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Black Mn-Fe crusts as markers of abrupt palaeoenvironmental changes in El Soplao Cave (Cantabria, Spain)

Fernando Gázquez¹, Jose Maria Calaforra¹ and Paolo Forti²

Abstract:

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Peculiar iron and manganese deposits coating walls, floors and ceilings of many galleries are one of the special features of the El Soplao Cave (Cantabria, Spain). These speleothems appear to have been deposited over wall clay deposits, as well as forming part of flowstones. Structure of crusts is essentially amorphous but several manganese and iron oxides were identified like goethite and birnessite, though all occur with a low degree of crystallinity. In the outer layer of the crusts, alteration iron minerals appear that derive from previous minerals in a process probably mediated by microorganisms. EDX microanalyses report fairly high values of Fe and Mn in the crusts, though the Mn/Fe ratio varies considerably as a function of distance from the substrate/bedrock. The present study proposes a genetic model for crust speleothems in El Soplao, based on oscillations of the phreatic level. The origin of these deposits is related to mobilization, under phreatic conditions, of polymetallic sulfides in the host rock. Metal ions (including Fe²⁺ and Mn²⁺) released into the cave under reducing conditions, are oxidized and fixed in a process mediated by bacteria, giving rise to oxides and hydroxides of low crystallinity. The presence of various black intercalated layers in aragonite flowstones indicate periods when cave conditions suddenly changed from vadose, when aragonite is precipitated, to phreatic and epiphreatic conditions, when the Mn-Fe deposits are precipitated. Subsequently, vadose conditions were re-established, leading to the final stages of precipitation of aragonite recorded in the flowstone and recent aragonite helictites on the surface of the Mn-Fe crusts.

Keywords: El Soplao Cave, manganese iron crust, speleothems

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INTRODUCTION

Polymetallic oxides and hydroxides are minerals frequently encountered in caves, and iron and manganese ones are especially abundant in subterranean environments (Hill & Forti, 1997). Over the last fifty years, the mineralogy, morphology and genesis of this kind of speleothems has been studied in a variety of caves (Crabtree, 1962; Moore, 1981; Gascoine, 1982; Hill, 1982; Kashima, 1983; Peck, 1986; Jones, 1992; Onac, 1996; Onac et al., 1997; White et al., 2009). In some cases, research focussed on the role of microorganisms in the precipitation of these oxides (Peck, 1986; Boston et al., 2001; Spilder et al., 2005).

Manganese, soluble in its divalent form (Mn²⁺) is oxidized to trivalent (Mn³⁺) or tetravalent manganese (Mn⁴⁺) in superficial environments at low temperature in a process that is generally mediated by microorganisms (Calvert & Pedersen, 1996; Jürgensen et al., 2004).

Oxides of Mn³⁺ and Mn⁴⁺ have a complex mineralogy and a wide range of crystalline structures (Post, 1999). The mineralogy of some manganese oxide speleothems is not easy identifiable in many cases (Looney, 1969; White et al., 2009). In few cases, the manganese minerals have sufficient crystallinity to identify them (Onac et al., 1997; Boston et al., 2001; White et al., 2009). The main manganese minerals deposited in caves are birnessite, romanechite and todorokite (Hill and Forti, 1997), though ranciéite and pyrolusite have also been identified (White et al., 2009). Also, the clay minerals are closely linked to the formation of Mn oxides and hydroxides, such as vernardite, ranciéite, birnessite and todorokite (Chukhrov et al., 1980).

Manganese oxides usually occur in caves as black crusts on walls and floors. Sometimes they form the base of speleothems, but they rarely form part of stalactites, stalagmites or flowstones (Hill & Forti, 1997). "Fossilized" layers of Fe and Mn oxides into other speleothems have only been described in a few studies (Peck, 1986; Provencio & Polyak, 2001).

