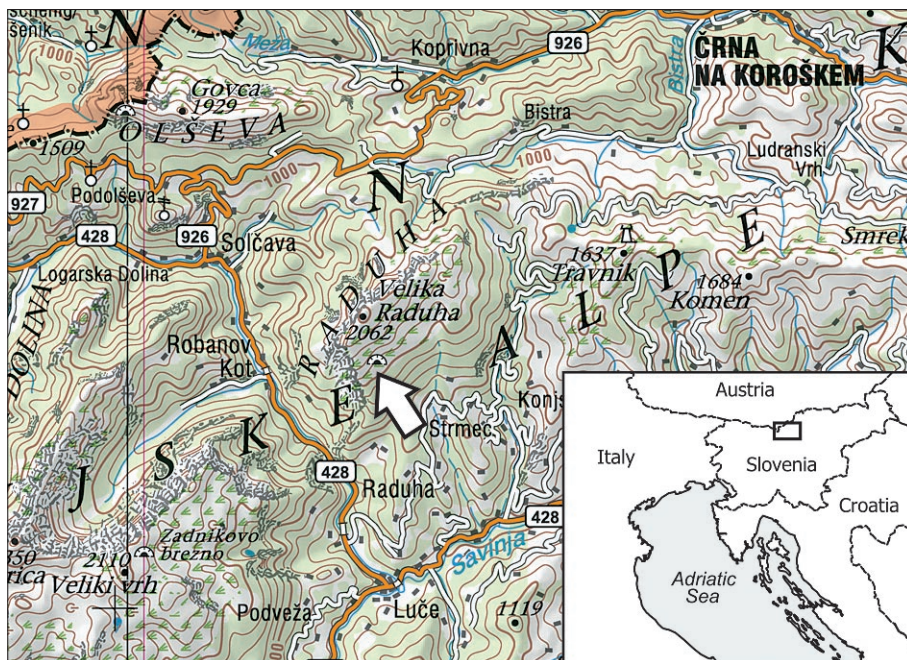


Fig. 1: Location of Snežna Jama in the Kamnik-Savinja Alps, N Slovenia.

cal map by Celarc (2004), the first part of the main cave passage, with a general ENE-WSW direction, lies in the Cordevolian formation. The second, SE-NW oriented part, developed in the Ojstrica Formation (Celarc 2004): a major change in the general passage trend corresponds to a fault separating both formations. Cave deposits are very diverse. Fluvial sediments consisting of laminated clays and sands with pebbles are found all along the cave and can reach a thickness of 10 m in some areas (Bosák *et al.* 2002). Large massive calcite speleothems (draperies, flowstone sheets and domes, stalagmites and stalactites) are abundant in most areas of the main gallery (Zupan Hajna *et al.* 2008). Studies performed in flowstones reveal a minimum age of 1.2 Ma based on U-series data,

and older than 1.77 Ma based on magnetostratigraphy (Bosák *et al.* 2002). The central part of the cave passage (Naraglav & Ramšak 1990) is characterised by thick, actively precipitating calcite moonmilk speleothems (Košir *et al.* 2010; Košir *et al.* 2012). In the more internal part of the cave, aragonite and Mg-carbonate speleothems such as coralloids, stalactites and crusts are predominant.

The cave's average annual temperature is 4.5 °C whereas the relative humidity varies between distinct parts of the cave (Zupan Hajna *et al.* 2008). Fossil remains of *Ursus spelaeus* found in the terminal part of the cave indicate the existence of another cave entrance during the Pleistocene (Zupan Hajna *et al.* 2008), probably strongly affecting the cave microclimate in the past.

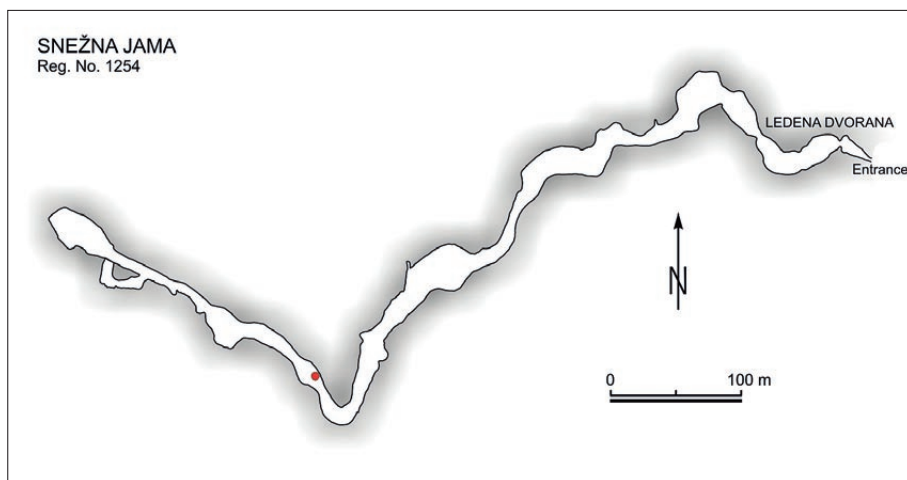


Fig. 2: Simplified plan map of Snežna Jama, taken from Zupan-Hajna *et al.* 2008. The red dot shows the sampled area.

DOLOMITE AND ARAGONITE SPELEOTHEMS

Dolomite appears in the area of the cave that is dominated by aragonite speleothems (Fig. 3A), growing on dolostone host rock.

Dolomite is associated with aragonite forming extensive crusts that cover the host rock on the cave walls (Fig. 3B-D). The dolomite crusts are between

3 and 6 cm thick (Fig. 3E) and display a globular surface morphology with globules varying from a few mm up to 5 cm in diameter (Fig. 3F). The surface of the crust is dry and does not show signs of present-day mineral precipitation. Some globules are partly covered with small white patches of moonmilk (Fig. 3G). Small

