Boxwork and ferromanganese coatings in hypogenic caves: an example from Sima de la Higuera Cave (Murcia, SE Spain)

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Abstract

This paper examines the greyish-blue deposits that were recently discovered in the lower levels of the Sima de la Higuera Cave (Murcia, SE Spain) which occur as patinas over the walls and ceilings, as well as coating *boxwork* formations. Their mineralogy was determined using XRD and micro-Raman spectroscopy, while EDX microanalysis was used to determine their elemental composition. The mineralogical analyses revealed the presence of Mn oxides (todorokite and pyrolusite) and Fe with a low degree of crystallinity, whereas EDX microprobe showed elevated concentrations of Mn (38.2 % wt), Fe (15.2 % wt) and Pb (8.1 % wt). The ferromanganese oxyhydroxides occur as botryoidal aggregates overlying blades of calcite that have a visibly sugary texture. The speleogenetic model proposed describes (1) an initial phase of precipitation of hydrothermal calcite veins (of hypogenic origin) within the fissures of the host rock under phreatic conditions and (2) a subsequent vadose phase involving preferential corrosion of the carbonate host rock caused by lowering of the pH resulting from CO_2 diffusion in condensed water and oxidation of Fe and Mn under aerobic conditions, probably mediated by microorganisms. It is this later phase that gave rise to the *boxwork*. The *boxwork* of the Sima de la Higuera Cave is a singular example of a

formation that is generated by dissolution-corrosion of the rock due to acidification caused by oxidation of iron and manganese.

Keywords: speleothems, ferromanganese oxyhydroxides, boxwork, hypogenic caves, corrosion, Sima de la Higuera Cave.

1. Introduction

The mineralogy, chemistry and genetic aspects of the oxides and hydroxides of iron and manganese speleothems have been extensively studied in many caves (Crabtree, 1962; Moore, 1981; Gascoine, 1982; Hill, 1982; Kashima, 1983; Peck, 1986; Jones, 1992; Onac, 1996, 1997; Northup et al., 2003; Spilde et al., 2006; White et al., 2009; Rossi et al., 2010; Gázquez et al., 2011; Gázquez et al., 2012).

Manganese, soluble in its divalent form (Mn^{2+}) oxidises to trivalent (Mn^{3+}) or tetravalent (Mn^{4+}) manganese in superficial environments and at low temperature, in a process that is frequently attributed to bacterial mediation (Calvert and Pedersen, 1996; Jürgensen et al., 2004). Microorganisms accelerate the rate of oxidation of Mn^{2+} by several orders of magnitude with respect to abiotic catalysis, so it is accepted that the precipitation of oxides of Mn^{3+} and Mn^{4+} depends on biological processes (Nealson et al., 1988). This recognition has led to a number of investigations focusing on the role played by microorganisms in precipitation of these oxides (Peck, 1986; Boston et al., 2001; Spilde et al., 2005, 2006; Rossi et al., 2010).

Originally, it was thought that the ferromanganesic deposits were corrosion residues that derived exclusively from dissolution of the carbonate substratum due to condensation (Queen, 1994), or from acid corrosion in hypogenic caves (Davis, 2000; Provencio and Polyak, 2001). However, recent work has proposed the source of Fe and Mn to be from mobilization of these elements contained in mineralizations of the host rock (Gázquez et al., 2011; Gázquez et al., 2012) or from dissolution of these elements in vadose parts of the cave (Spilde et al., 2006). One way or the other, ferromanganesic speleothems in caves tend to be of two distinct types:

(1) The first group consists of Fe-Mn minerals, usually with smooth surfaces, deposited on the cave walls, floors and ceilings (Onac et al., 1996; White et al., 2009; Gázquez et al., 2011). Sometimes, these types of crust are intercalated with detrital material or

"fossilized" inside carbonate speleothems (Peck, 1986; Provencio and Polyak, 2001; Yusta et al., 2009; Gázquez et al., 2011). As a general rule, these ferromanganesic speleothems are usually deposited by moving water and the underlying substrate does not appear to be weathered.

