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Phreatic overgrowths on speleothems (POS) from the Mallorca caves: Morphology, mineralogy, and crystal fabric classification

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Abstract

Phreatic overgrowths on speleothems (POS) are unique precipitates that are found in a small number of coastal caves around the world, like those in the Mallorca Island. Their growth is directly related to the water level of the brackish lakes connected to the sea characteristic of these caves and, therefore, they can be very reliable indicators of past sea levels. The study presented here characterizes and classifies an important number of POS samples collected in the coastal caves of Mallorca. The characterization includes not only the observations made on 117 handheld samples and on 102 thin sections from POS, but also the study of their mineralogy and their location in the caves. This study has provided the basis for a systematization of all these characteristics, some of which are reported here for the first time in POS samples. The results indicate that (1) most of the POS precipitate on stalactites, (2) calcite POS show branched internal and external texture and their most common crystal fabric is mosaic calcite and (3) aragonite POS show globular external texture and fan-shaped internal texture, and their principal crystal fabric is needle-like. All the aragonitic samples have been found above or at the same heights as the current sea level, which indicates that they have probably formed during warmer climates. The calcite POS have been found at heights above and below the present sea level and are interpreted as to have formed during cold and rainy periods. The systematization proposed in this paper could be applied and checked in other POS worldwide. Additionally, the combination of these results with the information obtained from studies on the present precipitation of these phreatic speleothems in some Mallorca caves has provided an insight on their formation conditions which will enlarge the utility of these speleothems as palaeoenvironmental indicators.

KEYWORDS
aragonite, calcite, phreatic overgrowths on speleothems (POS), crystal fabric, morphology, texture

1 | INTRODUCTION

Phreatic overgrowths on speleothems, known as POS, are carbonate precipitates that grow over a substrate (predominantly on existing speleothems) at the air–water interface in brackish lakes inside coastal caves. As the level of the water in those lakes is directly related to the sea level, their precipitation is produced at the altitude of the sea level at the time of their formation (Boop et al., 2013), which makes them meaningful sea-level index points (e.g., Dumitru et al., 2018; Onac et al., 2022) of the position of the past seawater levels.

These unique speleothems have only been found in a few locations around the world, including Mallorca (Spain), where they were defined and have been widely studied (Dorale et al., 2010; Dumitru et al., 2019; Dumitru, Austermann, et al., 2021; Dumitru, Polyak, et al., 2021; Ginés, Ginés, Fornós, Tuccimei, et al., 2012; Onac et al., 2022; Tuccimei et al., 2006; Vesica et al., 2000). Other places around the world include Sardinia (Italy; Mucedda et al., 1997; Tuccimei et al., 2007, 2012), Bermudas (British Overseas Territory in the North Atlantic Ocean; Harmon et al., 1978), Nansei Islands (Japan; Urushibara-Yoshino, 2003), Cuba (Bontognali et al., 2016; De Waele et al., 2017, 2018) and the Kvarner region in Croatia (Lončar et al., 2022). Their rarity and their specific significance in terms of palaeo-sea levels make their study one of the most promising in the identification of these levels.

The first observations on the Mallorca POS were reported by Rodés (1925) and Joly (1929) and subsequently in the 1960s by Butzer and Cuerda (1962). However, their detailed study started mainly in the 1970s with the works from Ginés and Ginés (1974), Butzer (1975), Pomar et al. (1976, 1979) and Pomar and Cuerda (1979). These authors indicated the relationship between the heights at which these precipitates appear and the height of various fossil beach deposits corresponding to interglacial periods. Since then, many studies have been published about the relation between the POS and the sea-level changes together with other works on the timing of their formation by U–Th dating and on their oxygen and carbon isotopic signatures for rainfall and temperature reconstruction (Csoma et al., 2006; Dorale et al., 2010; Dumitru et al., 2018, 2019; Fornós et al., 2002; Ginés, 2000; Ginés et al., 2001, 2002, 2003; Ginés & Ginés, 2007; Ginés, Ginés, Fornós, Bover, et al., 2012; Onac et al., 2006, 2022; Polyak et al., 2018; Tuccimei et al., 1997, 2006, 2009, 2010, 2011, 2012; Vesica et al., 2000). The Mallorca POS have been found at current heights ranging from 46 m above to 23 m below the present-day reference sea level, their ages range from Upper Miocene to Holocene and they correspond to more than 30 different Mediterranean Sea palaeolevels (Boop et al., 2017; Dumitru, Polyak, et al., 2021; Fornós et al., 2002; Ginés, 2000; Ginés, Ginés, Fornós, Bover, et al., 2012; Ginés, Ginés, Fornós, Tuccimei, et al., 2012). These studies have provided important palaeoclimatic information, mainly related to the eustatic curve evolution of the western area of the Mediterranean basin during MIS 5 and, although in less detail, back to the upper Miocene.

Despite all these works, detailed studies on the texture and mineralogy of the POS are scarce. The descriptions and systematics existing for common speleothems (stalagmites, stalactites and flowstone) cannot be applied to POS due to (1) the differences in their genesis and (2) the fact that there are many morphological variations in the POS at hand-specimen scale that do not exist among common speleothems. Pomar et al. (1976, 1979) reported the first detailed descriptions of crystalline fabrics in some samples of POS from Mallorca, and some years later, Ginés (2000), Ginés, Ginés, Fornós, Bover, et al. (2012) and Ginés, Ginés, Fornós, Tuccimei, et al. (2012) presented a synthesis of the results from their study of 13 POS samples from eight Mallorcan caves. Another interesting contribution about the crystalline fabric is the one from Csoma et al. (2006), who studied samples drilled from a wall in the Cova de Sa Bassa Blanca (Mallorca), but in this case, they were mixed deposits from the Middle Pleistocene composed of flowstone and POS.

The work presented here focuses on the study and characterization of POS at two different scales, hand size (characterizing size, morphology, etc.) and thin section (from centimetre to micrometre scale, identifying mineralogy, crystalline fabric, growth mechanism, etc.) together with the description of their altitudinal position in the caves. This study is a continuation of those from Ginés (2000) Ginés, Ginés, Fornós, Tuccimei, et al. (2012) but extended to a whole set of POS sampled in 23 different littoral caves in Mallorca: a total of 117 different POS samples in hand size and 102 thin sections. The objective is to increase the knowledge on their mineralogical, morphological and crystallographic features in a similar way to what has already been done for common speleothems (stalactites, stalagmites and flowstones) in Frisia et al. (2000, 2002), Fairchild et al. (2010), Frisia and Borsato (2010), Chiarini et al. (2017), Martín-Chivelet et al. (2017) and, especially, in Frisia (2015).

Moreover, a preliminary evaluation of the genetic conditions recorded in all these characters has been performed using the general knowledge about carbonates precipitation along with the complementary studies conducted by this research group on the precipitation of phreatic speleothems at present.

2 | POS

The main characteristics of these precipitates have been thoroughly described by many authors (e.g., Ginés, Ginés, Fornós, Tuccimei, et al., 2012 and references therein), and here, only a summary is presented. POS are speleothems that precipitate over different substrates at the air–water interface in the lakes inside coastal caves (Ginés, Ginés, Fornós, Tuccimei, et al., 2012; Tuccimei et al., 2010). These lakes are formed by brackish waters created by the mixture between meteoric and seawaters with which the coastal caves are directly connected and therefore their growth at the air–water contact makes them direct indicators of the sea level at that moment (Ginés, 2000; Ginés & Ginés, 1974; Pomar et al., 1976). A combination of geochronological information, based on U–Th or Pb dating, and altitudinal position of the POS enables the reconstruction of the past sea level with decimetre precision (Boop, 2014; Dumitru, Austermann, et al., 2021; Ginés, Ginés, Fornós, Tuccimei, et al., 2012). Previous authors (Ginés, Ginés, Fornós, Tuccimei, et al., 2012; Vesica et al., 2000) related the positive elevations of POS alignments with respect to the current sea level to transgressions associated to interglacial periods (warm events); and they associated the negative alignments (POS located below the current sea level) to regressions linked to glacial periods (cold conditions).

The POS start their growth from any carbonate substrate: cave walls, fallen blocks or previous speleothems (stalactites, stalagmites or columns; Figure 1a). Their precipitation, as in most of the speleothems, is due to the CO_2 outgassing from the water to the atmosphere inside the cave promoted by their different CO_2 partial pressures (Boop et al., 2014; Csoma et al., 2006; Dorale et al., 2010; Pomar et al., 1976, 1979).

Mineralogically, the POS can be composed of calcite (either high-Mg calcite [HMC] or low-Mg calcite [LMC]; Vesica et al., 2000; Ginés, Ginés, Fornós, Tuccimei, et al., 2012), which is the most common, but also of aragonite. Morphologically, these precipitates form a bulky overgrowth with the thicker part located at the air–water interface, corresponding to the average sea level (see Figure 1b). The thickness decreases upwards and downwards and the total length (around 0.5 m maximum) is interpreted as being related to the combined influence of the tidal range and the changing barometric pressure (Entrena, Gómez-Pujol, et al., 2024; Fornós et al., 2002; Pomar et al., 1979; Tuccimei et al., 2006). In general, the complete

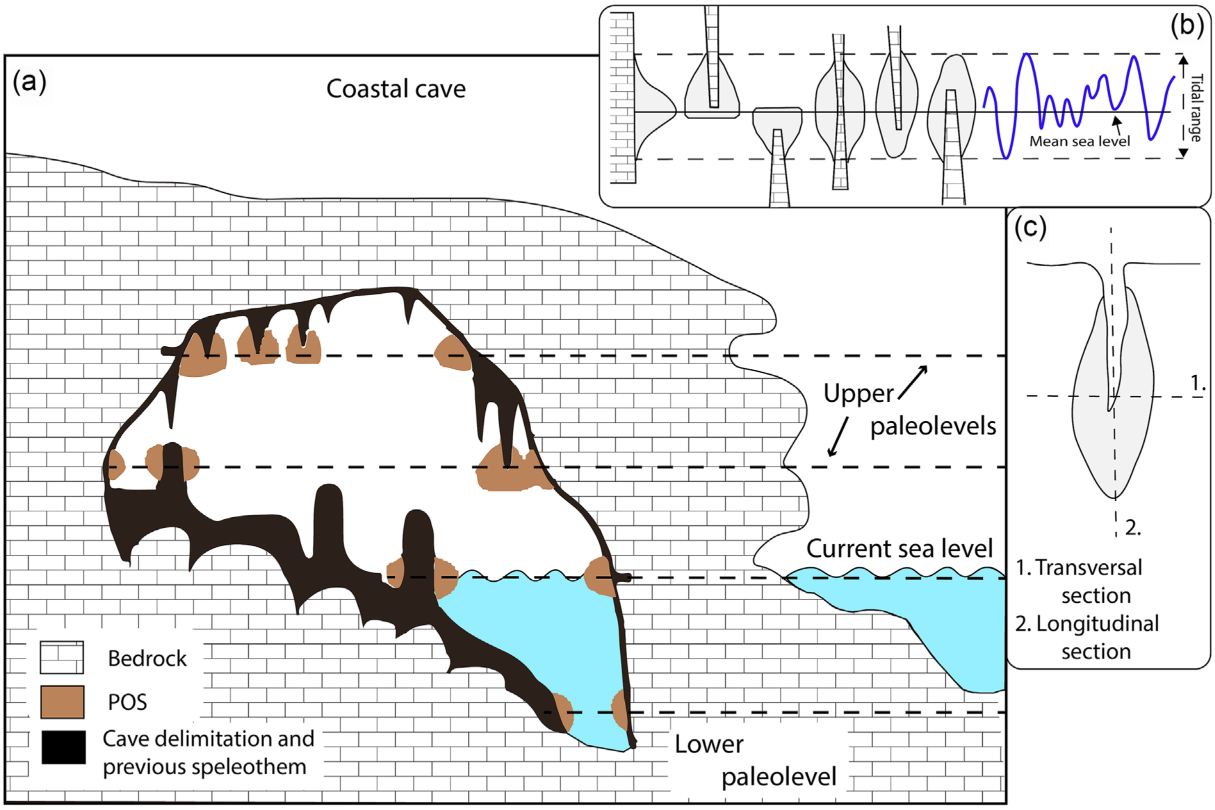

FIGURE 1 (a) Scheme of a generic Mallorca coastal cave with four different levels of POS, two of them represent upper palaeolevels, another one a lower paleolevel and the fourth one represents the current growth related to the current sea level (modified from Ginés, Ginés, Fornós, Tuccimei, et al., 2012). (b) Scheme of POS ubication and morphology in reference to the sea level and the variations of tides (modified from Tuccimei et al., 2010). The growth of the different morphologies of POS from stalactites, stalagmites, columns and walls can be seen in both schemes. (c) Sketch of the cutting directions of the bulk speleothems used to make the polished and the thin sections.

morphology of the POS is an ellipsoid, but in some cases, depending on the substrate over which it grows, the morphology can be different, not representing the full tidal range (see, e.g., the range of stalactite and stalagmite represented in Figure 1b).