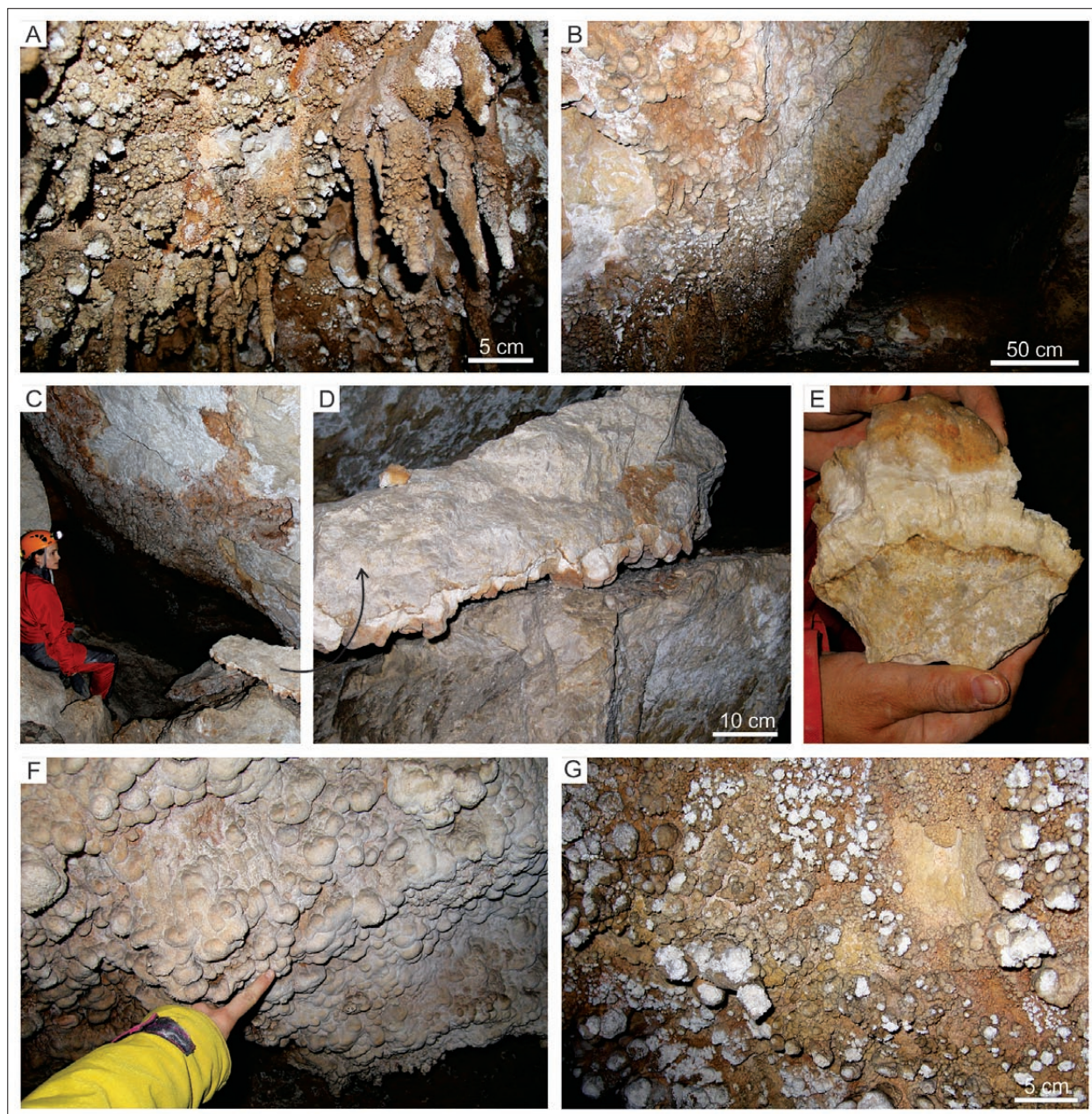


Fig. 3: A) Aragonite stalactites partly covered with patches of moonmilk. B, C) Botryoidal crusts of dolomite and aragonite. In some areas they had broken and fallen on the floor (arrow). D) Block of dolomite host rock covered by a botryoidal crust (bottom). E) Hand specimen of host rock with crust. F) Detail of the botryoidal appearance of the dolomite crusts. G) Botryoidal-coralloid crust covered with globules of moonmilk.

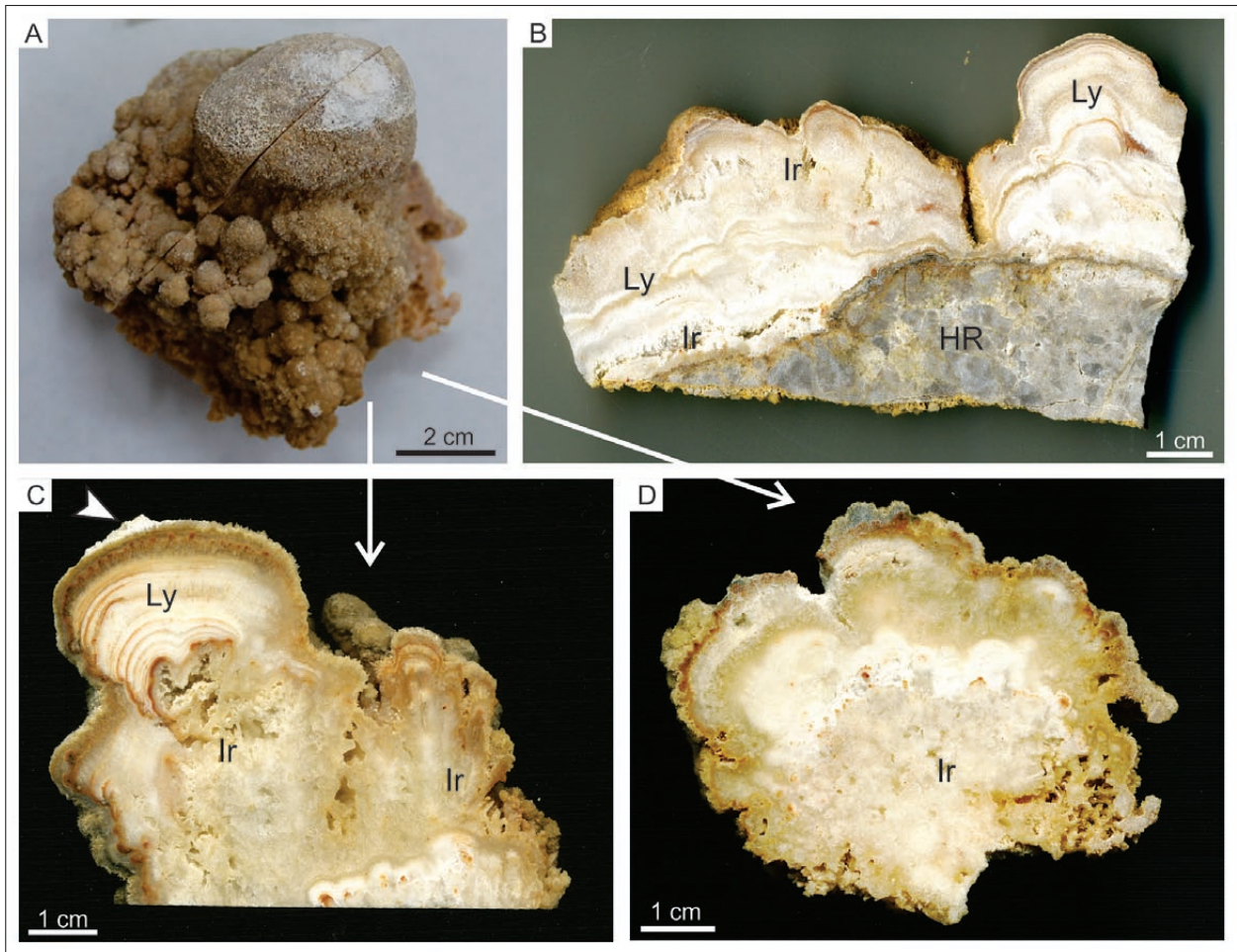


Fig. 4: Hand specimen (A) and polished slabs (B, C and D). C is a cross-section of A, perpendicular to the wall. C is a longitudinal section of A, cut parallel to the wall. HR: host rock. Ly: layered texture. Ir: irregular texture. The arrow in C points to a patch of moonmilk.

amounts of calcite have also been identified in some parts of the crusts.

Internally, the crusts (Fig. 4A) show two main textures: a) The **laminated texture** is defined by the alternation of translucent layers with opaque white layers. This layering characterises the bigger globules (Fig. 4B, C); and b) an **irregular porous texture**. The smaller glob-

ules and the inner part of the crusts display arborescent textures and high porosity (Fig. 4B, C, D). Both textures are composed of aragonite and dolomite (Fig. 5A). The moonmilk which covers some globules (Fig. 4A, C) is composed of hydromagnesite ($\text{Mg}_3(\text{CO}_3)_4(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$) (Fig. 5B).

PETROGRAPHY OF THE DOLOMITE CRUSTS

DOLOSTONE HOST ROCK

The host rock is a brecciated crystalline dolostone, with calcitic cements filling the fractures in some areas. The dolomite textures vary from xenotopic mosaics of crystals up to 2 mm in size (Fig. 6A) to idiotopic-hypidiotopic mosaics of rhombic crystals of highly variable sizes (10–2000 μm)

(Fig. 6B). Some of the dolomite rhombs appear enclosed in larger calcite crystals that fill the fractures.