(2) The second group consists of precipitates that have the aspect of rough patinas deposited over the cave walls and ceilings, usually on top of visibly altered carbonate substrates, dubbed "punk rock" by Hill (1987). The presence of this type of ferromanganesic deposits is relatively scarce compared to the abundant crust deposits of the first group and their origin seems to be linked to weathering of the host rock. The most significant examples of this typology are found in hypogenic cave such as Spider Cave and Lechuguilla Cave (Carlsbad Caverns National Park, New Mexico) (Davis, 2000; Provencio and Polyak, 2001; Northup et al., 2003; Spilder et al., 2005, 2006), in Jewel Cave and Wind Cave (South Dakota) (Chelius and Moore, 2004; White et al., 2009) and Cupp-Coutunn Cave (Turkmenistan) (Maltsev, 1997).

The present work studies a new example of this second group of ferromanganesic deposits, which has been recently discovered in the Sima de la Higuera Cave (Murcia, Southeast Spain) (Ferrer, 2010), also of hypogenic origin. The mineralogical and geochemical data obtained have enabled us to establish a scheme of evolution to describe the genesis of this peculiar speleothem, based on corrosion of the host rock, which in this case leads to the formation of unique *boxwork* coated with ferromanganese oxyhydroxides. The term "*boxwork*" refers to mineral veins in the bedrock which, due to the greater resistance of the calcite in these veins, protrude from the cave wall after dissolution and/or corrosion of the surrounding host rock (Hill and Forti, 1997).

2. Geological setting

The Sima de la Higuera (Fig tree Cave) is located in the Sierra de Espuña, in the municipal district of Pliego (Murcia Region). Its entrance lies 485 m a.s.l., crowned by a large fig tree that gives the cave its name. Speleological exploration of the cave began in 1997, although there is some evidence that it was discovered earlier than this date (Club Cuatro Pico and Club Pliego Espuña, 2001; Ferrer, 2010). Its surveyed length is around 5500 m and the maximum depth is 156 m below the cave entrance, and 82 m below the base of the entrance sinkhole (Fig. 1B).

The cave lies in Oligo-Miocene detrital and marly limestone. Interlayered carbonate conglomerate also appears below the -110 m level, where the ferromanganese deposits studied in this work are emplaced. The carbonate sequence is quite fractured due to NW-SE pressure that has given rise to a series of joints and faults that subsequently determined the cave's morphology, particularly its deeper levels. Mineralizations of metallic sulfides do not appear in the cave setting. In contrast, manganese minerals such as pyrolusite, have been identified in the Tertiary carbonate sequence within the cave, and also appear outside the cave. Significant hydrothermal springs arise in the vicinity of the cave, with temperatures that range from 30 to 50 ºC. These include those of Mula and Archena, 10 and 20 km from the cave, respectively. The high heat flux is due to the relative thinning of the earth's crust and the presence of recent magmatic masses produced by volcanic eruptions that occurred a million years ago (Pinuaga-Espejel et al., 2000).

The mouth of the cave gives access to a subvertical sinkhole 74 m deep, which is developed along the length of a diaclase that runs E-W and finally opens out in the Junction Chamber (Sala de la Unión). This chamber and the galleries that communicate with it form one of the upper levels of the cave, which also run E-W. On this level appear several, small hanging lakes (Coral Lake - Lago de los Corales, and the Bath Chamber –Sala de la Bañera). Beyond this point, the cave morphology changes considerably, with larger galleries and chambers, such as the Ghost Chamber (Sala de los Fantasmas) or Paradise Chamber (-95 m level, Sala Paraíso), which occupy an intermediate level. Lastly, the deepest levels include labyrinthine galleries (three-dimensional "*maze caves*") that are smaller in size, and it is here where the ferromanganesic speleothems, which are the subject of this study, are found (Manganese Gallery) (Fig. 1C).

The cave contains strong evidence of a hypogenic origin. In this study, we use the term "hypogenic" as postulated by Palmer (2011), who suggested that hypogenic caves form due to the upward flow of deep-seated water or by solutional aggressivity generated at depths below the ground surface. In the Sima de la Higuera Cave the hypogenic mechanism is evidenced by the presence of types of speleothems and geomorphological features that are typically related to hypogenic caves such as calcite raft cones, tower cones, mammillary crusts (cave clouds) and folia, specific corrosion forms, copula and condensation domes, scallops, etc. (Audra et al., 2002, 2009; Klimchouk, 2009). The location of these elements in the cross-section of the cave (Fig. 1C) suggests an upflow

of thermal water during the cave speleogenesis, as indicated in other hypogenic caves (Audra et al., 2009).