There are very few studies on the hydrogeochemical characters of the current environments in which these speleothems precipitate. The most relevant are the works from Vesica et al. (2000), Csoma et al. (2006) and Boop et al. (2014) who integrated the hydrochemical study on the lakes present in some of the Mallorca coastal caves with the characterization of common speleothems, POS and rafts. Although POS and rafts have some differences in their formation and preservation, both of them form at the water–air interface in the brackish lakes of these coastal caves. Moreover, the fact that some calcite and aragonite rafts have been found associated with currently forming and fossil POS (see below), supports the evidence that both speleothems precipitate under the same conditions.

The three studies mentioned above cover an important number of the caves (11) where some of the POS studied in this paper were sampled. Vesica et al. (2000) study the Late Pleistocene POS in the caves known as Cova de na Barxa, Cova de na Mitjana, Cova del Dimoni, Coves del Drac, Coves del Pirata, Cova del Pont, Cova de Cala Falco, Cova de Cala Varques B and Cova des Serral. Csoma et al. (2006) study POS, rafts and common speleothems found in Cova Sa Bassa Blanca and formed during the entire Pleistocene period. And, finally, Boop et al. (2014), instead of studying the precipitates, focus on the characterization of the current waters from the lakes in Pas de Vallgornera and Drac caves. All these authors indicate that the waters in the coastal cave lakes are a mixture of meteoric and seawater and that this is the conditioning factor for their geochemical and mineralogical characters. They also consider that the main control on the precipitation in the water–air interface is the CO_2 degassing (Herman et al., 1985; Pomar et al., 1979) from the lake waters to the atmosphere of the cave, which promotes the oversaturation of the waters with respect to calcium carbonate minerals and their precipitation in the form of POS and/or rafts.

Vesica et al. (2000) report a relation between heavier $\delta^{18}O$ and $\delta^{13}C$ values and higher proportion of sea water in the brackish lakes (closer distance to the open sea) and associate them to warm climatic episodes. Csoma et al. (2006), based on the information from primary fluid inclusions, indicate that the mixing ratios between fresh and marine water in the settings where the POS precipitate can be as high as 1:1, indicating that they probably formed during interglacial stages, when the sea level was higher than at present (Pomar et al., 1979). Boop et al. (2014) report an increase in salinity and $\delta^{18}O$ in the brackish lake waters with depth, (increasing influence of seawater), pCO_2 values greater in the waters than in the air and Mg/Ca ratios around 1.17 in Vallgornera and 1.02 in Drac caves. They indicate that the precipitation of one or another carbonate polymorph depends on this ratio and on the combination of other factors like temperature, pCO_2, pH, salinity, trace elements, mineralogy of the seed material and activity of microorganisms.

More recent studies (Entrena, 2023; Entrena et al., 2020; Entrena, Auqué, et al., 2024; Entrena, Gómez-Pujol, et al., 2024) have provided additional information on the environmental conditions associated to the present precipitation of POS and rafts in Coves del Drac and in Cova dets Ases. They confirm the important influence of the mixing between meteoric waters and the Mediterranean seawaters in the hydrogeochemical characters of the lakes and, therefore, in the chemical, isotopical and mineralogical characters of the solids precipitated from them. They also support the fact that Mg/Ca molar ratio (dependent on the percent of marine water in the mixture) is the principal factor controlling the mineralogy but the effects of other factors, such as the CO_2 degassing rate and the saturation state of the waters with respect to calcite and aragonite, are also important. Additionally, Entrena, Gómez-Pujol, et al. (2024) indicate that the variations in the level of the hypogeous lakes in Coves del Drac and the local sea-level variation of the Mediterranean Sea show a clear dependence on the tidal movements in the sea with a 55% reduction in the vertical movement and a delay of 1.7 h. This has been interpreted as a contact between both water masses through the fracture network characteristic of the Miocene materials in which the cavity is embedded.

This information on the general characters of the POS and the waters where they precipitate is essential in the characterization of the samples studied in this paper and in the interpretation of their environmental settings.

3 | GEOLOGICAL AND GEOGRAPHICAL LOCATION

Mallorca is the largest island of the Balearic archipelago (3667 km^2) and is located in the western Mediterranean basin (Figure 2; Fornós et al., 2002). The Balearic archipelago is the emerged part of the Betic Range, which is the result of the collision between Euroasiatic and African plates (Fornós et al., 2002), that occurred during the compressive stage of the Alpine Orogeny. This compressive stage created the horsts that correspond to the mountain ranges of the island of Mallorca: Tramuntana, Central and Llevant ranges, all of them with a NE–SW preferential direction and formed by pre-Miocene basement (Figure 2), the oldest materials of the island. The horsts are separated by grabens (Gelabert et al., 1992) that developed during the extensional stage of the Alpine Orogeny and correspond to the basins Inca-Sa Pobla, Palma and Campos (Gelabert et al., 1992). These basins have been filled with upper Miocene horizontal carbonate materials followed by the most modern Plio-Quaternary sediments.

The studied POS have been sampled from the caves indicated in Figure 2 and Table 1, which are located in the following sedimentary units (Ginés, Ginés, Fornós, Tuccimei, et al., 2012):

1. Limestones and breccias from the Lias (Lower Jurassic) located in the Tramuntana Range. The caves developed in these lithotypes are characterized by a telogenetic karst (Ginés & Ginés, 2007; Mylroie, 2013; Figure 2, blue dots). They are irregular, with an important structural control, pseudocylindrical morphologies and a clear vertical development. In some cases, they are deep enough to have reached the seawater level in the past and at present and, therefore, to have developed internal lakes and allowed the precipitation of the POS (Ginés & Ginés, 1987).
2. Calcarenites and reef limestones from the Tortonian–Messinian (Upper Miocene). These materials filled-in the Neogene basins, and they are now forming a characteristic tabular platform (Watkinson et al., 1997). These caves are related to eogenetic karst systems (Ginés & Ginés, 2007; Mylroie, 2013). In contrast to the caves developed in the Jurassic materials, they have a general horizontal development (Ginés & Ginés, 2011) and are in direct contact with the water table and the sea (Figure 2, yellow dots) which is the main reason for the presence of submarine zones and also of some vadose and aerial zones. They show large chambers with vadose and phreatic speleothems and with deposits of allochthonous material. Most of the studies on POS have been done on the Miocene cavities located in the south-eastern Mallorcan coast, where these speleothems are more abundant (Csoma et al., 2006).

The development of these coastal cavities began with small voids produced by dissolution in the mixing zone between fresh and marine waters (Vesica et al., 2000) and probably associated to the bedrock fractures, joints and porosity. The proto cavities continued their growth with successive collapses due to instabilities and readjustments associated with the variation of the sea level during the

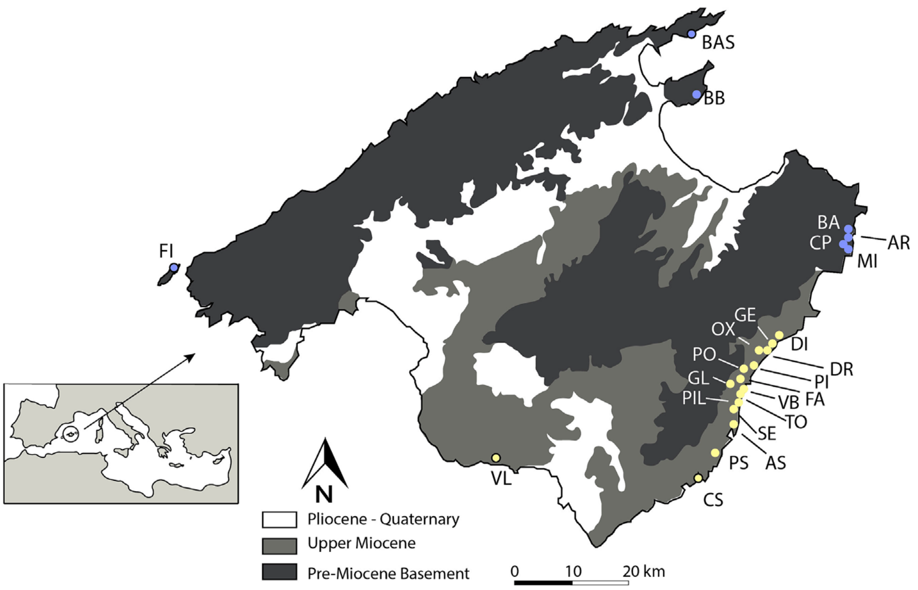

FIGURE 2 Mallorca location in the Mediterranean Sea and simplified map of the geology of the island with the location of the caves. The caves in the Jurassic materials are indicated with a blue dot and the ones in the Miocene with yellow dots. The equivalences between the names of the caves and the acronyms are listed in Table 1.

TABLE 1 Compiled information of the caves, the host rock where the caves are located, the number of thin-section samples, the code of the hand-size samples studied, the type of substrate over which they precipitate (ECT, stalactite; EGM, stalagmite; wall) and the height where the samples were located and the mineralogy.

Cave	Host rock	No. thin sections	Hand specimens	Type	Height (m)	Mineralogy
1. Cova del Serral	M	2	SE-D1/1	–	1.4	LMC
2. Cova des Pas de Vallgornera	M	2	VL-D1	ECT	–	ARA
			VL-D2	EGM	–	LMC
			VL-D3[b]			ARA
			VL-	ECT		
3. Cova des PONT	M	3	PO-D2[a]	–	–	HMC LMC
			PO-D3/D5	ECT	−3.2/−3.6	LMC
			PO-D4		−7	
4. Cova Genovesa o d'en Bessó	M	3	GE-D1	Wall	2	
			GE-D2	–	−13.1	
			GE-D3	ECT	−19.3	HMC LMC
			GE-D4		−13.8	LMC
			GE-D08	EGM	0	
5. Cova de Cala Falco	M	1	FA-D2	Wall	–	ARA, HMC
			FA-4	–	2	
6. Cova d'en Bassol (Passol)	M	6	PS-D1/D3/D5/D6/D7	ECT	−8/−10.5/−18/−23/?	LMC
			PS-D2	–	−10.5	
			PS-D4	EGM	−13.5	
7. Cova de Sa Gleda	M	14	GL-D1/D3	ECT	−15/−17.5	
			GL-D4/D8/D9/D13/ D10		−1.5/−20.3/−20.5/1.5/ −14.5	LMC
			GL-D5		−16	LMC, HMC
			GL-D6/D14		−17/−14	
			GL-D15	Wall		
			GL-D11/D12	ECT	¿?/−13.5	LMC
8. Coves del Pirata	M	0	PI-D1[a]	EGM	2.1	HMC
9. Coves del Drac (Cala Santanyí)	M	4	CS-D1	–	−13.5	LMC
			CS-D2/D3/D4	ECT	−15/−17/−15	
10. Coves del Drac (Manacor)	M	14	DR-D16/D9/D13/D6/ D7	ECT	−15/−5/0/?/0	
			DR-D24/D3/D11/ D12		−2/−9/−12	LMC
			RP-D1	–	0	
			DR-D1	EGM		LMC
			DR-D4/D14/D15/ D18	ECT	3.3/0/0/0	ARA
			DR-D5			ARA, LMC
11. Cova Dets Ases	M	7	AS-D02	Wall	1.25	
			AS-D03	ECT	0	ARA
			AS-D04/D07	Wall	1.3/06	LMC
			AS-D05/D06	–	1.2/1	
			AS-D08	Wall	0.5	LMC, HMCC[a]
12. Cova de Cala Varques B	M	6	VB-D0 VB-SA[a]	–		HMC
			VB-D2[a]	ECT	1.4	
			VB-D2bis			
			VB-D3	–	1.5	LMC
			VB-D4/D6/D5	ECT	¿?/?/−16.5-	
			s/n	EGM	0	