ARAGONITE

It appears as acicular crystals whose size varies from 10 to 500 μm in width and from 50 μm to 5 mm in length

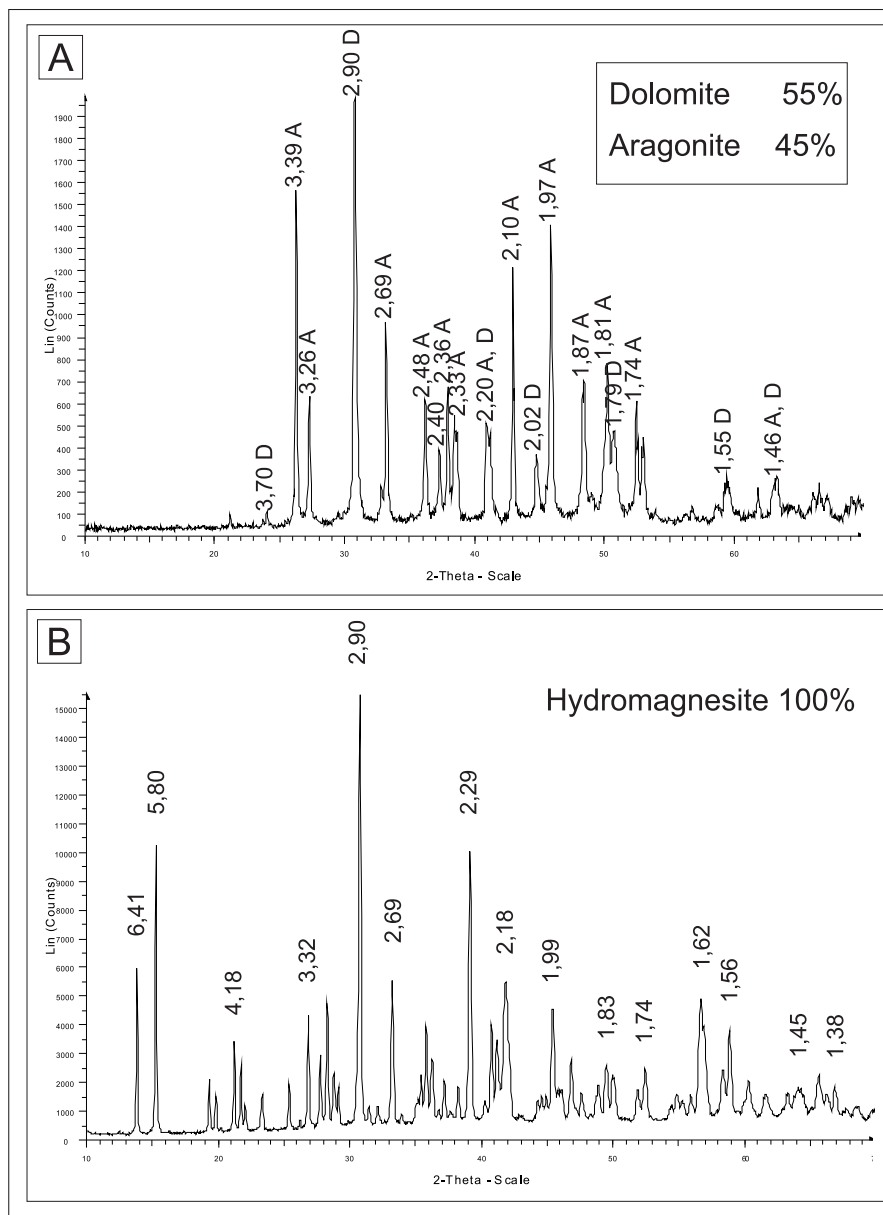


Fig. 5: XRD diagrams of botryoidal crust (A) and moonmilk globule (B).

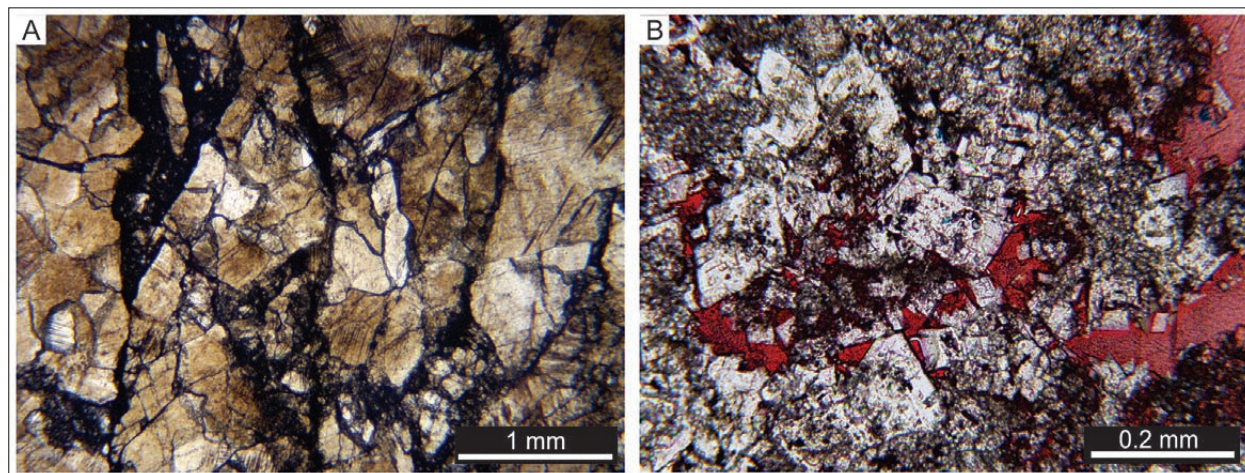


Fig. 6: Petrography of the host rock. Plane polarised light (PPL) A) Xenotopic mosaics of dolomite crystals of variable size. B) Hypidiotopic mosaics of rhombic dolomite crystals of highly variable sizes. Poiquilotopic calcite cements (red) filling intercrystalline porosity.