In addition, its ambient temperature is elevated compared to the annual mean outside temperature of 13.8 ºC; the current cave temperature oscillates between 18.6 ºC and 21.7 ºC, increasing slightly in the deeper parts (Club Cuatro Pico and Club Pliego Espuña, 2001) which indicates a significant positive thermal anomaly. Relative humidity of the cave air is between 87.5 and 90 % (Club Cuatro Pico and Club Pliego Espuña, 2001).

Although the evidence points to deep hydrothermal water flowing through the caves in the past, present-day water inflow is entirely from infiltration of meteoric water. There are only a few vadose speleothems generated from dripwater (stalactites, stalagmites, etc.) in the shallowest levels, around -74 m, and above the level of the Bath Chamber.

3. Materials and methods

3.1. Description of the samples

The sample analysed consists of a fragment of a "*boxwork*" blade (SHG), taken from the roof of the Manganese Gallery, situated in one of the deeper levels of Sima de la Higuera Cave, at the -110 m level (Fig.1). The sample comprised a mineral lamina, 5-10 mm thick with a sugary texture, whose outer surface is covered by greyish-blue deposits, rough in texture and dull (Fig. 2A, B).

In places, the *boxwork* projects from the cave wall more than 30 cm into the cave void (Fig. 2D) and covers hundreds of meters of cave wall and ceiling, especially in the galleries of the mid-lower levels of the cave. Nevertheless, the *boxwork* can also be observed in shallower parts of the cave, though much of the time it is barely visible, having been totally eroded away or widely covered by more recent speleothems, like coralloids or *popcorn*.

In places, the dark deposits are accompanied by others, pink or reddish in colour (Fig. 2E) and, less frequently, these coloured patinas cover calcite spar, some of them centimetric in size (Fig. 2B). In this case, the crystal surfaces are also rough, although the crystal shapes are usually well preserved. In the deep galleries, there is also a stratum of conglomerates whose pebbles are totally covered in a similar dark patina (Fig. 2F,G).

3.2. Analytical methodology

SEM microphotographs were taken using a HITACHI S-3500 instrument in high vacuum mode. The samples were previously dried and coated with graphite to increase electron transmissivity. The elemental chemistry was determined by EDX (Energy dispersive X-ray spectroscopy) microprobe at nine points with different typology over the *boxwork* sample (Fig. 3). Semiquantitative 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 such as Fe, Mn, O, Si, Al, Ca, Mg, Pb and Ba to be analysed (Table 1). Carbon concentration was not measured due to masking by the graphite coating.

A subsample of these dark materials was extracted using a needle for later mineralogical analysis by XRD (X-ray diffraction). The mineralogy of the internal crystalline lamina was also determined by XRD of a powdered sample. 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. Mo_{Ka} cathode radiation was used ($\lambda = 0.71073$Å) 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 mg) but carries the disadvantage of low resolution in the resulting diffractograms.

The mineralogical nature of the two clearly differentiated zones was also studied *in situ* by micro-Raman spectroscopy. The excitation source was a Laser Research Electro-Optics (REO) working at 632.8 nm. The spectrometer used was a KOSI HoloSpec f/1.8i model from Kaiser, with Rayleigh scattering of 633 nm, a spectral range of Raman displacement of 0-3800 cm^{-1} and spectral resolution of 5 cm^{-1}. The CCD used was a DV420A-OE-130 model from Andor. The Raman head used was KOSI MKII, HFPH-FC-S-632.8 model from Kaiser coupled by optical fibre. Microanalyses of up to 5 μm diameter spot were undertaken with a Nikon Eclipse E600 microscope. The microscope was coupled to the Raman probe and a JVC TK-C1381EG videocamera. For all of the spectra, the laser power used on the sample was 15 mW, and the irradiance, 2.4 kW/cm^2 at 50X. This ensures no thermal damage to the samples. Acquisition time was 6 s and 5 accumulations were done. The sample was manually scanned, while the height of focus was varied in order to optimize the intensity of the spectra signals. The spectra obtained

were compared with the RRUFF Raman mineralogical database standard (http://rruff.info/) for calcite and Fe-Mn oxyhydroxides and our own database.