(Continues)

TABLE 1 (Continued)

Cave	Host rock	No. thin sections	Hand specimens	Type	Height (m)	Mineralogy
13. Cova de Ses Tortugues	M	4	TO-D1/D2/D3	ECT	1.5/1.5/−21.5	LMC
			TO-D4		0	HMC
14. Cova de s'Onix	M	1	OX-D1	–	3	HMC
15. Cova del Dimoni	M	8	DI-D1/2	Wall	2.5	ARA, LMC
			DI-D3[a,b]	ECT	2.5	ARA
			DI-D4[b]	ECT	1.1	HMC
			DI-D5/1	–	1.3/?	
			DI-2	EGM		
			DI-3/4	ECT		
16. Cova de Cala Pilota	M	1	PIL-D1	–		LMC
17. Cova de na Barxa	J	1	BA-2/3[a]	ECT	2/?	LMC, ARA, HMC, HMCC
18. Cova de Na Mitjana	J	6	MI-D1[a]/D2[a]/D3/05	–	3.9/4.9/5.8/5.6	HMC
			MI-04[a]	–	2.5	
			MI-06	ECT	5.6	HMC
19. Cova Sa Bassa Blanca	J	1	BB-01	ECT	35	
20. Cova des Bastons	J	2	BAS-D1/D2	ECT	−14/−12	HMC
21. Coves Petites	J	5	CP-01	ECT	33.7	
			CP-02/05	–	33.7/33.3	LMC
			CP-03	–	25.08	
			CP-04	ECT	33.3	LMC
22. Coves d'Arta	J	10	AR-01	ECT	27.29	
			AR-02	–	31.79	
			AR-03/05/07	–	23.58/25.08/22.58	
			AR-04/19	Wall	22.58/14.27	LMC, ARA
			AR-06/22	ECT	30.36/8	LMC, ARA
			AR-08		27.29	LMC
			AR-20	Wall	16	
			AR-21	ECT	8	ARA
23. Cova de sa Finestra	J	1	FI-D1	EGM	−16	HMC
Total		102	117			

Abbreviations: ARA, aragonite; LMC, low-magnesium calcite; HMC, high-magnesium calcite; HMCC, high-magnesium calcite with more than 11% of Mg.
[a]The mineralogy of these samples comes from Ginés, Ginés, Fornós, Tuccimei, et al. (2012).
[b]The mineralogy of these samples comes from Tuccimei et al. (2010).

Pleistocene (Ginés & Ginés, 2011; Vesica et al., 2000). During the Upper and Middle Pleistocene, vadose and phreatic speleothems developed inside the caves and allochthonous sediments were also deposited there by flowing waters (Entrena et al., 2022; Ginés et al., 2011). As mentioned above, one of the most distinctive features of the Mallorca coastal caves is the abundance of brackish lakes connected with the sea. This is seen today, but it must have been the case in the past as it is evidenced by the presence of fossil POS (Tuccimei et al., 2006).

The hydrogeology of the island shows the typical features of the carbonate islands with a lenticular body of fresh water above the saline intrusion of seawater. Currently, the mixing zone between these waters is located in the coastal caves, and the proportion of meteoric and marine water is directly associated with several factors at different scales. For example, during wet years, meteoric water can be seen as the main component of the cave lakes, while in dry years, the saline component dominates (Csoma et al., 2006). Depending on the mixing proportions, the characteristics of the environment and the water chemistry are different and, most probably, also the speleothems mineralogy. The relation between the littoral cave pools and the Mediterranean Sea levels has also been evidenced by the presence of alternating phreatic, vadose and aerial stages in the caves showing the same altimetric evolution as the sea level since the Pleistocene, when they were formed (Ginés & Ginés, 1974; Pomar et al., 1979).

4 | MATERIALS AND METHODS

A total of 117 POS samples have been collected since the 1970s when the study of these precipitates started. The sampling was done with the permission of the different institutions responsible for the conservation and protection of the islands' caves over the years (lately the 'Conselleria de Medi Ambient I Territori, Direcció General de Espais Naturals I Biodiversitat de les Illes Balears'). These samples are now part of the University of the Balearic Island (UIB) collection. The POS were sampled from 23 caves (Figure 2 and Table 1) mainly in the Miocene of the eastern part of Mallorca (Marina de Llevant). Most of the POS samples were packed and stored with the information files containing their labels, the name and location of the cave and their position (horizonal and vertical) inside of the cave. There were some cases in which the information about the sample was incomplete due to sampling difficulties (e.g., associated with deep samples obtained by speleodiving) and/or to the fact that they were taken many years ago (e.g., the POS growing on walls). These samples have been treated with caution in the interpretations.

All the hand specimens were examined in detail describing their morphology, the crystal size and their external and internal structure in sections cut longitudinally and/or transversally to the development with respect to the substrate (Figure 1c). This information was used to establish a first characterization encompassing all principal macroscopic characteristics and also to select the best samples for petrographic study. One hundred and two samples were selected to make thin sections, and except for eight samples without a clear orientation, all of them were done from the previously polished longitudinal or transversal sections (see Figures 4 and 6) and most of them include the contact with the pre-existing speleothem. The focus on the inner area of the POS is to ensure the correct interpretation of their orientation; however, it has limited the amount of information on the external parts of them. A Carl Zeiss Jena (JENAPOL model) binocular petrographic microscopy was used. The thin sections were made in the General Research Support Service (SAI) of the University of Zaragoza.

A total of 64 samples were studied by X-ray diffraction (XRD) in order to determine their mineralogical composition: very HMC (Mg > 11%), HMC (Mg > 4%), LMC (Mg < 4%) and/or aragonite. These samples were analysed by a Bruker D8-Advance X-ray diffractometer at the University of Balearic Islands, with 40 kV voltage, 40 mA current, CuKα radiation and the XRD patterns were acquired using the Diffrac Suite EVA v. 4.4 software.

5 | RESULTS

The need for more detailed studies based on the mineralogical, morphological and crystallographic characters of the POS, together with the location in the interior of the cavities, was evidenced in previous works, and a thorough description of these characters is presented in this section. Due to their large morphological variability in hand specimens (not observed in common speleothems) and the important variety of crystalline fabrics and mineralogy in thin section, a classification of the specimens studied here is also proposed.

5.1 | POS mineralogy, bedrock location and height above sea level

The mineralogical analyses carried out by XRD on 64 of the studied POS samples, together with the results from previous works (Ginés, 2000; Ginés, Ginés, Fornós, Tuccimei, et al., 2012; Tuccimei et al., 2011) and the extrapolation of these results to samples located in the same cave with equal aspect, morphology and crystal fabric, provide a total of 80 samples (out of the 117) with detailed mineralogical information (Table 1 and Figure 3).

- 41 of the 80 samples mineralogically analysed are formed only by LMC, and they are located in caves on the miocene materials (Figure 3b);

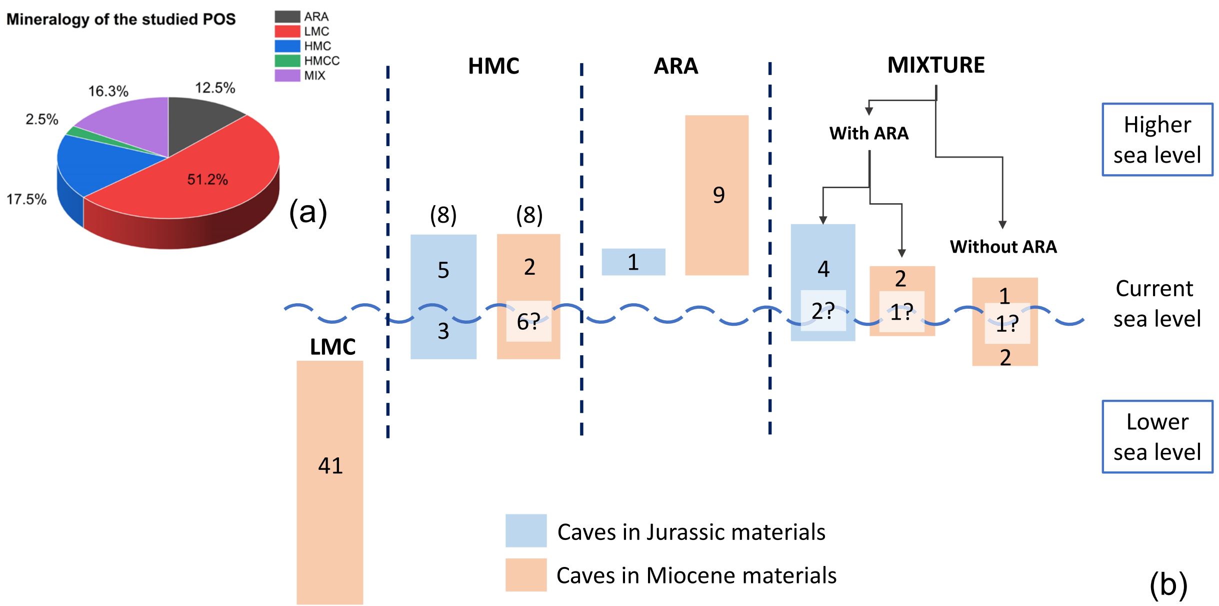

FIGURE 3 (a) Mineralogy of the studied POS samples ($n = 80$). ARA, aragonite; LMC, low-Mg calcite; HMC, high-Mg calcite; HMCC, high-Mg calcite with more than 11% Mg; MIX, mixture of these mineralogies. (b) Schematic summary of the number of samples associated to different mineralogies, their position above or below the current sea level and the materials in which the caves are carved. The question mark besides some numbers indicates the lack of information on the position of those samples in the caves.

- 16 samples are formed only by HMC (Figure 3b), and they appear in caves from both the miocene (eight samples) and the jurassic materials (eight samples);
- 10 samples are formed only by aragonite, and except for one found in jurassic rocks (Figure 3b), the rest have been found in caves located in miocene materials; and
- the 13 remaining samples are formed by a mixture of these mineralogies, although the most common combination is aragonite and LMC, and they have been found in caves located in jurassic and miocene materials (Figure 3b).

Based on the relations extracted from the study of the morphological characteristics in hand-size scale, another eight samples were assumed to be composed by aragonite and 29 by calcite. In summary, these results indicate that the studied POS are mainly composed by LMC and aragonite. This contrasts with the results from Ginés (2000) and Ginés, Ginés, Fornós, Tuccimei, et al. (2012) who reported HMC as the principal mineralogy in their study performed on a small number of POS samples.

Another important finding in this study is the location of the POS in the caves with respect to the current sea level (Figure 3b). The pure aragonite samples are located above the present sea level, and in the case of the samples with replacement of aragonite by calcite (observed in thin sections), three of them appear 14 m (and more) above that level, and the other one is related to the present sea level. On the other hand, the calcite POS samples can appear above and below the present sea level; however, the samples with some aragonite (related to replacement or with changes in the mineralogy associated with two different growth stages), but dominated by calcite, appear either with positive heights or at the current level of the sea. These locations are consistent with previous works based on a limited number of samples (Csoma et al., 2006; Ginés, Ginés, Fornós, Tuccimei, et al., 2012; Pomar et al., 1976).

5.2 | Hand-size characterization

The first hand-size characterization and classification of POS were made by Ginés and Ginés (1974) and Pomar et al. (1976), who differentiated three groups based on their surface morphology: (1) smooth, (2) rough and (3) angular-cracked surfaces. In both works, Group 1 is associated with aragonite crystals and Groups 2 and 3 to calcite crystals. In the study presented here, additional criteria were applied (Figure 4): (a) the external shape of the POS, which is conditioned by the type of substrate from which they grow, and (b) their external and (c) internal texture.