This paper analyzes the chemistry and mineralogy of the manganese crusts on the ceilings and walls of the El Soplao Cave and their relation with other deposits of the cave. Mineralogical and geochemical data are presented; these enabled a model of the genesis of these peculiar speleothems to be constructed, related

¹Water Resources & Environmental Geology, University of Almería, La Cañada de San Urbano s/n, 04120 Almería, Spain (jmcalaforra@ual.es).

²Italian Institute of Speleology, University of Bologna, Via Zamboni 67, 40126 Bologna, Italy (paolo.forti@unibo.it).

to extreme changes in water level in the cave. Some of these pavement deposits has been recently analyzed (Rossi et al., 2010) with a “stromatolitic” interpretation for their genesis but no palaeoclimatic interpretation have been provided.

GEOLOGICAL SETTING

El Soplao Cave (43°17'45, 42°N - 4°26'45, 76°W) lies in the Sierra de Arnero, in the Escudo de Cabuérniga mountain range (Cantabria, North Spain). The Sierra de Arnero is a chain of mountains running parallel to the Cantabrian Coast, between the Bustriguado and Nansa valleys (municipal districts of Valdáliga, Rionansa and Herrerías) (Fig. 1).

The cave entrance is at 540 m a.s.l and it extends over 20 km length, with difference in level of barely 50 metres. The cave runs mainly NW-SE, with a secondary axis NE-SW. El Soplao has been open as a show cave since 2005. An artificial mine mouth (Isidra Gallery) serves as an entrance for touristic visits. There are also two natural cave entrances: Torca Ancha and Torca Juñosa, but access to the cave is difficult. Preliminary studies inside and outside the cave suggest other entrances to the cave may exist, which influence the microclimate dynamics and cave environment.

El Soplao Cave is excavated in Aptian rocks formed in a shallow continental platform of marine carbonates (Florida Unit). Permo-Triassic bed consists of siliciclastic conglomerate and shale. This region contains considerable metallogenic interest because of the large patches of dolomitization that have occurred in the carbonates (López-Cilla et al., 2009). Important deposits of lead and zinc sulfides (galena and spharelite) occur in the Florida mine and in the Soplao Cave itself (García-Mondéjar et al., 1996; Quesada et al., 2005). These ore minerals contain up to 320 ppm of Mn (Velasco et al., 2003).

Fig. 1. Location and geological setting of El Soplao Cave, and a plan view of a cave part. Situation of sampling points: 1, Campamento Gallery, manganese crusts on the walls and ceiling (SPL-MNC, SPL-ARA, SPL-PRO) and on the floor (SPL-FLO), 2, Pasillo de los Cubos, aragonite flowstone with layers of manganese oxide and detrital deposits (SPL-FLW-07). Cartography modified from IGME (1976); cave topography courtesy of El Soplao S.L.

DESCRIPTION OF THE SAMPLES

Samples of the black crusts were collected from the ceiling of Campamento Gallery (SPL-MNC-01). The crusts consist of 0.01 to 3 cm thick lamina that coat earlier clay detrital deposits on the walls and ceiling of the gallery. These crusts form a continuous layer over the gallery walls, though the crust has been dislodged in places, exposing the underlying detrital material. The crusts are consolidated and their surfaces are smooth (Fig. 2A), though there are some superficial marks related to capillarity flows over the surface (Fig. 3A). The convex surfaces of the cave roof often display abundant aragonite and/or calcite helictites and anthodites. These aragonite speleothems (SPL-AAR-05) are also analysed in this paper (Fig. 2B).

Ferromanganese oxides also cover the floors of the galleries. They have a marked biogenic character and display soft consistency. These sediments have also been studied by Rossi et al. (2010) and consist of sand and gravel intercalated between Mn oxide-rich layers. They were sampled (SPL-FLO-06) in order to compare them to other Fe and Mn deposits in the cave (Fig. 3B). On occasions, these deposits form the base of other calcite and aragonite speleothems (Fig. 2C).