4. Results

The SEM microphotographs allowed two visibly different zones to be broadly identified (Fig. 3A). The first comprises sub-millimetric euhedral calcite crystals, some of which have a sphenoidal habit with well-defined faces and edges. Over this mineral lamina appear botryoidal structures which, observed in BSE (Back-scatter electron imagery) mode, show a lighter colouration than the underlying calcite crystals (Fig. 3B). This fact suggests that the coating layer is composed of relatively heavier elements than those comprising the hydrothermal calcite blades, which seems to be intensely altered, particularly in the zones covered by these botryoidal features (Fig. 3C). The areas that lack this covering also appear to have been altered, although to a lesser degree (Fig. 3D).

The morphology of the altered calcite varies from hexagonal or pseudohexagonal (Fig. 3F) to scalenohedral forms (Fig. 3H), aligned with the habit of the calcite crystals. In the most altered zones, one is left with three-dimensional voids that also have a hexagonal pattern (Fig. 3G). Within the cavities are filaments with a markedly biotic aspect, which suggests that the cause of the alteration could be microbial activity (Fig. 3I).

The Raman spectroscopy identified that the dark botryodial features that appears partially covering calcite crystals are metallic oxides-hydroxides. The Raman signals detected at 633 and 594 cm^{-1} are indicative of polymetallic oxides and/or hydroxides, probably Fe-Mn minerals, which usually give Raman signals in this range (Dunn et al., 2003; Mironova-Ulmane et al., 2009) (Fig. 4A). However, the precise mineralogy of these substances could not be identified using this technique, since there was no correspondence in the RUFF mineralogical database. The signal at 488 cm^{-1} was assigned to the vibration of the Si-O-Si bonds that typifies clays (Frost, 1995). With respect to the other Raman signals encountered, the well-defined bands at 1086, 711 and 281 cm^{-1} are evidence of the presence of calcite (Rutt and Nicola, 1974).

Lastly, the sugary-textured mineral substrate (Fig. 3D), over which the ferromanganesic deposits have developed, verified that it was calcite (Fig. 3C); it presented the typical

signals for this mineral at 1435, 1744, 1086, 711 and 281 cm^{-1} (Rutt and Nicola, 1974) (Fig. 4B).

Additionally, mineral analysis of the same dark patina deposited over the *boxwork* (Fig. 3E) using X-ray diffraction found Mn phases to be present, including todorokite ($NaMn_6O_{12}·3H_2O$) (22 %) and pyrolusite (MnO_2) (16 %). These minerals are in addition to calcite (42 %) and amorphous phases (20 %), probably poorly crystalline Fe oxides that were also confirmed using the EDX microprobe (Fig. 4 A).

The chemical composition of the patinas was determined by EDX microprobe at nine points with differing typology found over *boxwork* from the Sima de la Higuera (Table 1). Although the percentage weight of Fe and Mn is relatively low in the total sample (62 and 32 ppm, respectively, as determined by XRF), high concentrations of these elements were detected using EDX microanalysis (Table 1), so corroborating the mineralogic nature of these deposits. The points analysed over the botryoidal structures (SHG-1, SHG-3 and SHG-6 in Fig. 3) revealed Mn concentrations ranging between 29.2 - 38.2 % wt. whereas Fe concentrations range between 10.3 - 15.2 % wt. There were also relatively high concentrations of elements not detected in the underlying calcite, such as Pb (up to 8.1 % wt.) and Ba (up to 2.7 % wt.).

The microanalyses done on the sugary-textured calcite show that the unaltered zones (SHG-2, SHG-5 and SHG-9 in Fig. 3) contain low concentrations of Mn and Fe, below 2.8 and 1.5 % wt., respectively. The concentration of these elements over the zones of altered calcite (SHG-4, SHG-7 and SHG-8 in Fig. 3) is similar to the unaltered zones (without botryoidal features), falling below 1 and 2.2 % wt. for Mn and Fe, respectively.

5. Discussion

The Mn-Fe deposits in the Sima de la Higuera Cave have characteristics that are totally different from those normally described in ferromanganese speleothems. In general, the crusts reported in other caves have a plastic texture like a gel (Onac et al., 1997), or else occur as laminae, frequently intercalated with detrital material (Rossi et al., 2010; Gázquez et al., 2011); their origin is usually related to flowing water or alternating vadose and phreatic conditions.

However, there is clear evidence that the Mn and Fe deposits of Sima de la Higuera Cave have a completely different origin, starting with the striking arrangement of these

minerals in the deepest galleries of the cave. They commonly form a rough patina coating the *boxwork* blades, whose structure is visibly altered and fragile.