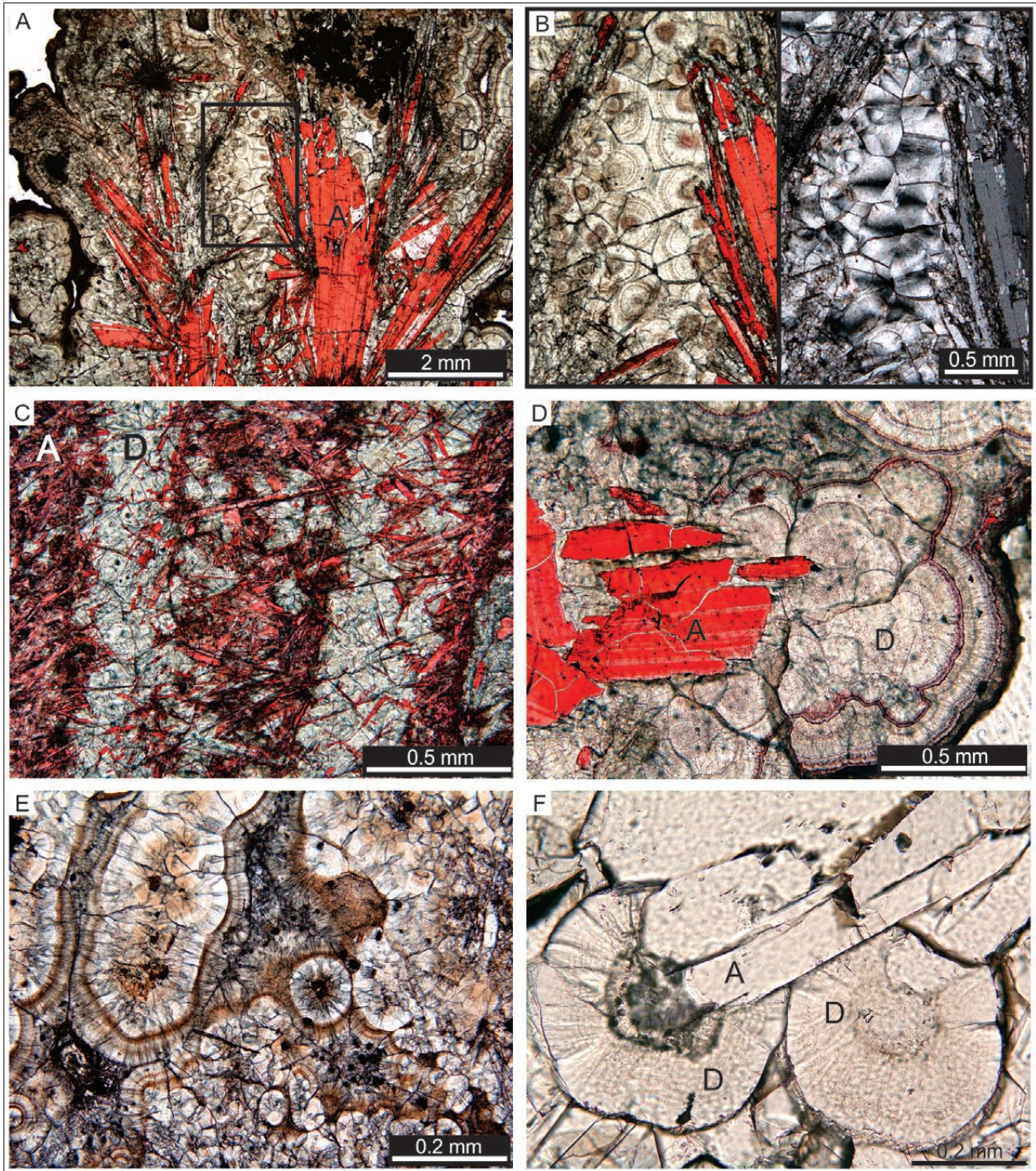


Fig. 7: Petrography of the crusts. Samples A to D are stained with alizarine. A) General view of the irregular texture of the crusts (PPL). Aragonite crystals (A) form fans which are covered by coarse dolomite (D) that also cement the space between them. B) A detail of A, with plane (left) and cross (right) polarised light. A mosaic of coarse dolomite showing a fibrous-radial texture and concentric bands in the crystals. The cross-like extinction pattern suggests that these dolomite crystals are true spherulites. C) Alternating layers of coarse dolomite and aragonite fans (red) forming the layered textures, PPL. D) Big crystals of spheroidal banded dolomite coating aragonite, PPL. E) Coarse dolomite mosaic. Although no relics of aragonite are visible, the alignment of crystals in the top left area could indicate the replacement of aragonite fibrous crystals, PPL. F) Dolomite spheroids growing on aragonite, PPL.

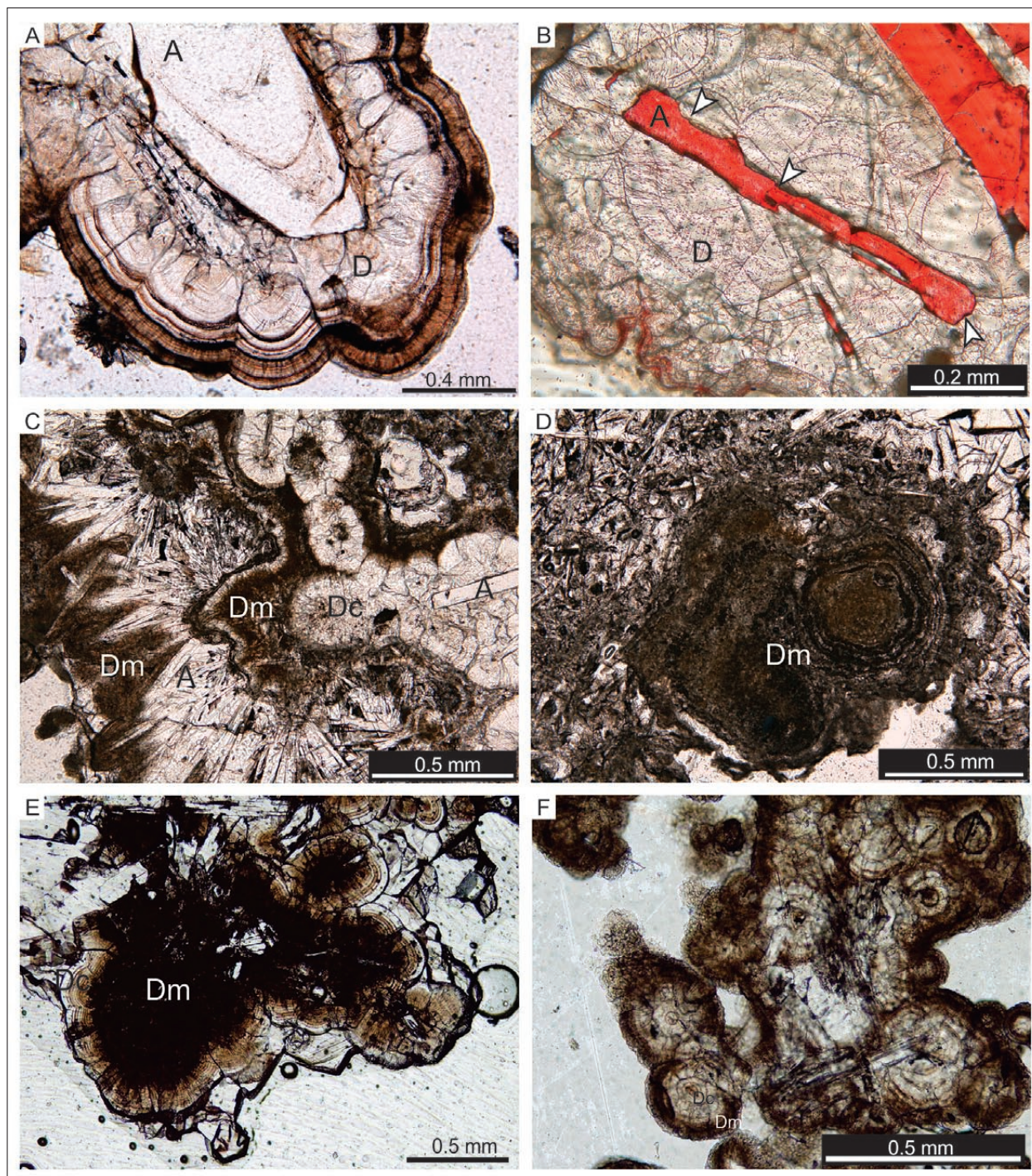


Fig. 8: Petrography of the crusts. Sample on B is stained with alizarine. All pictures taken with plane polarised light (PPL). A) Coarse dolomite forming coatings over an aragonite crystal. The dolomite crystals show concentric patterns. B) Coarse dolomite growing over and replacing aragonite crystal, as evidenced by the interpenetrated contacts between the crystals (arrows). C) Alternation of aragonite (A) and coarse (Dc) and microcrystalline dolomite (Dm). Microcrystalline dolomite appears here as structure-less aggregates over spheroidal dolomite and aragonite fans. D) Aggregates of microcrystalline dolomite showing concentric layering. E) A globule of microcrystalline dolomite coated by coarse dolomite. F) Spheroids of dolomite, alternating transparent bands with dark bands of microcrystalline dolomite.

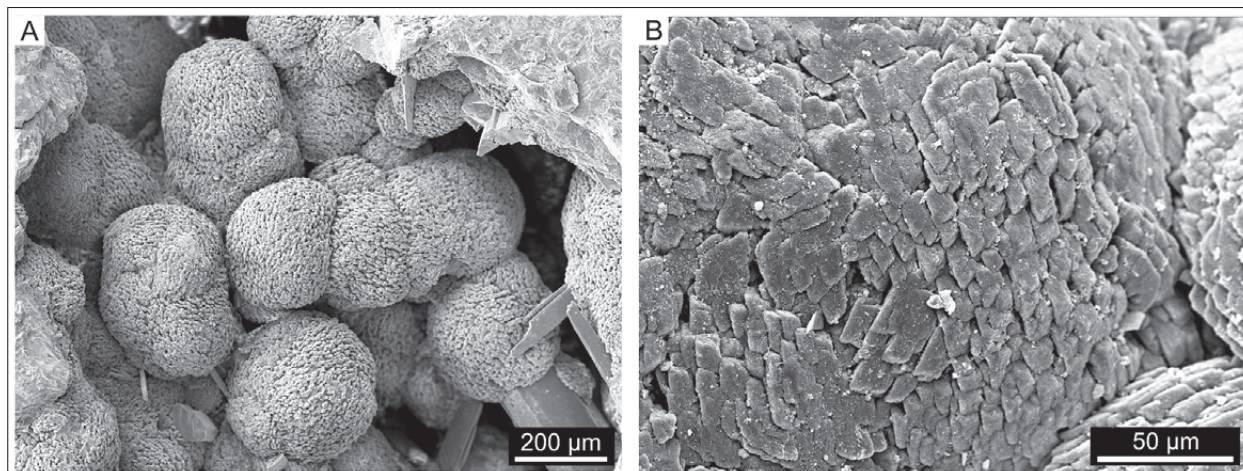


Fig. 9: SEM image of the coarse dolomite (A). The dolomite spheroids are composed of rhombic subcrystals (B).