Thirty metres away from Campamento Gallery a small passageway known as Pasillo de los Cubos can be reached (Fig. 1). This part of the cave exhibits a flowstone of intercalated aragonite and cemented detrital material (SPL-FLW-07). The final phases in the formation of this speleothem incorporated dark layers about 0.5 mm thick, which have been “fossilized” by a 5 mm-thick aragonite layer (Gázquez et al., 2010) (Fig. 2D). Detrital materials also appear covering aragonite and calcite stalactites in the Campamento Gallery (Fig. 2E).

METHODOLOGY

SEM microphotographs were taken using a HITACHI S-3500 instrument in high vacuum mode. The samples were previously dried and metalized with a 15 nm coating of Au. EDX microanalyses (energy dispersive x-ray spectroscopy) used the same instrument coupled to an Oxford INCA 7210 X-ray detector, using a voltage of 20 kV. The diameter of the beam was approximately 1 µm. The limit of detection of this technique enables major elements like Fe, Mn, O, Si, Ca and C to be analysed (Table 1). The detrital substrate in contact with the inner part of the crust was analyzed (SPL-MNC-01a and SPL-MNC-01b). Several microanalyses were performed, both in the external surface of the crusts (SPL-MNC-02a and SPL-MNC-02b) and the surface in contact with the underlying clay (SPL-MNC-03a, SPL-MNC-03b, SPL-MNC-03c and SPL-MNC-03d). Alteration minerals on the external crust surface (SPL-MNC-04a and SPL-MNC-04b) and six points through a section of the crust (SPL-PRO, 01 to 06) were also analysed. Floor Mn-Fe sediments were investigated by means of EDX (SPL-FLO-06c, SPL-FLO-06d, SPL-FLO-06e and SPL-FLO-06f). Finally, a Mn-Fe layer of the Pasillo de los Cubos flowstone was analyzed (SPL-FLW-07).

Mineral analysis using X-ray diffraction (XRD) was done at ambient temperature in a single-crystal diffractometer using a BRUKER APEX CCD area detector, modified for analysis of powdered samples.

Fig. 2. A. Crusts of Mn-Fe overlying clay deposit on the ceiling of the Campamento Gallery. B. Helictites on the ferromanganese crusts in the Campamento Gallery indicate that the crusts cannot be relatively recent formations. C. Deposits of Mn-Fe oxides covered by aragonite helictites on the wall of Campamento Gallery. D. Aragonite flowstone with intercalations of cemented detrital material derived from flood events in the Pasillo de los Cubos. The arrows point two dark layers of Mn-Fe oxides (SPL-FLW-07). E. Campamento Gallery. Aragonite stalactites coated in clay indicate flood events.

$\text{Mo}_{\text{K}\alpha}$ cathode radiation was used ($\lambda = 0.71073 \text{ \AA}$) using the ω scanning method, within angular limits $1.96 < \theta < 23.298$. This technique allows minimal quantities of samples to be analysed ($< 0.05 \text{ mg}$) but carries the disadvantage of low resolution in the resulting diffractograms. Both samples from ceiling (SPL-MNC-02) and from floor (SPL-FLO-06) were analyzed.

Quantitative chemical analysis of samples was done using X-ray fluorescence (wavelength dispersive XRF) with a BRUKER S4 Pioneer instrument. Total samples of sediments taken from the cave floor were analysed (SPL-MNC-06a and SPL-MNC-06b), along with aragonite needles that had developed over the crusts (SPL-AAR-05). All analyses were performed at the Technical Services Area of the University of Almeria (Spain).

RESULTS

Mineralogical analysis of the crusts by XRD detected various mineral phases of ferromanganese oxides, including goethite and birnessite, though all the crusts had a low crystallinity and were poorly defined in the diffractogram. Dolomite and quartz were

detected on the surface of the crusts using XRD and Fe oxide-hydroxides were also found and analysed using EDX (Table 1). The mineralogy of the floor deposits from Campamento Gallery is very similar to the ceiling crusts, with Mn-Fe oxides and some unidentified clay phases. Eventually, aluminium oxyhydroxides also appear in some floor crusts samples detected by EDX (Fig. 3C and SPL-FLO-06f in Table 1).