This type of thin blades made of reticulate crystalline laminae (*boxwork*) has been described in other caves (Hill and Forti, 1997). The genesis of the majority of these is related to the infill of fractures in the host rock with minerals that are slightly more resistant than the surrounding carbonate material, which are generally more readily eroded by condensation-corrosion mechanisms (Palmer, 1981). Calcite veins precipitated at low temperature are common (Hill and Forti, 1997), though some cases have been reported where the infilled calcite has been precipitated from hydrothermal water, as in the case of the *boxwork* in Wind Cave (South Dakota). There, the temperature of formation of speleothems is estimated to have been 55 ºC, based on analysis of fluid inclusions in the *boxwork* veins (LaRock and Cunningham, 1995). While, in the case of the *boxwork* from the Sima de la Higuera Cave, there is no information about fluid inclusions, the phaneritic sugary texture of the calcite that composes these blades, together with the great profusion of features that are typical of hypogene speleogenesis (mammillary crusts, bubble trails, tower cones, folia, calcite spar and others) suggest that these infills were precipitated under phreatic conditions from thermal water in a subaqueous environment, prior to the *boxwork* formation. This theory is also supported by the emplacement of spar-like and phaneritic calcite infills, that occasionally reach centimetric dimensions (Fig. 2B), in the upper levels of the cave and which, in other caves, have also been proposed as indicators of thermal conditions prevailing during their genesis (Lundberg et al., 2000). Occasionally, the centimetric calcite crystals of Sima de la Higuera Cave are also covered by rough greyish-blue patinas. Nevertheless, these spar crystals are not totally dissolved like the submillimetric crystals of the *boxwork* blades. Corrosion could affect both types of spar crystals equally; however, this alteration is only visible at microscopic scale using SEM.

In places, the calcite veins are arranged in a three-dimensional network, which also appears covered by ferromanganese oxyhydroxides. In this case, hydrothermal calcite crystals were precipitated, infilling the abundant cracks of the bedrock that had been previously fractured by tectonic forces (Figs. 5A, B). During a later stage, *boxwork* like that of Fig. 2E formed under vadose conditions.

Subaerial condensation corrosion occurred after the cave drained. Condensation and CO_2 diffusion in the condensed water are identified as being the precursor processes for dissolution of the carbonate rock both in caves that were epigenic and non-thermal in

origin (Jameson, 1991; Tarhyle-Lips and Ford, 1998; Freitas and Shemekal, 2006), as well as in hypogenic caves, exhibiting specific patterns of dissolution (Cigna and Forti, 1986; Bakalowicz et al., 1987; Sarbu and Lascu, 1997; Audra et al., 2007).

In the Sima de la Higuera Cave, the rising of hot air loaded with water vapour from the deepest levels of the cave led to condensation over the walls of the Manganese Gallery, whose temperature was slightly lower than that of the air rising from depth. This dissolution process could have been enhanced as a consequence of the CO_2 concentration in the cave air. Currently, this concentration usually reaches 2000 ppm in the lower and intermediate cave levels and it might have been greater in the past due to degassing of hydrothermal water. This mechanism of CO_2 diffusion has also been proposed as the precursor of corrosion of host rock in other thermal caves (Sarbu and Lascu, 1997).

Nonetheless, current processes of condensation in Sima de la Higuera Cave do not seem very active, particularly in the Manganese Gallery where there is no condensed water on the gallery walls and relative humidity is below 90 % (Club Cuatro Pico and Club Pliego-Espuña, 2001). The great profusion of Fe-Mn oxyhydroxides coating the gallery surfaces suggests that corrosion of the host rock and of the hydrothermal calcite blades themselves could have been due to oxidation of Fe^{2+} and Mn^{2+} that were precipitated as ferromanganese oxyhydroxides.

From this perspective, the “in situ” dissolution processes of the host rock, which could contain the Fe and Mn in their reduced form, would involve oxidation of these as they came into contact with the cave atmosphere, and they would remain attached to the bedrock surfaces (Cunningham et al., 2005). Although iron and manganese are elements that are frequently found as co-precipitates of marine carbonates (Morse and McKenzie, 1990), other studies have highlighted that the volume of manganese and iron usually precipitated in this type of crust is much greater than could have come from “in situ” dissolution of the host rock (Spilde et al., 2005). This imbalance is even more striking in cases where the profusion of ferromanganesic structures is so spectacular, such as in Lechuguilla Cave (Davis, 2000) or in the current case of the Sima de la Higuera Cave. The significant quantities of the iron and manganese precipitates in these caves may have derived from dissolution of the host rock overlying these galleries.