(Figs. 7 and 8). The crystals can grow perpendicular to the nucleation surface, forming palisades, but most commonly they grow radiating from a centre outwards to form fans. Bigger crystals form arborescent, frostwork-like structures that constitute the skeleton of the crust (Fig. 7A, B). Smaller fans of crystals can coalesce to form the layers that define the laminated textures (Fig. 7C).

COARSE DOLOMITE

This type of dolomite consists of crystals of rounded, fan-shape or spheroidal morphology (Figs. 7 and 8A-C), which range in size between 50 to 300 µm and generally exhibit an undulose extinction. They are colourless or light-brown and commonly show concentric zoning (Fig. 7B, D, and E) defined by the alternation of dark microcrystalline bands and crystalline and transparent ones. The number and thickness of the bands are highly variable. In many cases, they also display an internal fibrous-radial texture and pseudo-uniaxial cross-extinction patterns so they can be considered spherulites (Fig. 7B). This type of dolomite forms part of both the laminated and the irregular texture.

A few different types of coarse dolomite have been observed: *Isolated spheroids* (Fig. 7F). *Layers of dolomite* (Fig. 7C): mosaics of anhedral or rounded crystals which form around 0.2 mm thick layers that alternate with layers of aragonite, defining the laminated textures. *Dolomite cements*: clean mosaics of crystals that show radial and concentric patterns and straight crystal contacts. They fill the space between the large aragonite crystals (Fig. 7A, B). *Coatings*: fan-shape crystals that nucleate on the surface of aragonite and coalesce forming continuous botryoidal coverings of uniform thickness (Fig. 8A). The crystals display a radial structure, and the concentric pattern is continuous across the coating. *Replacement textures*: in some cases, the contacts between aragonite

and dolomite are not sharp, showing embayments and interpenetrated features that indicate a replacement process (Fig. 8B). This process is also inferred in dolomite mosaic fabrics containing only a few corroded aragonite relics or in cases where there are no relics but the spheroidal crystals are aligned in the direction of aragonite fibres (Fig. 7E).

SEM observations show that the surface of the dolomite spheroids is composed of aggregates of rhombic crystals 10 µm in size (Fig. 9).

MICROCRYSTALLINE DOLOMITE

In hand specimens, this type of dolomite makes opaque-white to orange masses in both the inner irregular part of the crusts and in the layered globules. Under the microscope, it forms brown to dark-grey microcrystalline aggregates. Microcrystalline dolomite can appear as shapeless aggregates over aragonite crystals, and forming discontinuous layers between layers of aragonite fans (Fig. 8C). They can also form globular aggregates, which can be homogeneous or display an arrangement in irregular concentric layers (Fig. 8D). Microcrystalline dolomite can be coated by spheroidal dolomite (Fig. 8E) or be part of the dolomite spheroids as a thick external band (Fig. 8F).

HYDROMAGNESITE

It forms globular moonmilk deposits on the external surface of the crusts. In thin section, hydromagnesite forms homogeneous aggregates of colourless to brown crystals of acicular shape, 2 to 20 µm long (Fig. 10A, B). In some cases, the crystals display a radial arrangement, forming fibrous radial globules or spheroids, around 200 µm in diameter (Fig. 10C, D). Under SEM, hydromagnesite appears as homogeneous aggregates with high porosity, formed by randomly oriented euhedral platy crys-

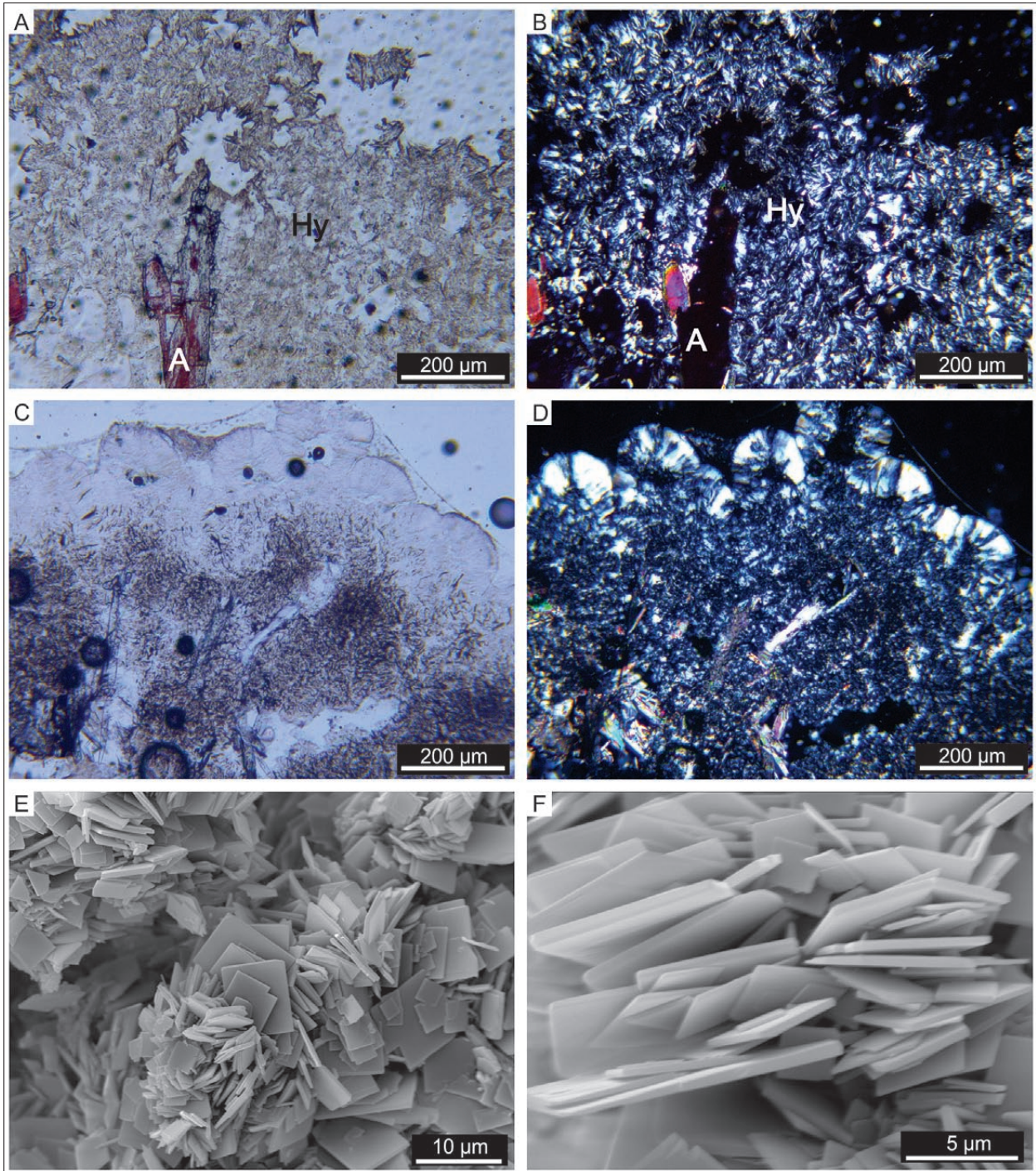


Fig. 10: Petrography of the moonmilk. A) Aggregates of hydromagnesite (Hy) surrounding aragonite crystals (A), plane polarised light, (PPL), B) Same as A, taken with cross-polarised light, (XPL). C) Transitional textures in the hydromagnesite aggregates. In the bottom part of the image the crystals are randomly oriented, while at top they are arranged growing radially from a common point forming spheroids of around 150 µm diameter, PPL. D) Same image as C, taken with cross nichols. E and F) SEM images of the hydromagnesite crystals. They are euhedral platelets of only a few microns thick, randomly oriented.

tals up to 10 μm in size and less than 1 μm in thickness (Fig. 10E, F).