The shape of the POS around the previous substrate, although not very helpful for genetic differentiation, gives a useful information to understand the evolution of the cave. There is also a limitation in the application of this criteria because in several cases, only fragments of the POS are available and/or the written information about the sampling does not exist. In those cases, the reconstruction of the previous substrate has been impossible. Based on the available data and considering this criterion, three different groups have been separated according to their shape: (1) ellipsoid, (2) spherical or hemispherical and (3) stripe (Figures 1b, 4 and 5a,b).

1. The *ellipsoid* forms are thicker in the central zone and progressively thinner upwards and downwards. This morphology is associated with the ideal description of POS because it indicates the maximum, the minimum and the mean sea level, as described in Section 2 (Figure 1b).

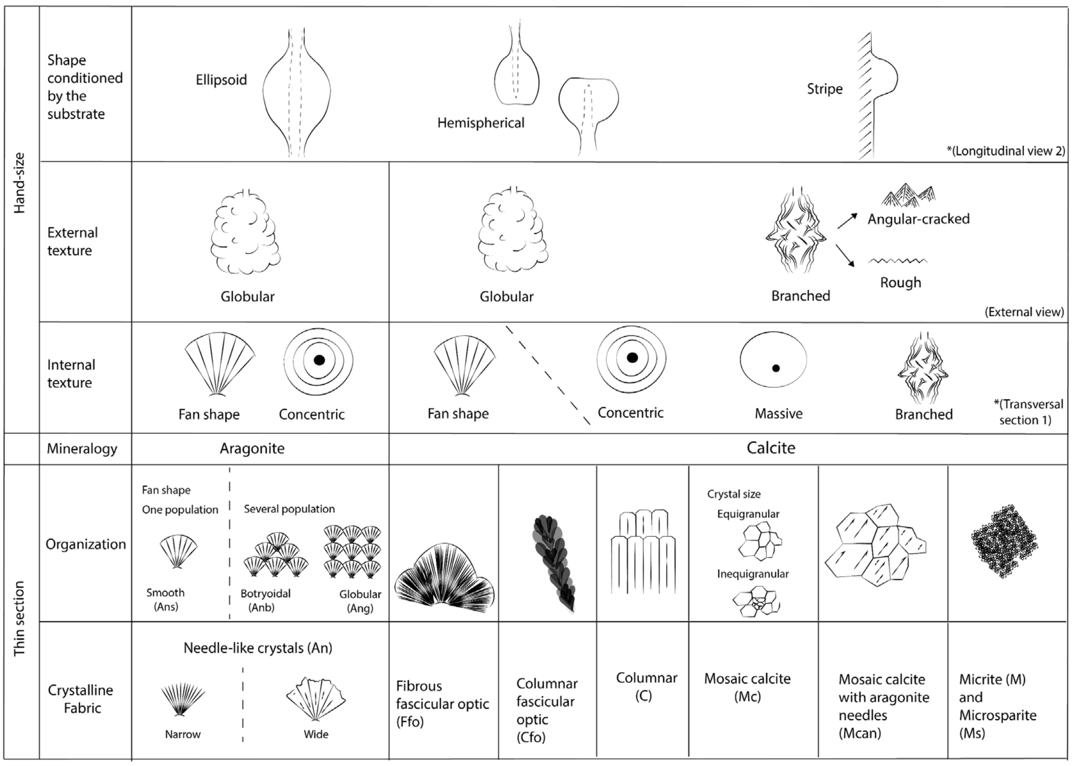

FIGURE 4 Macro-scale and micro-scale classification proposed here for the POS. *Refers to Figure 1c.

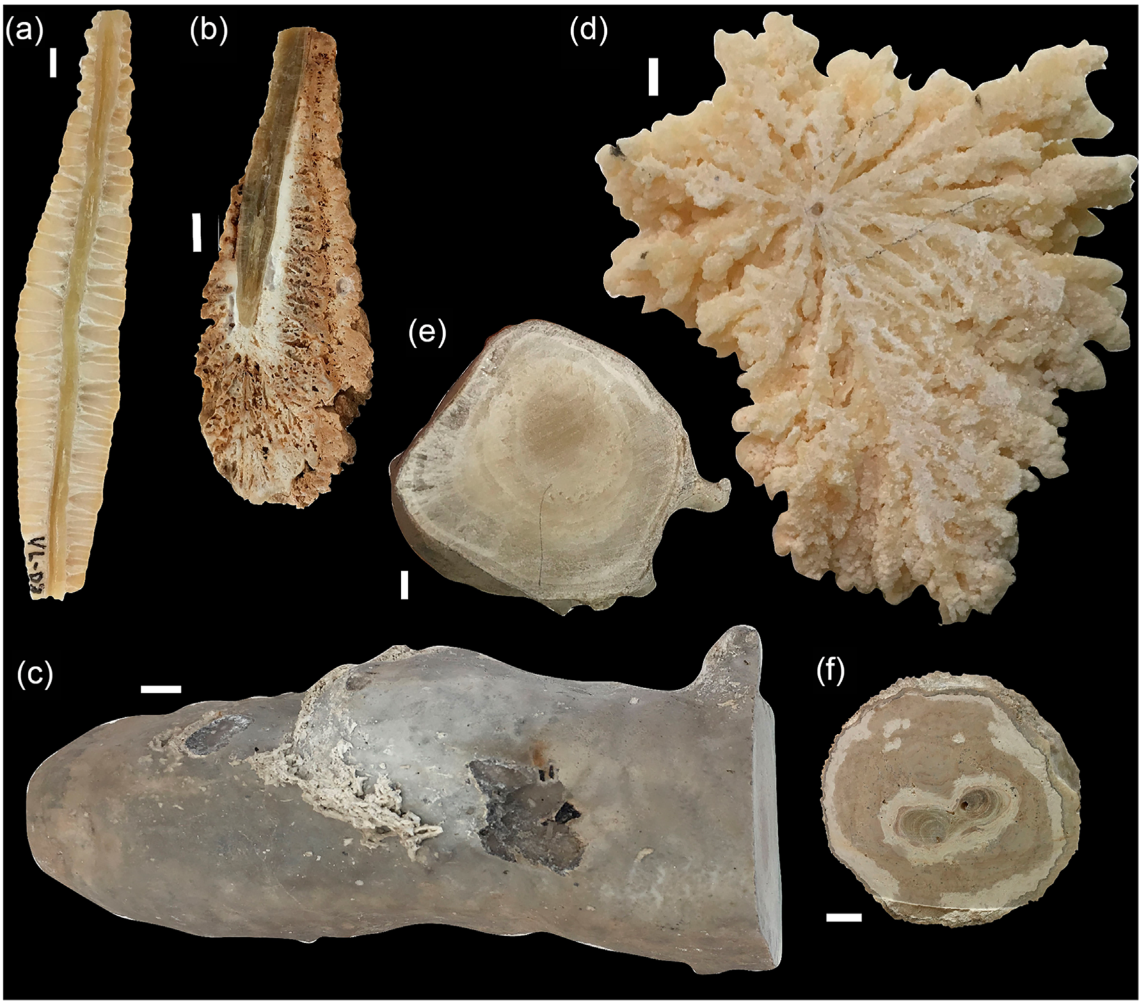

FIGURE 5 (a–c) Longitudinal and (d–f) transversal sections of some POS hand samples. (a) Longitudinal section of sample VL-D1 showing an ellipsoid morphology around a stalagmite; (b) sample PS-D1 in a longitudinal section with a hemispherical morphology around a stalactite; (c) exterior view of sample DR-D1 showing a globular external texture; (d) sample GL-D5 in a transversal section and perpendicular to the previous stalactite; the typical branched external and internal texture (with angular-cracked aspect) can be clearly seen in the photograph; (e) sample DR-D1 in a transversal section presenting a concentric internal texture growing on a stalagmite; and (f) sample BA-2, with a massive internal texture, growing up on a stalactite.

2. The *spherical or hemispherical* morphologies develop the central thicker part but grow only in one of the directions, either upwards or downwards. This morphology grows in the cases in which the substrate of the POS are short stalagmites or stalactites. If it is a short stalagmite that does not reach the height of the maximum tide, the POS does not grow upwards, and if it is a short stalactite that does not reach the minimum of the tide, the lower part of the ellipsoid does not develop (Figure 1b).
3. The *stripe* morphology is usually related to POS growing from walls with a vertical cross section of a half ellipsoid or from other special structures that can give other irregular forms (Figure 1b).

According to the criterion of the external texture of the POS, two general groups have been described (Figures 4 and 5c,d):

1. The first group is characterized by a *globular* appearance with smooth surfaces (Figure 5c,e) on which the crystals cannot be differentiated, and it is usually related to aragonitic mineralogy although some aragonite crystals may appear replaced by calcite. This group corresponds to the ‘smooth morphology’ type proposed by Ginés and Ginés (1974) and Pomar et al. (1976).
2. The second group shows a clear differentiation of crystals which grow in *branches* from the previous support to the open space and leaving spaces among them. The crystals are well developed and can be either angular cracked (with millimetric size; Figure 5d) or rough (with micrometric size; Figure 5b), as suggested in the classifications of Ginés and Ginés (1974) and Pomar et al. (1976).

The final criterion used in the hand-size classification is based on the internal texture of the POS. This has been evaluated in polished transversal sections (see scheme in Figure 1c and photographs in Figure 5) which show the appearance of the samples to the naked eye in terms of their texture and/or mineralogy. As this criterion was not evaluated by the previous authors, a specific systematization is suggested here (Figure 4). Four different types have been distinguished in the studied samples: (1) concentric, (2) fan-shaped, (3) massive and (4) branched (Figures 4, 5d–f and 6).