Thus, manganese and iron could be mobilized in the vadose zone by dissolution of the Oligocene-Miocene carbonate enclosing the cave. In fact, manganese minerals, such as pyrolusite, appear in the Tertiary carbonate sequence in which the cave is developed. It

is likely that dissolution of these metallic oxides under anoxic conditions could liberate these elements in their reduced forms (Mn^{2+} and Fe^{2+}). Subsequently, metals were carried by flowing water through fractures, and even through the intercrystalline pores of the hydrothermal calcite veins. Eventually, the solution reached the cave where metals oxidized under subaerial conditions (Fig. 5D).

The process of oxidation of these metals is frequently mediated by microorganisms that use reduced manganese and iron (Mn^{2+} and Fe^{2+}) as their energy source (Nealson et al., 1988; Spilde et al., 2005) (Fig. 5D). Microorganisms in the Fe-Mn crusts of Sima de la Higuera Cave have been detected in various voids, where one can observe intricate bacterial filaments that are probably linked to the oxidation of Fe and Mn, according to the reactions:

$$2\ Mn^{+2} + O_2\,(g) + 2\ H_2O \rightarrow 2\ MnO_2\,(s) + 4\ H^+$$

$$4\ Fe^{+2} + O_2\,(g) + 10\ H_2O \rightarrow 4\ Fe\,(OH)_3\,(s) + 8\ H^+$$

As can be deduced from these chemical transformations, oxidation of manganese and iron gives rise to protons that acidify the medium, and so lead to corrosion of the calcite beneath. In this way, formation of *boxwork* is encouraged by preferential dissolution of the microcystalline host rock, which is more soluble than the blades of sugary-textured hydrothermal calcite.

On the other hand, the calcite veins that remain exposed are also affected by corrosion caused by the oxidation of the iron and manganese and CO_2 diffusion in condensed water, as seen in Fig. 3, where calcite "*ghosts*" (molds around former calcite) can also be seen either with a pseudohexagonal (Fig. 3C) or scalenohedral (Fig. 3H) structure, depending on the degree of corrosion. The scalenohedral forms appear in the less corroded areas, frequently on the faces of the rhombohedric calcite $\{10\bar{1}4\}$ (Fig. 3H). The same pattern has been observed on a microscopic scale in experiments relating to the initial phases of superficial dissolution of calcite (Astilleros et al., 2008). The initial phases of dissolution by corrosion are characterized by regression of the exfoliation laminas and by generation and enlargement of dissolution pits, which have a characteristic rhomboid form with sides parallel to the direction $\langle\bar{4}41\rangle$ (Astilleros et al., 2008). They ultimately result in the scalenohedral corrosion forms that are visible on the crusts. On the other hand, the pseudohexagonal “ghosts” of formed calcite appear as reticules over the surface of the crusts in areas where there is a higher density of

botryoidal Fe-Mn precipitates (Fig. 3C). On other occasions, the pseudohexagonal morphology appears in tridimensional structures generated by the dissolution of the preceding calcite crystals (Fig. 3G). In both cases, the hexagonal morphology seems to be related to a more advanced phase of calcite corrosion. Differences in the magnitude of the condensation mechanism at microscopic scale could have played a significant role in the differential dissolution-corrosion pattern of the calcite blades.

6. Conclusions

Two stages can be differentiated during the genesis of the ferromanganese *boxwork* in the Sima de la Higuera Cave: (1) precipitation of sparitic calcite veins in the fissures of the carbonate host rock when the cave was submerged in the thermal aquifer water; and (2) corrosion of carbonates by acid generated due to CO_2 diffusion in condensed water and oxidation of reduced Fe-Mn in aerobic conditions. The acid attack preferentially dissolved the carbonate host rock, which has a microcrystalline structure, while the veins of sparitic calcite, precipitated in earlier phases, present greater resistance to corrosion. In this way, the calcite blades projected into the cave in the form of a *boxwork.*

The *boxwork* in the Sima de la Higuera Cave is a singular example of structures generated by dissolution-corrosion of the rock due to acidification resulting from the diffusion of CO_2 in the cave atmosphere and most probably as a consequence of oxidation of iron and manganese by microorganisms.