CALCITE

Calcite was detected in minor amounts in the XRD analyses. It can form late cements between dolomite crys-

tals. Using microprobe and SEM (backscattered electron mode) observations (Fig. 11), it was also identified as very thin bands intergrowing with dolomite in dolomite spheroids.

GEOCHEMISTRY OF THE SPELEOTHEMS

The elemental composition of the dolomite of Snežna Jama was analysed in a microprobe which was also used, in backscattered electron mode, to characterise the fabric of the crusts (Fig. 11).

The banding of the spheroidal dolomite is due to differences in porosity and composition. The dark bands, seen under an optical microscope, show a high abundance of pores of submicron to micron size and relative

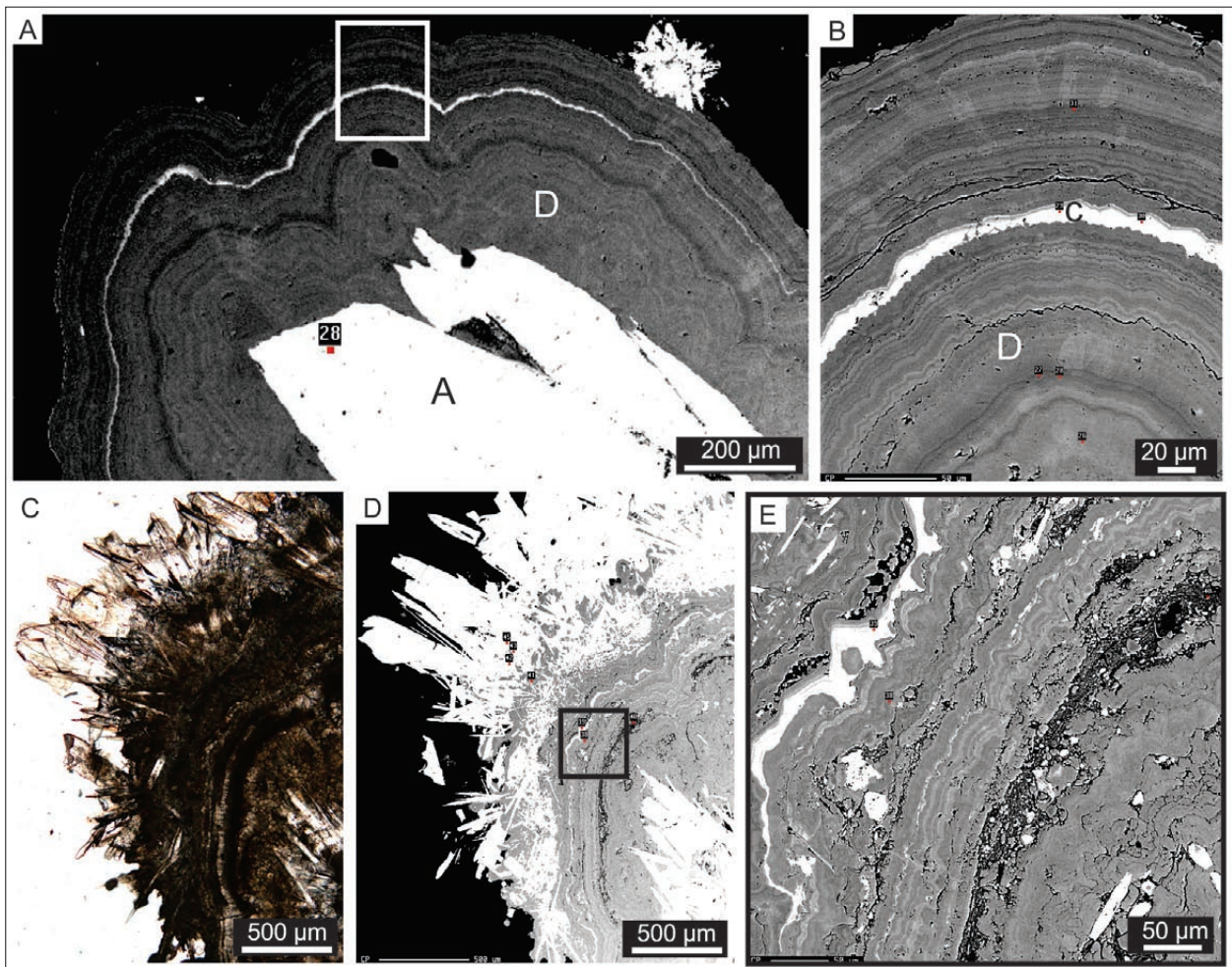


Fig. 11: A) Image 8A observed in backscattered electron mode of the microprobe. The different tone of grey of the banding reflects variations of the Mg and Ca contents. B) Detail of A. The middle white band is calcite (C). C-E) Backscattered electron observations reveal that the micritic masses which appear between the aragonite needles in C correspond to dolomite (grey colour, D). They present abundant detrital material and display compositional banding reflecting variations in Mg and Ca.

Tab. 1: Microprobe results showing mol percentages of Mg, Ca, Fe, Mn, Sr, Na, K and Ba of dolomite (D), aragonite (A) and calcite (C) crystals. The Mg/Ca ratio for dolomite is also shown. n: number of analyses. b.d.: below detection limit.

min	% MgCO ₃	% CaCO ₃	% FeCO ₃	% MnCO ₃	% SrCO ₃	% Na ₂ CO ₃	% K ₂ CO ₃	% BaCO ₃	Mg/Ca	n
D	40.5–49.9	50.0–58.8	bd–0.06	bd–0.07	bd–0.2	bd–0.08	bd–0.03	bd–0.04	0.7–1.0	28
A	bd–0.16	99.3–99.7	bd–0.01	bd–0.02	bd–0.5	bd–0.07	bd	bd		4
C	2.7–25.4	74.4–97.1	bd–0.06	bd–0.09	bd–0.2	bd	bd	bd–0.02		8

enrichment in magnesium (Fig. 11A, B). The transparent homogeneous bands are comparatively much less porous and, when observed with backscattered electrons, show an internal compositional variation, presenting laminae of dolomite about 5 µm thick with different amounts of Ca and Mg, and thin bands of calcite (Fig. 11B).

All types of microcrystalline dolomite, including the one that looks homogeneous under an optical microscope, show the alternation of darker and lighter bands when observed in the microprobe in backscattered electron mode (Fig. 11C-E). These alternations are also due to variations in amounts of Ca and Mg. In these cases, the bands are less continuous than in the spheroidal dolomite, they present higher porosity, small detrital grains and high heterogeneity (Fig. 11E).

Microprobe analyses also enabled aragonite and calcite to be distinguished based on the MgCO₃ content which is <0.5 % mol in aragonite and between 2.7 to 25.4 % mol in calcite (Tab. 1).

Elemental analyses show that the dolomite is rich in Ca, with values of mol % of CaCO₃ varying between 50 % and 58.8 % and MgCO₃ values ranging between 40.5 % and 49.9 % mol (mean values are 55.3 % and 44.5 % mol, respectively). Mg/Ca ratios vary from 0.70 to 1.00. The maximum FeCO₃ content is 0.06 % mol, MnCO₃ content is <0.07 % mol, Na₂CO₃ <0.08 % mol, SrCO₃ <0.20 % mol, K₂CO₃ <0.03 % mol and BaCO₃ <0.04 % mol. Elemental compositions of the spheroidal and microcrystalline dolomite do not reveal any significant differences.

DISCUSSION

Most of the reported occurrences of dolomite in caves share a number of characteristics (Tab. 2): a) dolomite appears together with aragonite, huntite, magnesite and hydromagnesite; b) it forms part of moonmilk, coralloids and crust speleothems; and c) the host rock of the cave is dolostone. All of these characteristics are interrelated, but the presence of Mg in the host rock is the most important constraint. The high Mg/Ca ratios in the cave waters favour the precipitation of aragonite versus calcite (Cabrol 1978; Rowling 2004; Wassenburg *et al.* 2012) due to the inhibiting role of hydrated Mg²⁺ ions in the nucleation and growth of calcite (Fernández-Díaz *et al.* 1996; De Choudens-Sánchez & González 2009). High Mg/Ca ratios are also necessary for the precipitation of huntite and hydromagnesite (González & Lohmann 1988). The type of speleothem is mainly controlled by the type of water flow and the cave microclimate, which includes processes like ventilation, condensation or evaporation (Hill & Forti 1997). Coralloids and crusts typically form in thin films of water, influenced by evaporation (Hill & Forti 1997).