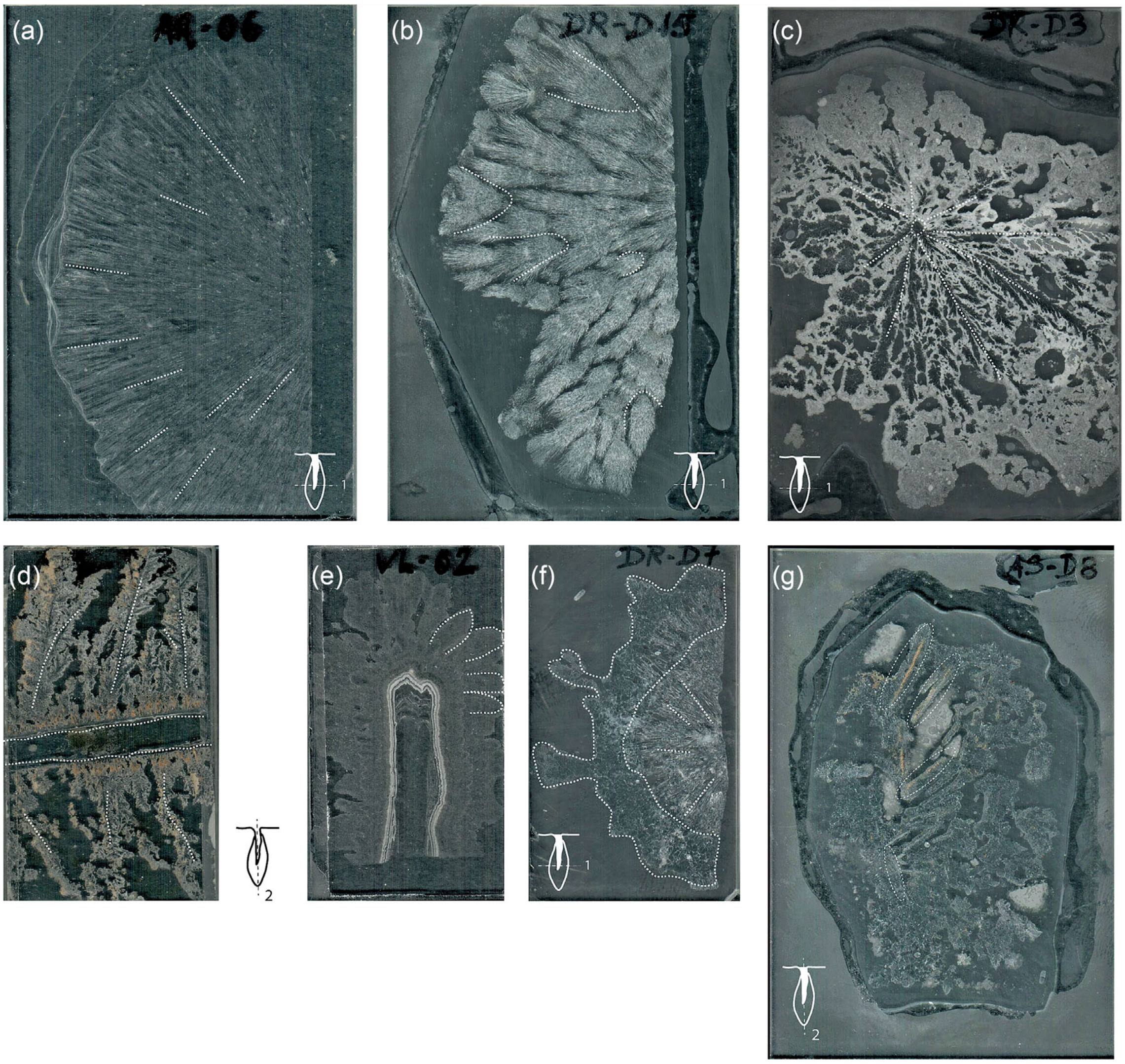

FIGURE 6 General view of some thin sections showing some details of the POS internal appearance and their relation with the previous substrate. The small schemes of the lower corners are in reference to the Figure 1c. The size of sections (a)–(c) is 5.2 × 7.5 cm, and for sections (d)–(g), it is 2.7 × 4.7 cm. (a,b) Samples AR-06 and DR-D15, both formed by needle-like aragonite crystals with fan-shaped internal texture to the naked eye; in the classification used for the fabrics, the first one shows only a population of fans, and it is considered smooth (Figure 4), while the second shows several populations of fans in a botryoidal organization; (c) sample DR-D3 (see also Figure 5d) with a branched internal texture; the original stalactite is shown by the black dotted circle in the centre, and the dotted lines show the axes of the branches; (d) sample PS-D3 also showing a branched internal texture with the axes of the branches in dotted line and the position of the previous stalactite on which the POS grows (two horizontal dotted line); the brown areas represent accumulations of detrital material (see Section 5.3.3); (e) sample VL-02, formed by columnar fascicular optic calcite crystals (delineated by dotted lines); (f) sample DR-D7, with two different areas, the internal one is formed by needle-like aragonite crystals with fan-shaped texture and the external one by calcite crystals with massive/branched internal texture; and (g) sample AS-D8, with a branched internal texture and showing the presence of calcite rafts (dotted ellipse) with random orientation.

1. In the *concentric* type, there are layers growing from the surface of the original support towards the outside (Figure 5e).
2. The *fan-shaped* appearance shows layers of crystals growing in fans from the previous support competing for the space (Figures 5a and 6a,b).
3. The *massive* appearance does not show visible crystals or internal structure (Figure 5f).
4. The *branched* appearance is formed by calcite crystals growing in all directions; sometimes, the crystals can be clearly differentiated by naked eye (Figures 5d and 6c,d,g).

The first three types (concentric, fan-shaped and massive) are usually found in the POS with a globular and smooth external texture, and therefore, they are mainly associated to aragonite (also to calcite in the case of massive texture). The branched internal texture is usually seen in samples that also have a branched external texture (Figures 5c and 6c,d,g).

5.3 | Thin-section characterization

The characterization of the 102 thin sections of POS presented here has been based on the scheme proposed by Frisia (2015), Ginés (2000) and Ginés, Ginés, Fornós, Tuccimei, et al. (2012). Frisia (2015) provides the most complete classification of calcite crystalline fabrics in common speleothems, while the others synthesize results from a few POS studied using hand specimens and thin sections.

Like in the previous studies, the first differentiation presented here is based on the POS mineralogy. Then, the different crystalline fabrics found in each group have been described and categorized.

5.3.1 | Aragonite POS

The typical crystal fabric of the aragonite POS is formed by crystals elongated along the *c* axis and perpendicular to the substrate they grow from (stalactites, stalagmites, walls, among others). These crystals show a fan organization from the centre outwards and present an undulatory extinction. This fabric has been reported in previous works about POS and common speleothems, and in most of the cases, the authors have differentiated two groups according to the specific crystal morphologies. Some of these works are the following: (1) Pomar et al. (1976) described fibrous and needle-like aragonite crystals in his work about the crystalline characteristics of some POS, (2) Ginés (2000) includes them all in his term 'needle-like' (Table 2), (3) Csoma et al. (2006) called them acicular aragonite crystals in a study of mixed speleothem deposits, (4) Frisia and Borsato (2010) described this fabric in common speleothems as crystals with a length/width (L/W) ratio higher than 6:1 distinguishing between 'ray and acicular' crystals and (5) the same two types were also reported by Perrin et al. (2014) in the speleothems of a French cave. Other authors use different terminologies like 'needle and prismatic or acicular' aragonite (Frisia et al., 2002; Wassenburg et al., 2016, respectively), 'needle and columnar' aragonite (Duan et al., 2012), 'fibrous and elongated' aragonite (Zhang et al., 2014) or just 'acicular fabric' in general terms (Alonso-Zarza et al., 2018; Martín-García et al., 2009, 2014, 2019; McMillan et al., 2005; Rossi & Lozano, 2016; Turgeon & Lundberg, 2001).

Two groups have also been distinguished in the samples that show this fabric in the set of POS studied here, but their specific characters are different from what was indicated by previous authors: (a) samples with wide crystals characterized by a L/W ratio between 6:1 and 900:1 (lengths between 16 and at least 50 mm and widths between 0.06 and 0.01 mm; Figures 6a and 7a,b) and (b) samples with narrow crystals characterized by L/W ratios higher than 900:1 (lengths between 12 and 40 mm and widths between 0.0125 and 0.005 mm; Figures 6b and 7c,d).

In both cases, the crystals show a fan organization with one or several populations. The cases formed by one population (one fan) have a smooth aspect (Ans; Figures 4, 6a and 7a,b), and the cases formed by several populations (several layers of fans) can either not show any specific organization (botryoidal shape, Anb; Figures 4, 6b and 7c,d) or grow organized on top of each other (globular shape Ang; Figure 4). Ginés (2000) did not differentiate between narrow and wide crystals instead he named the needle-like fabric organization as 'smooth' or 'botryoidal' for aragonite crystals and as 'globular' for fibrous calcite crystals (Table 2).

The POS characterized by this needle-like aragonite crystalline fabric (21 thin-section samples) usually show a globular external texture and a concentric and/or fan-shaped internal texture (Figures 4 and 5a,b).

5.3.2 | Calcite POS

The variety of fabrics found in the case of POS formed of calcite is larger than what was seen in the aragonite POS (Figure 4):

- Fibrous fascicular optic calcite (Ffo)

TABLE 2 Equivalences between the previous crystalline fabric classification of common speleothems proposed by Frisia (2015) and of POS proposed by Ginés (2000) and the classification used here.

	Common speleothems	POS crystalline fabrics			
Mineralogy	**Frisia (2015)**	**Ginés (2000)**		**This work**	
Aragonite	—	Needle-like/fibrousial and parallel	Smooth Globular Botryoidal	Needle-like (An)	Smooth (Ans) Globular (Ang) Botryoidal (Anb)
Calcite	Columnar fascicular optic (Cfo)			*Fibrous fascicular optic (Ffo)*	
		Elongated		Columnar fascicular optic (Cfo)	
	Columnar (C) Columnar open (Co) Columnar elongated (Ce) Columnar with lateral overgrowth (Ce_{lo}) Columnar radiaxial (Crf) Columnar microcrystalline (Cm)			Columnar (C)	
	Mosaic calcite (Mc)	Isometric		Mosaic calcite (Mc)	*Massive* *Branched*
	Mosaic calcite with aragonite needles (Mc_{an})			Mosaic calcite with aragonite needles (Mc_{an})	
	Micrite (M)	—		Micrite (M)	
	Microsparite (Ms)	—		Microsparite (Ms)	

Note: The names in italics and shaded in the column with the classification proposed for the POS studied in this work indicate no equivalence with previous terms in Frisia (2015) and Ginés (2000). The classification terms suggested by the previous authors that have not been found in the POS studied here have not been included in the table (term 'elongated' from Ginés, 2000 and terms 'dendritic' and 'replacive microsparite' from Frisia, 2015).

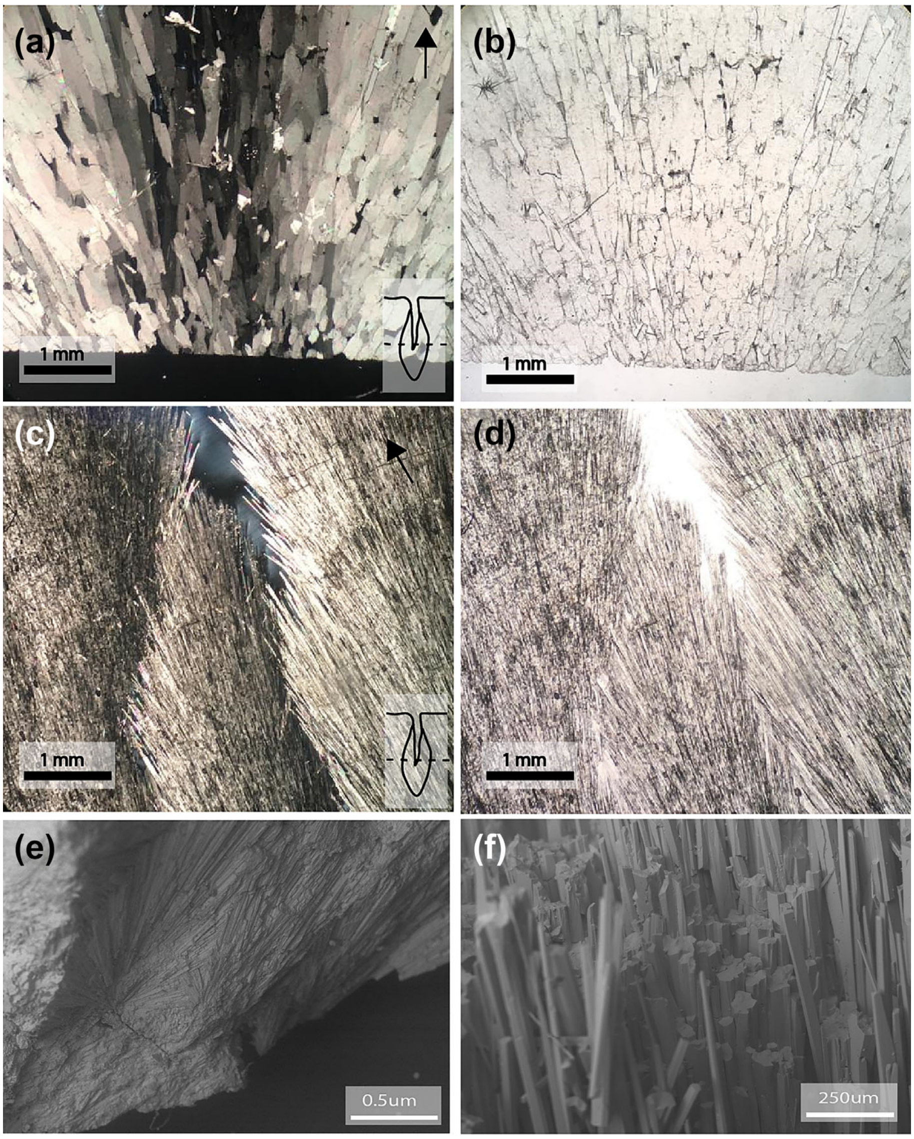

FIGURE 7 Thin-section photomicrographies and SEM images of POS samples with different aragonite fabrics. The black arrows in the upper right corner of (a) and (c) indicate the growth direction of the crystals and the small schemes in the lower right corner show the orientation of the thin sections with respect to the entire POS (see Figure 1c). (a,b) Sample AR-06 (see also Figure 6a) under crossed polarized light (XPL) and plane polarized light (PPL), respectively; they show one fan of wide aragonite needle-like crystals (An) and, as the section is not perfectly parallel to the fan growth, the complete longitudinal development of the needle-like crystals cannot be appreciated; (c,d) sample DR-D15 (see also Figure 6b) under XPL and PPL, respectively; they show an example of several fans of narrow aragonite needle-like crystals (Anb) whose terminations can be observed in the SEM image shown in (e) and (f); and (e,f) SEM image of sample BA-2 (see also Figure 5f) showing the fan-shaped organization at a different scale.