The major elements in the crusts from El Soplao are Mn and Fe, though the Mn/Fe ratio varies considerably depending on its distance from the host rock (Fig. 4). The chemical composition of the ferromanganese crusts varies according to the zone in which the microanalysis is done. The inner part of the crust, in contact with the detrital substrate (Fig. 3D), contains high concentrations of Si (50.2 wt%) and O (33.16 wt%), and this corroborates with the presence of quartz grains as detected by XRD. The outer crust surface contains alteration minerals with high Fe content (26.24 wt%), dolomite and detrital quartz. Microorganisms were detected on the rough surface of the crusts in Campamento Gallery (Fig. 3F).

Sr concentration is very low in the ferromanganese crusts (0.0082 wt%) (SPL-FLO-06a) compared to the analyzed aragonite helictites (0.6 wt%) (SPL-AAR-05). Zn appears in the majority of analyses in small quantities in the wall-ceiling crust ($< 7 \text{ wt\%}$), but its concentration is higher in the sediment sample taken from the cave floor (up to 23 wt%). Moreover, Co (0.133 wt%), Ti (0.8160 wt%), Pb (0.92 wt%) and

Fig. 3. Secondary electron images. A. Ferromanganese crust from the ceiling of Campamento Gallery. The white lines indicate the marks left by the condensation water flow. B. Stratification of a biogenic sediment composed on Mn-Fe oxides, which formed on the floor of Campamento Gallery. C. Aluminium oxides and hydroxides in the interior of the floor crusts. D. Clay substrate in Campamento Gallery, over which the crusts were precipitated. E. Alteration minerals (oxides-hydroxides of Fe) on the surface of a crust from Campamento Gallery. F. Bacteria on the surface of a ferromanganese crust taken from Campamento Gallery.

Table 1. Analyses of major elements. Analytical error ranges from ± 0.33 wt% for oxygen to ± 0.13 wt% for aluminium. Error in Fe and Mn measurements was ± 0.2 wt%.

Samples	O (wt%)	Fe (wt%)	Mn (wt%)	Si (wt%)	C (wt%)	Al (wt%)	Mg (wt%)	Ca (wt%)	Zn (wt%)	Mn/Fe	Sample description
SPL-MNC-01a	33.16	3.08	1.16	50.24	12.35	n.d	n.d	n.d	n.d	0.38	detrital substrate (SiO ₂)
SPL-MNC-01b	44.9	13.23	17.54	9.72	n.a	6.82	1.15	1.72	n.d	1.33	detrital substrate (clay)
SPL-MNC-02a	31.3	28.52	13.72	9.82	8	4.96	1.51	1.64	n.d	0.48	superficial crust
SPL-MNC-02b	26.84	21.65	33.35	5.68	2.97	2.87	1	2.83	1.59	1.54	superficial crust
SPL-MNC-03a	39.14	8.03	29.35	6.49	6.24	4.06	1.79	2.07	2.29	3.66	internal crust
SPL-MNC-03b	46.46	7.73	21.18	9.95	n.a	6.23	1.15	1.88	3.74	2.74	internal crust
SPL-MNC-03c	11.72	15.06	55.59	4.18	5.68	1.48	0.54	3.21	0.82	3.69	internal crust
SPL-MNC-03d	31.11	10.18	40.82	3.01	n.a	2.43	0.83	3.62	6.18	4.01	internal crust
SPL-MNC-04a	48.67	12.34	1.41	19.96	n.a	11.68	0.99	0.33	1.19	0.11	Alteration Fe minerals
SPL-MNC-04b	44.03	26.24	0.96	5.84	9.33	5.08	3.42	4.6	n.d	0.04	Alteration Fe minerals
SPL-AAR-05 ^F	n.a	0.1	0.006	5.9	n.a	n.a	1	n.a	n.d	0.06	aragonite helictite
SPL-FLO-06a ^F	30.51	13.36	14.73	7.17	n.a	10.09	0.61	2.1	4.814	1.10	Floor deposit
SPL-FLO-06b ^F	29.73	10.53	17.52	6.253	n.a	11.25	0.256	1.972	4.122	1.66	Floor deposit
SPL-FLO-06c	39.89	5.09	25.77	3.79	n.a	6.37	0.74	1.58	16.37	5.06	Floor deposit
SPL-FLO-06d	30.81	4.93	28.53	3.9	n.a	6.5	0.69	1.42	23.22	5.79	Floor deposit
SPL-FLO-06e	27.62	6.97	23.34	5.46	n.a	10.76	1.3	0.42	23.51	3.35	Floor deposit
SPL-FLO-06f	61.39	1.25	3.25	2.18	n.a	27.72	n.d	0.19	3.78	2.60	Floor deposit
SPL-PRO-01	15.91	9.73	35.11	0.94	34.11	n.d	n.d	0.33	1.98	3.61	Crust profile (1)
SPL-PRO-02	4.63	22.99	61.88	n.d	6.8	n.d	n.d	0.92	2.78	2.69	Crust profile (2)
SPL-PRO-03	14.2	12.39	42.78	0.79	27.2	0.4	n.d	0.48	1.76	3.45	Crust profile (3)
SPL-PRO-04	37.55	8.16	21.33	1.62	28.7	1.18	0.55	0.92	n.d	2.61	Crust profile (4)
SPL-PRO-05	8.42	27.96	37.08	0.6	22.38	n.d	n.d	0.54	2.22	1.33	Crust profile (5)
SPL-PRO-06	39.64	26.58	20.33	4.48	n.d	3.48	1.13	1.88	2.19	0.76	Crust profile (6)
SPL-FLW-07	45.97	4.83	11.9	6.93	n.a	3.94	1.47	10.45	14.62	2.46	Mn crust in aragonite flowstone