The dolomite of Snežna Jama cave shares most characteristics with previously reported dolomite in caves (Tab. 2). It grows in an area with dolostone host rock, forms part of coralloid and crust speleothems, and is as-

sociated with aragonite and hydromagnesite. The internal structure of the crusts suggests several stages of formation. In the first stage, fans of aragonite crystals formed frostworks, which established the skeleton of the crust. The acicular aragonite fibres probably precipitated in conditions of low discharge from a highly supersaturated solution affected by continuous degassing and evaporation (Frisia *et al.* 2002). In the next stage, the dolomite precipitated around the aragonite needles, eventually replacing them, with the result that the initial arborescent structures of the frostwork became globular. The precise physicochemical conditions for dolomite precipitation in caves are still not well constrained, but the change and alternation in the mineralogy reflects fluctuations in the chemistry of the water that still need further work to be understood. The deposit seems to have formed in vadose conditions; although it covers big areas of the wall, and globular/botryoidal morphologies have been described as formed in pools or lakes (Hill & Forti 1997), the fact that internal parts of the crust are porous but lack any sign of dissolution makes us believe that the deposit formed in subaerial conditions.

Concerning the inorganic precipitation of dolomite, it has been considered that the two main physicochemical factors affecting formation of dolomite are high

Tab.2: Compilation of dolomite occurrences in speleothems of different caves in the world. HR: host rock; D: dolostone/dolomitic marbles; L: limestone; S: shales and/or sandstones; M: magnesites; B: basalt; o: other.

Cave name	Speleothem type	Mineral paragenesis	HR	Reference	Origin
Saint-Cézaire, France	Moonmilk	Aragonite, huntite, dolomite , giobertite (=magnesite), illite	D	Pobeguín 1960	Not a weathering product, could have precipitated in normal P and T conditions
Lehman Caves, Nevada, USA	Coating aragonite anhydrites	Aragonite, dolomite	—	Moore 1961	Alteration of aragonite in contact with Mg-rich solutions
Titus Canyon Cave, California, USA	Moonmilk	Huntite, calcite, dolomite	—	Moore 1961	Alteration of huntite produces dolomite and calcite
Tecoma Crystal Cave, Utah, USA	Moonmilk	Dolomite	—	Halliday 1961	—
Carlsbad Caverns, New Mexico, USA	Wall-rock coating, popcorn	Aragonite, calcite, dolomite	L	Thrallkill 1968	Solid-state transformation of aragonite in contact with high Mg solutions. Possible but improbable transformation of hydromagnesite
Eibengrotte, Germany	Popcorn	Hydromagnesite, nesquehonite, dolomite , aragonite, calcite	D	Fischbeck & Müller 1971	Early diagenetic origin
Carlsbad Caverns, New Mexico, USA	Microcrystalline flowstone	Huntite, dolomite	L	Hill 1973	Direct precipitation from Mg-rich solutions
Baruta Cave, Venezuela	Flowstone	Calcite, aragonite, dolomite	D	Urbani 1997	Alteration of aragonite under the influence of Mg-rich seeping water
Sumidero Tenejapa, Mexico	Moonmilk	Hydromagnesite, magnesite, calcite, protodolomite	—	Broughton 1974	Solid-state transformation of aragonite in contact with high-Mg groundwater. Possibly an alteration from hydromagnesite. Presence of fungal hyphae and spores
Haitón de Sabana Grande, Venezuela	Moonmilk	Dolomite , gypsum	L	Urbani 1976	Not clear
Cango Caves, South Africa	Chalky crust	Dolomite , calcite	L, D, S, o	Martini 1987	Primary precipitation through evaporation
Carlsbad Caverns, New Mexico, USA	Pool deposits	Calcite, aragonite, dolomite	L, D	González & Lohmann 1988	Primary precipitation from waters of moderate Mg/Ca ratio, probably from fluids undersaturated with respect to calcite and aragonite
Soreq Cave, Israel	Conical stalactites, flowstones and cave corals	LMC, HMC, dolomite , aragonite	D	Bar-Matthews <i>et al.</i> 1991	Direct inorganic precipitation from local groundwater solutions enriched in Mg due to prior precipitation of LMC. Precipitation in thin adsorbed surface solution layers, where strongly variable Mg/Ca changes may have occurred

Cave name	Speleothem type	Mineral paragenesis	HR	Reference	Origin
Carlsbad Caverns, New Mexico, USA	Wall crust	Dolomite , trioctahedral smectite, quartz			
Hell Below Cave, New Mexico, USA	Moonmilk	Huntite, dolomite , magnesite and trioctahedral smectite	D	Polyak & Güven 2000	In water films, progressive evaporation and CO ₂ loss results in the sequential precipitation of Mg-rich calcite, aragonite, dolomite, huntite, and magnesite. This sequence of precipitation removes Ca and greatly increases the Mg/Ca ratio in the solutions
Spider Cave, New Mexico, USA	Floor crust	Dolomite , trioctahedral smectite, amorphous silica			
Basaltic Caves, Kauai, Hawaii, USA	Coatings, moonmilk and crusts	Aragonite, calcite, dolomite , gypsum, magnesite, kerolite, hydromagnesite	B	Léivellé <i>et al.</i> 2000	Combination of direct precipitation from solution by evaporation and CO ₂ degassing, alteration of precursor minerals, and (or) microbial processes and physicochemical conditions within microbial mats
Cueva de Nerja, España	Moonmilk	Huntite, dolomite , magnesite, calcite, aragonite	D	Casas <i>et al.</i> 2001	Prior precipitation of calcium carbonates, progressive water evaporation and loss of CO ₂
Bohemia Cave, New Zealand	—	Aragonite, calcite, hydromagnesite, dolomite , opal, Fe and Mn hydroxides, gypsum, sepiolite	D, S	Táslér <i>et al.</i> 2001	Dolomite precipitates from solution over aragonite
Spipola Cave, Italy	Moonmilk	Dolomite (minor calcite, gypsum and clay minerals)	G, o	Forti <i>et al.</i> 2004	Localised high-Mg concentration, evaporative conditions
Castañar Cave, Spain	Moonmilk, crusts, aragonite coatings	Aragonite, dolomite , huntite, magnesite, hydromagnesite	D, M, S	Alonso-Zarza & Martín-Pérez 2008	Transformation of huntite and aragonite
Cayman Brac, UK	Stalactites	Aragonite, calcite, gypsum, dolomite , Mg-Si needles	D	Jones 2010a	Microbes directly or indirectly promoted dolomite precipitation through modification of their surrounding microenvironment or by providing suitable nucleation sites
Santa Barbara Cave System, Italy	Cave clouds	Calcite, dolomite	L, D	Pagliara 2010	Pneumatic dolomite formed at temperatures above 40°C
József-hegy Cave, Hungary	Needles, rafts	—	L, D	Leél-Óssy <i>et al.</i> 2011	It formed from solutions condensed from vapour above warm water pools, in a hydrothermal cave
Caves of Guadalupe Mountains, New Mexico, USA	Finely crystalline precipitates, popcorn, botryoidal and mammillary crusts	Dolomite , calcite, aragonite, huntite, quartz, (sepiolite)	L, D	Palmer & Palmer 2012	Replacement and direct precipitation driven by evaporation processes
Cova des Pas de Vallgornera, Mallorca, Spain	Crusts	Aragonite, huntite, dolomite , calcite, and gypsum	L, (D)	Onac <i>et al.</i> 2014	Direct precipitation, transformation of aragonite and/or huntite, microbial mediation

Mg/Ca ratios, and high $\text{CO}_3^{2-}/\text{Ca}$ ratios (Müller *et al.* 1972; Davies *et al.* 1977; Morrow 1990; Machel 2004). In addition, in marine and related depositional settings, salinities substantially lower or higher than that of seawater also favour dolomite formation (Machel 2004).