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FIGURE CAPTIONS

Figure 1. A. Location and geological setting of the Sima de la Higuera Cave. Geological cartography modified from Kampschuur et al., (1972); B. Plan view of its development. The red circle indicates the location of the Manganese Gallery where the *boxwork* sample was collected. Cave topography courtesy of the Speleological Clubs: Cuatro Picos (Cartagena) and Pliego-Espuña (Pliego) (2001); C. Idealized cross section and location of the main hypogenic geomorphological features and speleothem formations in the Sima de la Higuera Cave. The red frame indicates the location of the Manganese Gallery.

Figure 2. Hypogene ferromanganese *boxwork* from the Sima de la Higuera Cave (Murcia): A. Manganese Gallery where it appears the ferromanganese *boxwork* studied in this work. The lower parts of the gallery walls are covered by clayey minerals that indicate a past water level. The ferromanganese oxyhydroxides also appear under these detrital deposits; B. Ferromanganese *boxwork* on the ceiling of the Manganese Gallery (-110 m); C. Calcite “spar” coating the cave walls beyond the “Bath Chamber”; D. Ferromanganese *boxwork* on the ceiling of the Manganese Gallery, partially covered with “*popcorn*”; E. Ferromanganese *boxwork* covered with coralloids; F, G. Clastic materials covered with ferromanganese oxyhydroxides and desiccation mud crust on the gallery floor; H. Large hydrothermal calcite veins filling fractures in the host rock which origin is related to the mechanisms that generated the *boxwork* (Photos: Victor Ferrer).

Figure 3. Secondary electron images of the manganese coatings on the *boxwork* of the Manganese Gallery: A. General view where it appears calcite euhedral crystals covered

by ferromanganese patinas; B. BSE (Back-scatter electrons) image showing zones of contrasting compositions. Clearer colour zones indicate Fe-Mn coatings while darker colour areas are composed of altered euhedral calcite crystals; C. Fe-Mn oxyhydroxides forming botryoidal structures over the visibly altered calcite substrate; D. Altered sugary-textured calcite substrate; E. Detail of the botryoidal features made of mineralizations of Fe-Mn oxyhydroxides; F. Details of the pseudohexagonal calcite "*ghosts*" related to the alteration caused by oxidation of Fe and Mn; G. Three-dimensional calcite "*ghosts*"; H. Scalenohedral calcite with molds; I. Biotic filaments inside the corrosion cavities. Note that the numbers indicate the location of the EDX microanalyses, whose results are summarised in Table 1.

Figure 4. Raman and EDX spectra of the Mn-Fe coatings from the Sima de la Higuera Cave: A. Raman spectrum and EDX spectrum of the Mn-Fe oxyhydroxides coating; B. Raman spectrum and EDX spectrum of the calcite blade substrate.

Figure 5. Genesis of the ferromanganese *boxwork* of the Sima de la Higuera: A. Karstification and initial hypogene speleogenesis linked to hydrothermal water rising. The cracks were enlarged by the hot water. Red = thermal water; B. Precipitation of "spar" crystals of hydrothermal calcite filling host rock fractures by means diminishing temperature. Yellow blocky pattern = calcite spar veins; C. Increasing cracks and voids formation due to hydrothermal flow. Dissolution of the carbonate host rock in underwater conditions and mobilization of Mn and Fe in their reduced forms; D. Walls and ceiling dissolution/corrosion under vadose conditions. Mn^{2+} and Fe^{2+} from the bedrock, both "in situ" and transported by flowing water coming from the vadose zone were oxidized when reached the cave (dark blue line = ferromanganese oxyhydroxides), probably via microbial activity in oxygenic environment. This reaction produces H^+ and pH lowering conducing to calcite corrosion. CO_2 diffusion in condensed water could also lead to acid corrosion. In places, clayey coatings and desiccation mud crusts appear on the floor of the Manganese Gallery.

Table 1. Analysis of major elements. Analytical error ranges from ±0.33 wt% for oxygen to ±0.13 wt% for aluminum. Error in Fe and Mn measurements was ±0.2 wt%. The location of the microanalysis samples is given in Fig. 3.