Calcite crystals with undulatory extinction, downward concave curvature of cleavage and divergent C axes. The crystals are elongated along the *c* axis with a L/W ratio >6:1. They grow perpendicular to the substrate with a fan organization from a nucleation point (Table 2 and Figure 8a,b) in what is considered by many authors a spherulitic growth (Frisia, 2015; Frisia et al., 2022; Mercedes-Martín et al., 2022; Nindiyasari et al., 2015). Ginés (2000) and Ginés, Ginés, Fornós, Tuccimei, et al. (2012) classified this fabric in POS as fibrous radial calcite (Table 2), and Frisia (2015) used the term columnar fascicular optic in common speleothems. Due to the similarities in morphology, extinction and type of growth between the fabric in the POS studied here, and the detailed petrographic description reported in Frisia (2015), the final decision has been to classify them as fascicular optic calcite (Ffo) although the word 'fibrous' (as in Ginés, 2000; Ginés, Ginés, Fornós, Tuccimei, et al., 2012) has also been added to differentiate this fabric from the next (while both have the same name according to Frisia, 2015; see Table 2).

Only 3 of the 102 studied thin sections show this fabric, and it is associated with other calcite fabrics such as columnar and mosaic (C and Mc). The three samples with this fabric show a fan-shaped internal texture and a globular external texture (Figure 4).

- Columnar fascicular optic calcite (Cfo):

Calcite crystals with undulatory extinction, downward concave curvature of cleavage and divergent C axes. The crystals are elongated along the c axis with a L/W ratio >6:1 like the one characteristic of the previous fabric, but in this case, they grow in palisade rather than in fan organization (Table 2 and Figures 6e and 8c,d). This palisade is perpendicular to the substrate on which the crystals grow. The term suggested here for this fabric, as mentioned above, is the one proposed by Frisia (2015) 'columnar fascicular optic fabric' in the classification of common speleothems (Table 2). Ginés (2000) did not consider this fabric in the classification of POS.

This fabric has been found in the studied POS associated to the same calcite fabrics as the previous one, columnar and mosaic (C and Mc). There is not a specific type of external and internal texture characteristic of these samples (Figure 4).

- Columnar calcite (C):

Calcite sparitic crystals, with uniform extinction, elongated along the *c* axis with a L/W ratio <5:1 (in common speleothems is <6:1). The crystals grow perpendicular to the underlying substrate and parallel to each other in a competitive scheme which gives them a columnar aspect (Figure 8e,f). This fabric is organized in layers but appears only in some areas of the entire POS (not forming the whole deposit as in

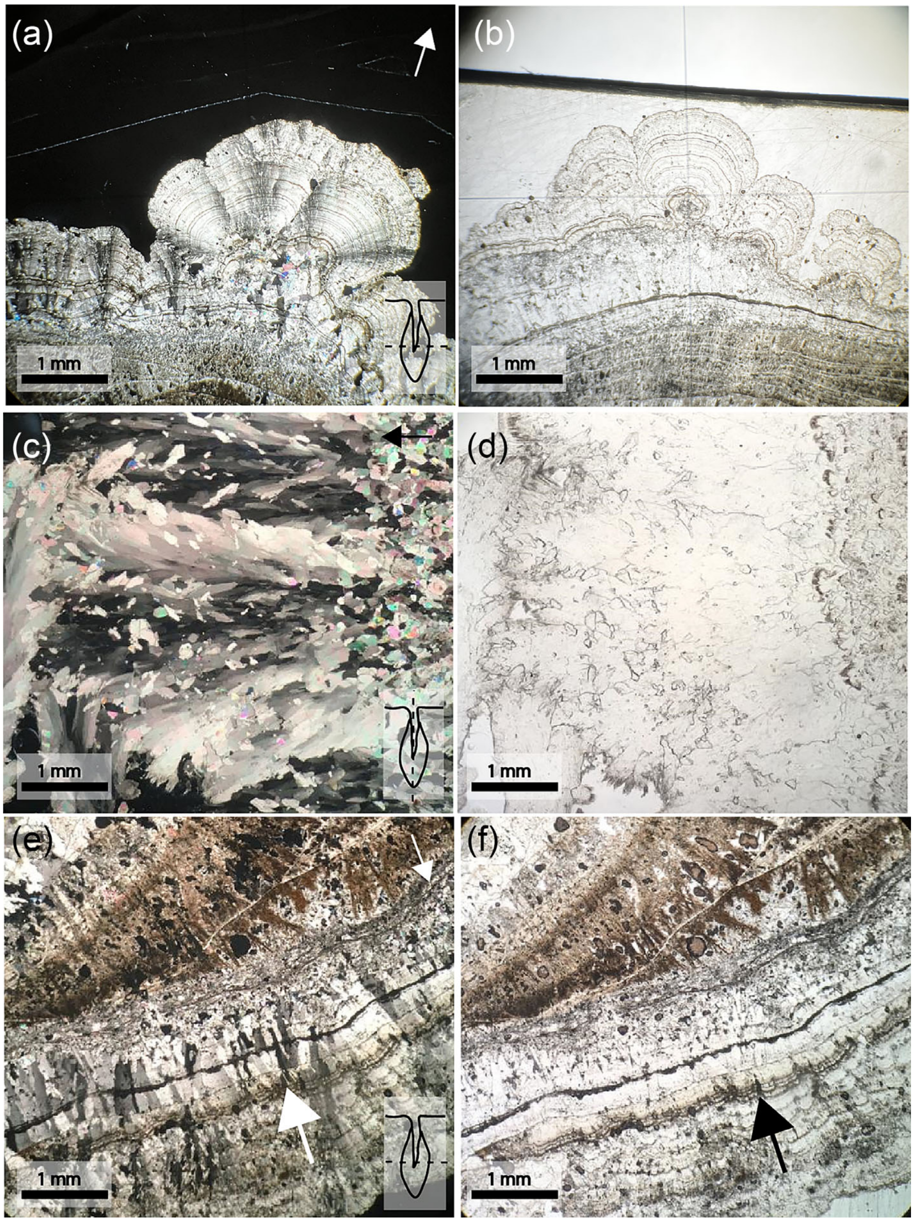

FIGURE 8 Thin-section photomicrographies of POS samples with different calcite fabrics. The arrows in the upper right corner of (a), (c) and (e) indicate the growth direction of the crystals and the small schemes in the lower right corner show the orientation of the thin sections with respect to the entire POS (see Figure 1c). Each row corresponds to a sample observed under PLX (left) and PPL (right). (a,b) Sample VB-D2bis: fibrous fascicular optic calcite fabric (Cr), (c,d) sample GE-D8: columnar fascicular optic fabric (Cfo) and (e,f) another detail of sample VB-D2bis in this case characterized by columnar calcite (C; arrow).

the case of the common speleothems) that show an optical crystallographic continuity and a uniform optical extinction.

This fabric was not considered in the POS classification of Ginés (2000), but it is mentioned in the classifications for common speleothems. Frisia and Borsato (2010) and Frisia (2015) proposed a great variety of fabrics within this columnar type (columnar open, columnar elongated, short columnar, among others; see Table 2). The variations in length, width and/or morphologies in the POS samples studied here are very subtle, and therefore, all the cases have been categorized as columnar (C) fabric in general.

As reported by many authors all over the world, this columnar fabric is the most frequent in common speleothems (e.g., Csoma et al., 2006; Fairchild et al., 2010; Folk & Assereto, 1976; Frisia et al., 2000; Perrin et al., 2014; Turgeon & Lundberg, 2001; Wassenburg et al., 2016), but it is not so frequent in POS.

In the POS studied here, this crystal fabric is usually found in samples whose hand specimen is incomplete and cannot have a clear classification. However, it seems to appear only in some specific areas and always mixed with others crystal fabrics.

- Mosaic calcite (Mc)

It is a fairly common fabric in all kinds of speleothems, including POS. It is formed by calcite crystals without a preferential orientation (Frisia & Borsato, 2010), and each crystal is in contact with, at least, another three (Figures 9a,b and 10a–d) with sizes between 30 μm and 1 cm (Frisia, 2015). The crystals can be euhedral or subhedral with plane intercrystalline boundaries and with no inclusions or remnants of previous crystals. This fabric could be considered as the 'isotropic fabric' in the classification from Ginés (2000). Previous works in Santa Catalina cave (Cuba; Bontognali et al., 2016; De Waele et al., 2018) described this fabric in a 'mushroom cap' (synonym of POS deposits) as calcite aggregates with a branched organization. It has also been described as mosaic calcite by Frisia and Borsato (2010), Frisia (2015), Wassenburg et al. (2016) and Alonso-Zarza et al. (2018) in common speleothems.

The mosaic calcite fabric has been found in the POS samples with branched external texture (angular cracked or rough, depending on the crystal size; Figure 4) and branched or massive internal textures.

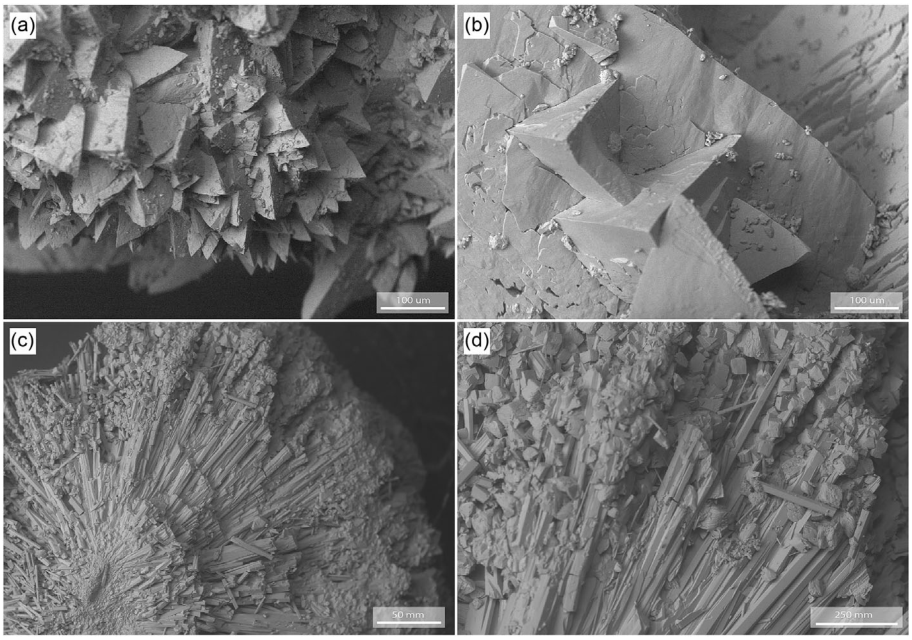

FIGURE 9 SEM images of POS samples with different calcite and aragonite crystals. (a) GE-D8 (see also Figure 8c,d): rhombohedral calcite crystals, (b) AS-D7: rhombohedral calcite crystals, (c) sample DR-D15 (see also Figures 6c and 7c,d): needle-like aragonite crystals replaced by rhombohedral calcite crystals and (d) detail of sample DR-D15.

- Mosaic calcite with aragonite needles (Mc_{an})

This has been applied to a special kind of mosaic fabric in which there are recognizable remains of a previous needle-like aragonite fabric (Figures 6f, 9c,d and 10e,f) indicating a replacement of aragonite by calcite. This replacement process has been reported in other speleothems (Folk & Assereto, 1976; Frisia et al., 2002; Martín-García et al., 2019; Zhang et al., 2014) in which the implications in the textural and chemical characteristics are also described. However, this is the first time that this fabric has been reported in POS.