In caves, the Mg/Ca ratios of waters can be increased by preferential removal of Ca during “prior precipitation” of calcite or aragonite (Fairchild *et al.* 2000; Sherwin & Baldini 2011; Wassenburg *et al.* 2012). Prior precipitation can take place in the epikarst before the water reaches the cave atmosphere, or inside the cave in the speleothems (Bar-Matthews *et al.* 1991). This last mechanism has been addressed by many authors to explain the formation of Mg-rich carbonates in speleothems (González & Lohmann 1988; Hill & Forti 1997; Polyak & Güven 2000; Casas *et al.* 2001), forming a precipitation sequence of different minerals driven by progressive degasification and evaporation. Calcite precipitates first in the speleothem, producing an increase of Mg/Ca in the residual waters. As degasification and evaporation proceed, aragonite precipitates, further depleting Ca in the water and thus further increasing the Mg/Ca, which promotes the precipitation of dolomite and huntite and, finally, hydromagnesite (Lippmann 1973; Hill & Forti 1997; Alonso-Zarza & Martín-Pérez 2008). Evaporation has been regarded as the main factor influencing dolomite precipitation in crusts of Cangoon Caves, South Africa (Martini 1987), moonmilk of Spipola Cave, Italy (Forti *et al.* 2004) and different late-stage speleothems of caves of the Guadalupe Mountains (Palmer & Palmer 2012).

The supersaturation of carbonate minerals in cave waters can be increased by forced degassing (Spötl *et al.* 2005), which can occur if the pCO_2 of the cave air is very low. This process can be driven by ventilation in caves with multiple entrances (Spötl *et al.* 2005; Melim & Spilde 2011). In Snežna Jama, the existence of shafts cross-cutting the main passage, and the existence of a former entrance on the opposite side of the current one (Zupan Hajna *et al.* 2008), could provide ventilation that would enhance CO_2 degassing. This factor, together with the Mg supplied by the dolostone, would establish the essential precipitation conditions for dolomite precipitation.

However, it is well known that in many cases, despite supersaturation of dolomite in the water, it does not precipitate (Morrow 1990; Land 1998; Warren 2000). This is due to kinetic reasons (Gregg *et al.* 2015), mostly the high hydration energy of Mg^{2+} ions (Morrow 1990; de Leeuw & Parker 2001), the highly ordered structure of dolomite (Lippmann 1973), certain self-inhibiting factors (Hu *et al.* 2005; Xu *et al.* 2013) and, in some settings, the presence of SO_4^{2-} ions (Baker & Kastner 1981; Wright & Wacey 2004). In many dolomite deposits all over the

world, the overcoming of these kinetic barriers is attributed to the activity of microorganisms (Vasconcelos & McKenzie 1997; Wright & Wacey 2005). Microbial metabolic activity can increase supersaturation by increasing alkalinity or by removing SO_4^{2-} (Baker & Burns 1985), the microbes can act as nucleation points (Van Lith *et al.* 2003a; Kenward *et al.* 2009), and the exopolymeric substances they produce can play a role in the dehydration of Mg^{2+} and Ca^{2+} (Krause *et al.* 2012; Bontognali *et al.* 2008, 2014).

Microbes can also participate in the precipitation of carbonates in caves (Jones 2010b), especially in certain types of speleothems such as pool fingers (Melim *et al.* 2001) and moonmilk (Curry *et al.* 2009), but their role in the precipitation is still not fully understood (Northup & Lavoie 2001). The dolomite of speleothems of Cayman Brac are in close spatial association with microbes, suggesting a genetic relationship (Jones 2010a). Lévillé *et al.* (2000) also found a microbiological influence in the precipitation of dolomite, kerolite, magnesite and hydromagnesite in speleothems of lava tubes of Hawaii.

In Snežna Jama we have not yet found any evidence of the presence of microorganisms to dolomite crystals. The spheroidal textures that this dolomite displays have been widely described in microbial deposits of dolomite (Gunatilaka 1989; Nielsen *et al.* 1997; Cavagna *et al.* 1999; Van Lith *et al.* 2003b; Lindtke *et al.* 2011) and other microbial carbonates (Buczynski & Chafetz 1991; Rivadeneyra *et al.* 2006). However, much work has recently focused in the influence of the organic molecules and biofilms in spherulitic morphologies (Braisant *et al.* 2003). Some recent studies have demonstrated the formation of spheroidal carbonates without the intervention of living cells, only mediated by the presence of organic substances (Zhang *et al.* 2012; Roberts *et al.* 2013; Bontognali *et al.* 2014) or even fully inorganically (Fernández-Díaz *et al.* 2006; Meister *et al.* 2011; Andreassen *et al.* 2012).

Another possible mechanism of dolomite formation is the transformation from precursor minerals. Recently, a few studies have reported inorganically produced dolomite and disordered dolomite via non-classic pathways of mineralisation (Wang *et al.* 2012) which involve the formation of intermediate amorphous Ca and Ca-Mg carbonate phases (Radha *et al.* 2012) regulated by the interplay of thermodynamic and kinetic factors (Wang *et al.* 2012). Kelleher and Redfern (2002) synthesised hydrous magnesium calcium carbonate that displayed spherulitic morphologies similar to those found in Snežna Jama.

Dolomite could also have formed by the transformation of a metastable mineral such as huntite or hy-

dromagnesite. This possibility was already discussed in the 1960s and 1970s (Moore 1961; Kinsman 1967; Lippmann 1973) but, so far, no studies have further investigated this possibility (Martín-Pérez *et al.* 2012). Despite the higher solubility of huntite and hydromagnesite, they could precipitate more easily than dolomite for kinetic reasons and, later on, transform into the more stable mineral dolomite (Lippmann 1973). The transformation of huntite into dolomite has been suggested in the speleothems of Titus Canyon Cave (Moore 1961) and Castañar Cave (Alonso-Zarza & Martín-Pérez 2008) and the transformation hydromagnesite-dolomite in Sumidero

Tenejapa, Mexico (Broughton 1974) and Carlsbad Caverns (Polyak 1992, cited in Hill & Forti, 1997). In Snežna Jama, the close spatial association between hydromagnesite and dolomite and the textural similarities could indicate a related origin. Microcrystalline dolomite has a similar crystal size to hydromagnesite and is located between the aragonite crystals (Fig. 8C) in a similar way as hydromagnesite (Fig. 10A, C). The size and texture of the dolomite spheroids are very similar to the spheroidal arrangement that hydromagnesite shows in some cases (Fig. 10C and D).

CONCLUSIONS

1. The botryoidal crusts covering the walls of some areas of Snežna Jama cave are mainly composed of Ca-rich dolomite and aragonite, and contain smaller amounts of hydromagnesite and calcite.

2. The crusts formed in different stages, which can be repeated and reflect fluctuations of water chemistry and/or cave microclimate. Acicular aragonite forms first and later on is coated and replaced by dolomite.

3. Aragonite displays acicular textures, and the crystals are arranged in fans and arborescent structures.

4. Dolomite occurs mainly as microcrystalline aggregates and coarse/spheroidal crystals, which can display fibrous radial (spherulitic) textures and often show compositional concentric banding.

5. The studied dolomite shares many characteristics with other cave dolomite around the world: dolostone host rock, botryoidal/coralloid morphology and an association with aragonite and hydromagnesite. However,

the spherulitic textures found in this cave are quite uncommon.

6. In Snežna Jama, the dissolution of dolostone host rock provides Mg, which favours the precipitation of aragonite, dolomite and hydromagnesite. The high Mg/Ca ratios necessary for hydromagnesite and dolomite formation can be produced by evaporation, prior precipitation of calcite and aragonite, and strong degasification produced by ventilation due to the presence of shafts which crosscut the cave and a former entrance on the opposite side of the cave.

7. The coexistence of hydromagnesite and dolomite, and the texture similarities between them, could point to a transformation from hydromagnesite into dolomite. Other hypotheses, like the possibility of a microbial influence in the precipitation of the dolomite, need to be evaluated by further research.

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