n.a. = not analyzed n.d. = not detected F = analyzed by XRF (Sr, Ti, Co, and Pb concentration are reported in the main text).

other transition elements (all < 0.1 wt%) were detected by XRF (SPL-FLO-06a and SPL-FLO-06b) in the floor crusts.

Aragonite needles (SPL-AAR-05), taken from the surface of the manganese crusts on the ceiling of Campamento Gallery, were low in Fe (0.1 wt%) and Mn (0.006 wt%). However, their silica content is significant (5.9 wt%); they have a similar Mg concentration to the crusts (1 wt%) and are enriched in Sr (0.6 wt%).

Data from other analysed speleothems (e.g., aragonite stalagmites) in El Soplao Cave showed negligible concentrations of Si. In contrast, Sr concentration was greater (approx. 0.4 wt%) than that obtained in the crusts, but similar to the aragonite helictites (0.6 wt%). These speleothems had concentrations of Mg (0.06 wt%), Fe (0.001 wt%) and Mn (0.0001 wt%), which were very far from the content in the Fe and Mn crusts.

Zn concentration in the black crusts that form part of the aragonite flowstone in the Pasillo de los Cubos (SPL-FLW-07) is considerably higher than in the Mn crusts on the ceiling of the cave, but similar to the floor deposits. Concentration of Mn and Fe are less than in the floor deposits analyzed and similar to the concentrations found in the ceiling crusts. In general it has been found that floor crust are enriched in Zn and depleted in Fe and Mn compared to the wall-ceiling crust.

DISCUSSION

Precipitation of iron or manganese oxides in caves depends to a certain extent on the pH of the medium. At around pH 6, precipitation of iron oxides is frequent, whilst close to pH 8.5 manganese oxides can be precipitated (Onac, 1996). Small changes in pH can cause precipitation of these oxides. At neutral pH, Fe and Mn oxides are precipitated simultaneously.