The presence of this fabric is associated to specific zones in the POS (not the entire deposit) and gives a globular external texture and concentric or fan-shaped internal texture.

- Micrite (M) and microsparite fabrics (Ms):

These are the last two fabrics described in the studied POS. The terms were used by Frisia (2015) for common speleothems (Table 2), but there are no equivalents in the classification of POS from Ginés (2000). The micrite fabric is constituted by microcrystalline calcite (<4 μm) recognized in thin section by mostly opaque, dark brown compact layers (Frisia, 2015; Frisia & Borsato, 2010) similar under plane and crossed polarized light (Figure 10g,h). The microsparite fabric is formed by slightly larger crystals (between 4 and 30 μm) organized in a mosaic also forming brown layers slightly less dark than the ones of micrite because of their larger size. Micrite and microsparite layers appear alternating with layers of sparite mosaics (see also Figure 8e,f).

As observed in common speleothems (Alonso-Zarza et al., 2018; Frisia, 2015), this fabric has been usually found associated to the needle-like fabric and located in transitional zones between calcite and aragonite fabrics and in the external parts of the POS (more susceptible to dissolution and reprecipitation processes). Micrite and microsparite fabrics have been observed in POS samples with globular external texture and concentric or fan-shaped internal texture.

5.3.3 | Special features

Some interesting additional observations have been made in the thin sections that deserve a separate description. These observations include (1) the presence of terrigenous material in some of the POS samples, (2) the presence of rafts attached to some of the POS and (3) the presence of 'triarmed crystals'.

Several of the samples studied in thin section show some infilling material adhered to the POS (Figures 6d and 11a,b). It appears as a dark material accumulated in layers in the inner and outer part and in holes or corners in the exterior of the deposits. It seems to be composed by a mixture of micritic carbonate (sometimes with microsparite crystals), silt-clay material and organic matter. The size of these layers is in general only a few millimetres thick, but they can be up to several centimetres which makes them distinguishable in hand sample. The presence of this material seems to be associated to water flows loaded with sediments.

Although not very common, some rafts have also been observed attached to the POS, locally adhered to their external zone or included inside them. The presence of rafts on POS has already been reported by Pomar et al. (1976), Ginés (2000), Vesica et al. (2000), Fornós et al. (2002) and Csoma et al. (2006) who call these formations 'floating calcite' or 'bladed calcite'. The fact that they appear attached in some specimens is the result of their more or less simultaneous precipitation. Their proximity in the surface of the water and the changes in the water level could produce their final attachment. The identification of the raft in thin section inside the POS is easy because its crystals (fans of needle-like aragonite or rhombohedral calcite; Figure 11c–f) shows a completely different orientation with respect to the specific POS growth direction (Figure 6g). In some cases, it is possible to recognize the aragonite raft replaced by calcite because there are still remains of the needle-like fabric inside.

Rafts have been located in 6 of the POS samples from four different caves. Mineralogically, three of these rafts are formed by calcite and another three by aragonite. The three calcite rafts are associated

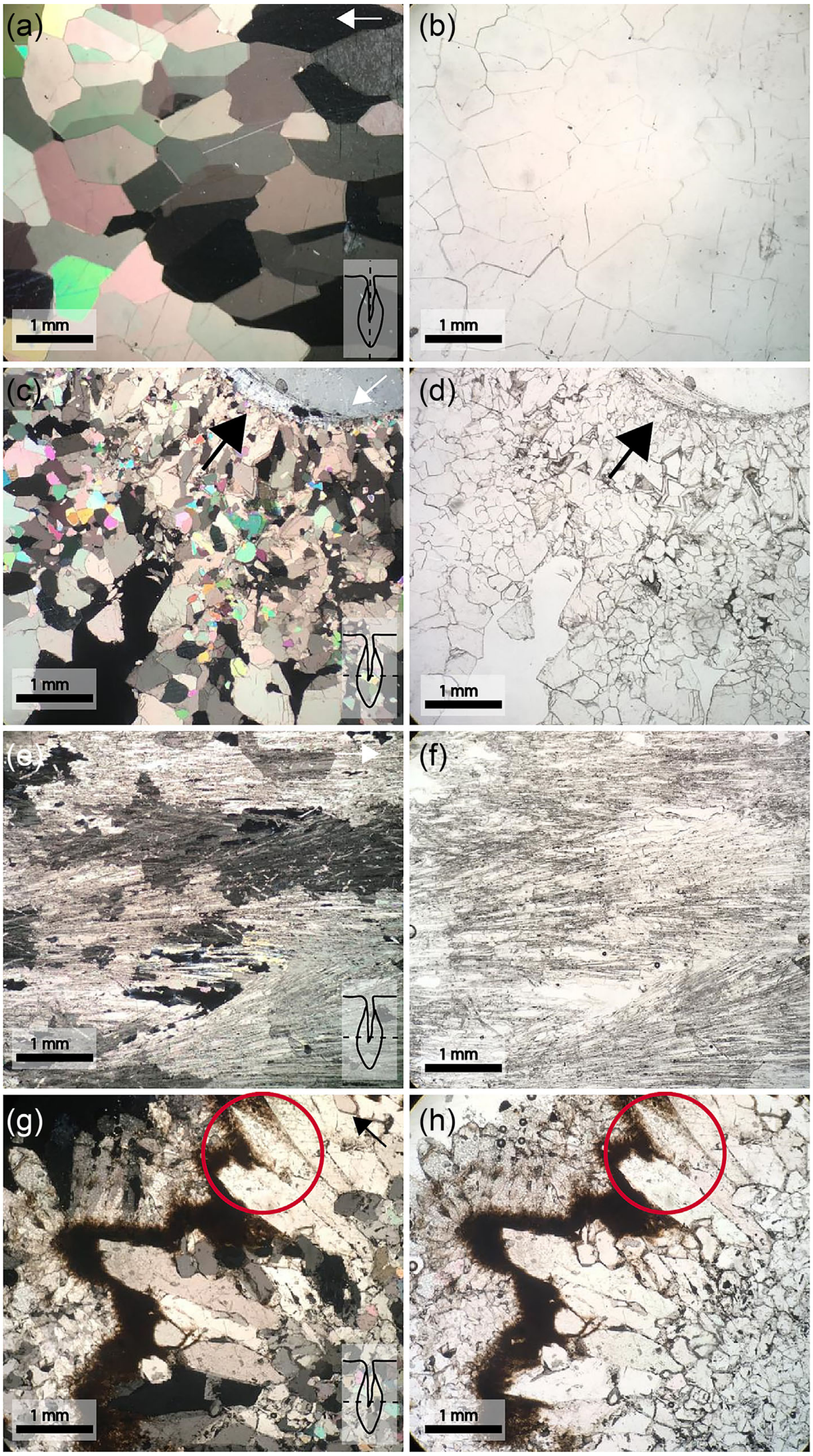

FIGURE 10 Thin-section photomicrographies of POS samples with different calcite fabrics. The arrows in the upper right corner of (a), (c), (e) and (g) indicate the growth direction of the crystals, and the small schemes in the lower right corner show the orientation of the thin sections with respect to the entire POS (see Figure 1c). Each row corresponds to a sample observed under PLX (left) and PPL (right). (a,b) Sample PS-D5 showing the mosaic calcite (Mc) fabric; (c,d) sample GL-D5: Mc with inequigranular crystals, the arrow points to the contact between previous speleothem and POS; (e,f) sample AR-07 showing a Mc with aragonite needles (Mc_{an}) and previous needle-like aragonite crystalline fabric; and (g,h) sample DR-D11 with a Mc fabric and the transformation of part of it into micrite and microsparite (M and MS), the red circle indicates the area in which the micritization process can be appreciated.

to calcite POS. Two of the aragonitic rafts appear in aragonite POS samples, and the third one is replaced by calcite, and it is associated to a calcite POS. The POS in which these raft samples have been found were located between 0 and 1.5 m above the current sea level.

The third special fabric observed in the studied POS is formed by accumulations of what is called the 'triarmed crystals' (Figure 11g–i). These calcite crystals present three arms organized in a 120° angle growing from a central point with uniform optical orientation. The thin sections of the samples where the 'triarmed crystals' have been found correspond to both, longitudinal and transversal cuts of the hand specimens, avoiding the possible confusion with a columnar fabric cut in odd angles and supporting the real presence of this type of crystal. One of the very few previous references to this fabric is from Gradziński et al. (2012), who associated this fabric with 'mammillary

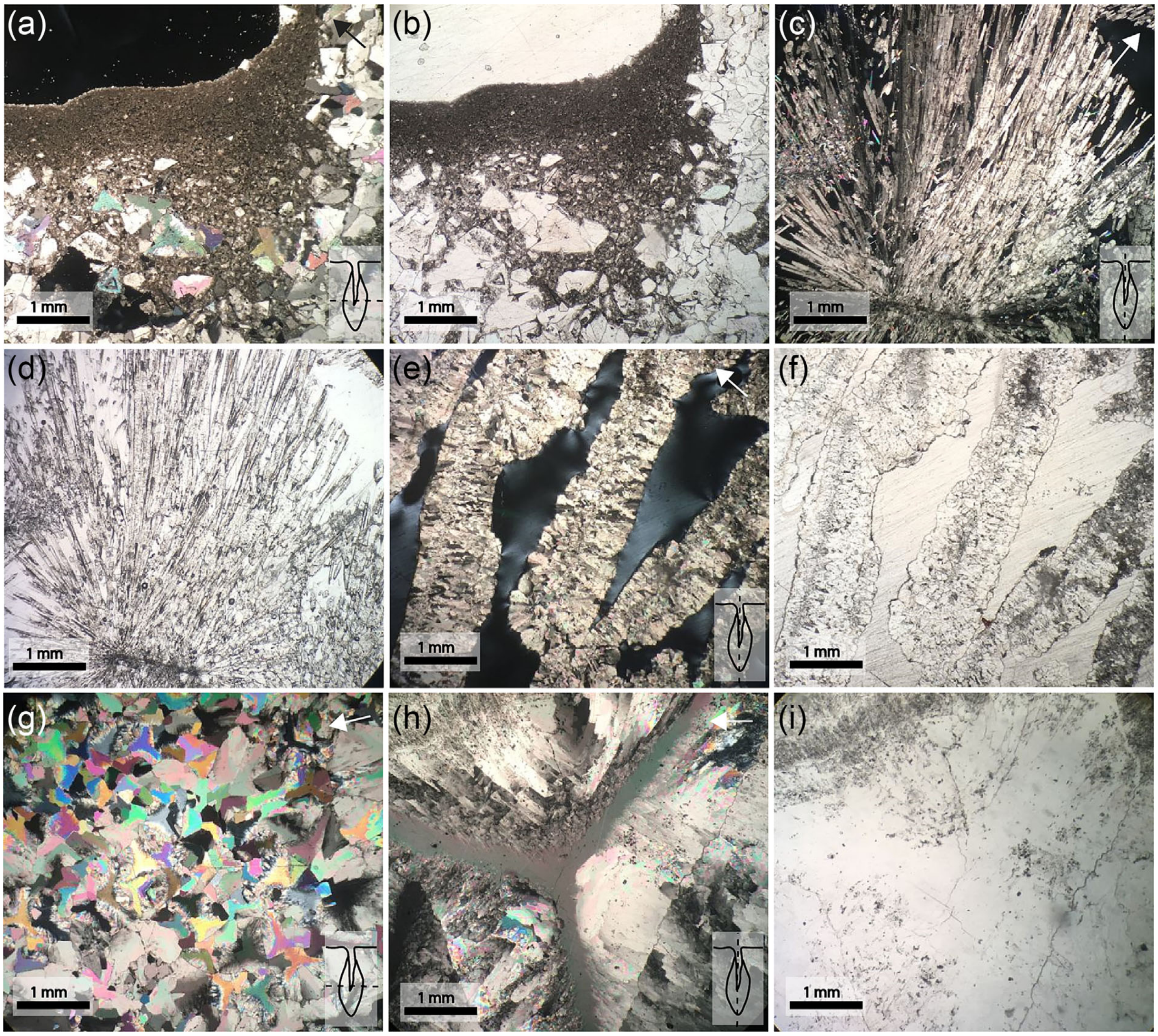

FIGURE 11 Thin-section photomicrographies of different structures. The arrows in the upper right corner of (a), (c), (e), (g) and (h) indicate the growth direction of the crystals, and the small schemes in the lower right corner show the orientation of the thin sections with respect to the entire POS (see Figure 1c). (a,b) Sample AS-D7 under XPL and PPL, respectively: accumulation of detrital black material (Figure 6d shows the same accumulations but in other sample); (c,d) sample DR-D18 under XPL and PPL, respectively: the photographs show a raft constituted by aragonite (based on their needle-like texture) in which the crystals located over the thin black layer that would be the own base of the raft, have a larger development than the ones below (see also Figure 6g); (e,f) sample TO-D4 under XPL and PPL, respectively: the photographs show several rafts made of calcite in which the thin layer from where crystals grow are easily observable (see also Figure 6g); (g) sample GL-D3 with an accumulation of 'triarmed crystals' (no PPL for this sample); and (h,i) sample CP-04 under XPL and PPL, respectively, presenting oversized 'triarmed crystals'.

sparry crust' and reported that the parallel direction of growth in these crystals present a calcite fan distribution, while the perpendicular direction presents these atypical morphologies.

A summary of the results presented in this Section 5 about the mineralogy of the POS, their location and their dominant morphologies and fabrics is included in Table S1. This information will be used in the next section as a support for the very basic interpretation of the precipitation conditions.

6 | DISCUSSION

As indicated above, the main objective of this paper is the systematic description and classification, at different scales, of the mineralogy and the different external and internal characters of 117 samples of POS deposits. The possibility of working with this important number of samples taken at different locations inside different caves and with some different characteristics, and studying them from different angles, has given the opportunity to find some relations between their characters and their possible genetic origin. Additionally, the available information on the precipitation of this kind of deposits at present in some of the studied caves has helped to relate their chemical and mineralogical characters with the hydrogeochemistry of the waters where they precipitated. There are, however, some uncertainties associated to this extrapolation because there is missing information in both sides. In the case of the old POS that have been characterized in this paper, the descriptions of their morphological, textural and crystalline characters are available, but the characters of the waters where they precipitate are unknown. In the case of the present precipitation of POS and rafts, the mineralogical and chemical characterization of the solids and the related waters are available but it is impossible to know what kind of crystalline fabric they will develop when they grow. Despite these uncertainties, this section presents the most plausible relations between the characteristics of the POS and their formation conditions.

The first finding to be highlighted is the presence of different mineralogies in the studied POS, aragonite and calcite with different Mg content (HMC and LMC). The precipitation of the two calcium carbonate polymorphs has been observed under different conditions, from typical carbonates in marine environments to those in continental environments associated with thermal springs (travertine deposits), lakes and rivers (tufas) and caves (common speleothems such as stalactites and stalagmites). What makes the POS special is that characters of marine and continental environments come together as their genesis is related to aqueous solutions that are a mixture of meteoric and seawaters. Despite the common presence of the two polymorphs and the amount of studies on the subject, it is still unclear which are the factors that control which of them precipitates (see, e.g., the thorough review from Jones, 2017). Some of the possible controlling factors include (1) CO_2 outgassing processes, (2) Mg/Ca ratio (these two are considered the most important in caves; Baker et al., 2016; Frisia et al., 2000; Martín-García et al., 2019 and references therein), (3) dissolved carbonate content, (4) temperature and (5) degree of calcium carbonate supersaturation, among others.

The need of CO_2 outgassing from the waters to the atmosphere of the cave for the precipitation of all the speleothems (including the POS) is clear, and the same can be said about the possible effects of its intensity on the precipitated mineralogy. In general, the higher the loss of CO_2 (and the increase of pH), the higher the increase in the dissolved carbonate and the most favourable precipitation of aragonite. In the case of the POS, the outgassing factor does not depend on the dripping rate as in the common speleothems but only on the variations of the CO_2 partial pressure in the recharge waters or the variations in the atmosphere of the caves. This last effect was observed in the study performed by Entrena et al. (2020) on the precipitation of POS at present in some lakes of the Drac caves, where a lower amount of precipitates and the absence of aragonite in them characterized the lakes with less ventilation and, therefore, less contrast between the pCO_2 in the waters and in the atmosphere.

Although there are several possible sources of Mg in the cave environments (interaction of the meteoric recharge with a bedrock rich in Mg—Alonso-Zarza et al., 2018; Frisia et al., 2002; Martín-García et al., 2009, 2014; McMillan et al., 2005; Perrin et al., 2014; Riechelmann et al., 2014; Rossi & Lozano, 2016; Wassenburg et al., 2016, or even Mg-rich deep-water sources—Boop et al., 2014; Merino et al., 2011; Puigserver et al., 2024), the Mg/Ca ratio in the mixed brackish lakes where the POS precipitate is mainly conditioned by the amount of seawater present in those waters (Entrena, Auqué, et al., 2024). In principle, the higher the seawater proportion, the higher the Mg/Ca ratio.

Irrespective of the Mg source, it is accepted that higher Mg/Ca ratios promote the precipitation of aragonite. However, the results observed in the studies developed by the research group of the authors of this paper (Entrena et al., 2020; Entrena, Auqué, et al., 2024) and in some laboratory experiments have shown that it is not only the Mg/Ca ratio but also its combination with other geochemical characters of the waters like, for instance, the degree of water supersaturation in calcium carbonate. For the same high Mg/Ca ratios in solution, the principal mineralogy will be aragonite if the supersaturation of the water in calcium carbonate is low (De Choudens-Sanchez & Gonzalez, 2009; Fernández-Díaz et al., 1996; Frisia et al., 2002; Martín-García et al., 2019; Zhang et al., 2014).

Assuming that the precipitation of aragonite will be favoured when the waters have higher Mg/Ca ratio, the presence of this polymorph could be related, in the case of the POS, to periods characterized by a larger percent of marine water in the mixture (in the case of the POS) and/or low availability of meteoric water (in the case of the POS and the common speleothems). Therefore, the aragonite POS could be associated to higher availability of marine water related to transgression periods. The results obtained from the POS studied here support some of these possible interpretations. All the aragonitic samples have been found at heights above the current sea level while the calcite POS were located above and below; the calcite POS with presence of aragonite have only been found above or at the present sea level. Previous studies on some of the Mallorca POS already associated the presence of aragonite POS in palaeolevels located above the current sea level to warm periods and less meteoric recharge (Csoma et al., 2006; Ginés, Ginés, Fornós, Tuccimei, et al., 2012; Pomar et al., 1976; Vesica et al., 2000). That is, periods in which the percentage of the marine water in the brackish lakes where the POS precipitate is larger.

Some additional considerations on the POS precipitation environment can be drawn based on the morphologies, fabrics and special features found in the studied samples.

Aragonite needle-like fabric (An) must be associated to stable and slow formation conditions over the time to allow the development of long crystals. Moreover, the presence of several populations in some fabrics could be interpreted as due to temporary alterations of these stable conditions. Some of the calcite fabrics can provide information about the CO_2 outgassing process. For example, the mosaic calcite fabric (Mc) must be related to a less intense and slower outgassing process that would allow the crystals to grow slowly and with larger sizes. The micrite fabric (M) would be related to high and fast CO_2 degassing ratios that provide numerous nucleation centres for small crystals competing for space. The observation of micritization processes could be indicative of either biological/organic activity (Frisia, 2015; Frisia & Borsato, 2010; Jones, 2010; Martín-García et al., 2009, 2014) or of the actuation of a condensation-corrosion process (Alonso-Zarza et al., 2011; Cañaveras et al., 2001; Folk & Assereto, 1976; Frisia, 2015; Jones, 1989; Martín-García et al., 2009, 2014). These dissolution processes in caves are indicative of a moment of pause in the growth of the speleothem (Martín-García et al., 2014). Changes in the conditions of the waters inside the cave can also be interpreted in the case of the mosaic calcite with aragonite needles fabric (MC_{an}) from environments favourable for the precipitation of aragonite to other environment that would dissolve that fabric and would promote the precipitation of calcite.

Finally, the presence of terrigenous material in a large number of POS samples provides an additional piece of information than can help to understand the climatic conditions around the caves during the precipitation of the POS. The study from Entrena et al. (2022) performed on the sediments found in Cova dets Ases concluded that they were related to a remobilization from different areas (inside or outside) due to events of important amount of water flowing inside the cave (meteoric or marine flooding events) followed by different transport and deposition mechanisms. However, the most relevant conclusion is that the presence of this terrigenous material indicates the absence of speleothem growth, and as mentioned by the authors, it would be very important in the dating/interpretation of periods without speleothem precipitation.

7 | CONCLUSIONS

A detailed description and classification of over 117 POS samples from almost all the Mallorca caves, at hand-size and thin-section scales, has been presented in this work. It emphasizes their large variability in morphology, fabric and crystalline texture compared with common speleothems (stalagmites, stalactites and flowstones). These morphological variations have been systematized in this work based on different criteria (Figure 4), and the detailed study of their crystal fabrics has given a better characterization of the specific features of POS with respect to those found in common speleothems.

This study has reported for the first time the presence in POS of some fabrics so far only described in common speleothems. They are (1) the columnar fascicular optic fabric (Cfo), (2) the columnar fabric (C), (3) the mosaic calcite with needle-like aragonite (Mc_{an}) and (4) the micrite and microsparite fabrics (M and Ms). On the contrary, some special features found associated to the studied POS are considered very rare or non-existent in common speleothems: the presence of terrigenous material adhered to the deposit, the presence of rafts attached to them and the triarmed crystals.

The very thorough study of many different characters in such an important number of POS samples, together with the conclusions obtained from previous studies of POS and rafts precipitation at present in some of the Mallorcan caves, has allowed us to establish some interesting relations. Aragonitic POS are less common than the calcite examples and preferentially precipitate on stalactites. They mainly show globular external texture and fan-shaped and concentric internal texture. Their characteristic crystal fabric is the needle-like aragonite (An) being the most common the fan-shaped organization with one population. All the aragonitic samples have been found above or at the same heights as the current sea level. They seem to be related to periods of higher sea levels probably associated to warmer climates. The calcite POS are the most common, and they precipitate on stalactites. The branched external and internal textures are, together with the mosaic calcite (Mc) organized in branches, the most common crystalline fabrics. The calcite POS studied here have been found at heights above and below the present sea level. Their location has been interpreted as related to periods of more meteoric recharge in the cave systems probably associated to cold and rainy climates.

This study evidences the differences between common speleothems and POS, at mesoscale and micro-scale, and the need to study them in more detail. The study of new POS samples from other caves in Mallorca (and in other parts of the world) will be a good test for the generalization of the systematization presented here. Moreover, the determination of their precipitation conditions in modern situations will also be a source of additional and more precise interpretations of the environmental factors that control the formation of this type of speleothems. In this way, the potential of POS as palaeoenvironmental indicators will extend further than their use as proxies of the sea-level variations.

AUTHOR CONTRIBUTIONS

Conceptualization: Ana Entrena, Luis F. Auqué, María J. Gimeno and Joan J. Fornós. *Funding acquisition*: Joan J. Fornós. *Methodology (including methodological development)*: Ana Entrena and Luis F. Auqué. *Investigation*: Ana Entrena and Joan J. Fornós. *Resources*: Luis F. Auqué, María J. Gimeno and Joan J. Fornós. *Supervision*: Luis F. Auqué and María J. Gimeno. *Writing—initial draft*: Ana Entrena. *Writing—reviewing and editing*: Luis F. Auqué, María J. Gimeno and Joan J. Fornós.

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DATA AVAILABILITY STATEMENT

All the data of the analyzed samples (cave name, height, mineralogy, precipitation place, etc.) are available upon request to the authors.

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SUPPORTING INFORMATION

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