Fig. 4 shows the Mn/Fe ratio over the growth sequence of a ferromanganese crust (600 μ m thick) deposited on the ceiling of Campamento Gallery. The Mn/Fe ratio diminishes with distance from the substrate rock. This fact indicates that iron oxides predominate in the outer crust, while Mn oxides are more abundant in the inner part. Since the Mn/Fe ratio depends on the pH of the medium in which it was precipitated, it is clear that close to the carbonate host rock, high alkalinity medium, Mn oxides are precipitated, while the lower pH in the later stages of formation, led to greater precipitation of Fe oxides.

There are two possible sources of Mn and Fe in El Soplao Cave. The origin of Mn-Fe that gave rise to formation of the crusts in El Soplao could be linked to mobilization of these metals from polymetallic sulfide mineralizations in the host rock. The phreatic conditions, when the cave was submerged under aquifer water, led to mobilization of these elements. Such a process is only possible in an anoxic medium,

Fig. 4. Mn/Fe ratio (wt%) through the stratigraphic sequence of a ferromanganese crust in Campamento Gallery. The Fe/Mn ratio is higher close to the substrate and diminishes towards the exterior. The Mn/Fe ratio is related to the preferential precipitation of oxides of Fe or of Mn, as determined by the pH of the medium (see text).

when Mn is in its reduced state (Mn^{2+}) (Calvert & Pedersen, 1996; Jørgensen et al., 2004). On the other hand, dissolution of dolostone host rock (Fig. 5A), rich in Mn-Fe (0.2 and 1.5 wt% respectively, Bustillo et al., 1992) under anoxic conditions, is a significant source of Mn and Fe that is released into the aquifer water.

During other periods, the cave was partly submerged. Due to massive inflow of water into the cave, the flow regime became turbulent (Fig. 5B) and carried large amounts of detritus in suspension. This material was later deposited in different parts of the cave. Evidences of these flood events inside El Soplao Cave are documented by following observations: while aragonite stalactites in some parts of the cave are white, those in Campamento Gallery are covered in clay and detrital deposits (Fig. 2E). Further evidence of old torrential flows is seen in the aragonite flowstone in the Pasillo de los Cubos, where detrital material has been trapped and fossilized between aragonite layers (Gázquez et al., 2010) (Fig. 2D).

Suspended solids were deposited on the cave walls, ceilings and speleothems when the flow energy decreased (Fig. 5C). During this phase, clays were adhered to the cave surfaces and decanted, serving as substrate for the formation of the Mn-Fe crust in Campamento Gallery and in the flowstone in Pasillo de los Cubos (Fig. 2D). The relatively high concentration of Mn (17.54 wt%) and Fe (13.23 wt%) in the clay substrate on which the crusts deposited conform our above scenario.

In our model we propose that, unlike the crust of Pasillo de los Cubos, in Campamento Gallery Mn and Fe are exuded from the clay and gives rise to ceiling and wall crusts in El Soplao. Under epiphreatic aerobic conditions, metals are oxidised on the surface of the clay, in a process that could be mediated by microorganisms (Fig. 5D) and ionic exchange at the water-clay interface. In the case of the crusts on the walls and ceiling of Campamento Gallery, condensation may have played a fundamental role in the oxidation of Mn and Fe. The surface of these crusts shows irregularities, which document the vertical downward water flow that favoured the oxidation and subsequent precipitation of Mn-Fe oxides.

Microbial involvement in the precipitation of Mn-Fe oxides and hydroxides seems clear, and has been already documented from other caves (Spilder et al., 2005). Microorganisms activity have been found within the Mn-Fe deposits in El Soplao (Rossi et al., 2010) and fresh microorganisms have been detected on the rough surface of the crusts in Campamento Gallery (Fig. 3F). Judging by their morphology, they are probably streptobacilli or actinomycetes. Their activity not only seem to be related to initial Mn-Fe crusts (Fig. 5D) but also must have to do with the alteration Fe minerals and maybe the dolomite that appear over the crusts (Fig. 5E).

On the other hand, dolomite in caves is frequently associated with other minerals such as calcite, aragonite, huntite and hydromagnesite. Recent studies have demonstrated that microbial activity can play a fundamental role in the precipitation of this mineral (Jones, 2010). Most research supports the idea that dolomite forms part of the cave speleothems through alteration of pre-existing minerals (Hill & Forti, 1997; Alonso-Zarza & Martín-Pérez, 2008). In the case of El Soplao Cave, dolomite could be related

Fig. 5. Genesis of the Mn-Fe crusts in El Soplao Cave. **A.** The host rock contains metallic sulfide minerals **B.** Cave flood events generated turbulent flow (i.e., $\text{Re} > 4000$) enhancing the transport of detrital material. **C.** Sedimentation of detrital material and mobilization of reduced ions (Mn^{2+} and Fe^{2+}) in a less turbulent flow (i.e., $\text{Re} < 2000$) **D.** Oxidation of metallic ions leads to the formation of Mn-Fe crusts in an epiphreatic environment. **E.** Alteration of Mn-Fe crusts in an aerobic environment and precipitation of Fe oxides-hydroxides (Note: Reynolds number is only an estimate for referring to the energy of the medium).

Fig. 6. Genesis of Mn-Fe oxide layers in the aragonite flowstone in the Pasillo de los Cubos **A. Phreatic period.** The Pasillo de los Cubos is submerged below aquifer water-level. Mobilization of metals derived from mineralized host rock occurs under anoxic conditions ($Eh \leq 0$) and laminar flow (i.e., $Re < 2000$) **B. Epiphreatic period.** Precipitation of Mn-Fe oxides and hydroxides due to a fall in the phreatic level that allowed the diffusion of oxygen in the sheet of water, causing oxidation of Fe and Mn ($Eh > 0$) under a laminar regime (i.e., $Re < 2000$) **C. Vadose period.** Precipitation of aragonite from laminar water flow under vadose conditions due to water degassing (Note: Reynolds number is only an estimate for referring to the energy of the medium).

to microbial activity and Fe-Mn crusts deposits. However, the origin of dolomite could also be linked to the dolostone host rock.

A general scheme of the precipitation sequence of El Soplao Cave flowstones could be as follows: (1) the anoxic-phreatic events favoured the enrichment of Mn-Fe ions in the water (Fig. 6A), (2) epiphreatic oxygenate conditions allowed Mn-Fe precipitation by metal oxidation of the black crusts over clay material (Fig. 6B) and finally (3) the precipitation of aragonite by water degassing (Fig. 6C). This situation also alternated with phreatic periods when detrital material was sedimented by floods occurred, especially in the early stages of the flowstone genesis (Fig. 2D). This final stage of aragonite precipitation is also reflected in the crusts in Campamento Gallery and over the biogenic sediments on the floor at various points of the cave (Fig. 2B and 2C).

CONCLUSIONS

Ferromanganese crusts in El Soplao Cave appear on the floor, walls and ceiling of certain galleries. On the cave floors, they take the form of biogenic sediments, and even appear inter-layered in aragonite flowstones. The crusts seem to have originated as a result of the alternation between phreatic and vadose periods. Mobilization of Mn^{2+} and Fe^{2+} from polymetallic sulfides occurred under anoxic conditions when the cave was submerged. Clays deposited on the surfaces of the galleries served as the substrate onto which the Fe-Mn crusts were precipitated. Under epiphreatic conditions, oxidation of Mn and Fe under aerobic conditions mediated by bacteria occurred. Finally recent bacteria activity favoured the precipitation of post-depositional minerals such as alteration Fe oxides and maybe dolomite.

Because the crusts also appear as intercalations between layers of aragonite in the flowstone speleothem indicate that vadose conditions (when aragonite was precipitated) alternated with phreatic and epiphreatic conditions (when Mn-Fe oxides and hydroxides were precipitated). Precipitation of aragonite could be associated with relatively dry periods inside the cave. In El Soplao Cave, these dry periods alternated with flooding phases that are unequivocally linked to pluviometric peaks in this region. Indirectly, the study of these special speleothems could help to date phreatic level changes in El Soplao Cave maybe linked to palaeoclimatic changes.

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