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# GENESIS OF PHOTOTROPIC BIOSPELEOTHEMS IN GUIZHOU (CHINA): OCCURRENCE OF BIOCORROSION, MICROPHANTOMIZATION AND ALGAL PRECIPITATION

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(5 figures and 4 plates)

**ABSTRACT.** The phototropic biospeleothems in tropical areas are mainly tufa stalactites and speleothems directed towards the daylight. The studied examples in Guizhou province show a type of limestone alteration and calcite precipitation almost *in situ*, located in the condensation zone. Petrographic examinations show: 1/ a corrosion contact between the rock (or a former deposit) and the biospeleothem, 2/ a corrosion front into the rock, 3/ the chemical precipitation of CaCO<sub>3</sub> in a micrite clotted fabric, 4/ some microstromatolites, 5/ algal filaments visible into micrite and microstromatolite. The laminated structure is probably due to periodic condensation (dry season/wet season). The micrite clotted fabric (or thrombolite) is related to the micrite process by algal filaments as in the genesis of algal limestones. The biocorrosion / bioprecipitation process underlines the influence of microbes in the rock chemical alteration (e.g.: isovolumic alteration) and the genesis of some speleothems.

Keywords: Karst, phototropism, micrite, stromatolite.

RESUME. Genèse des biospéléothèmes phototropiques du Guizhou (Chine) : biocorrosion, microfantômisation et précipitation algaire. Les biospéléothèmes phototropiques, fréquents en zone tropicale, se présentent sous la forme de stalactites de tufs et de formes en aiguilles orientées vers la lumière du jour. Les exemples étudiés dans des grottes du Guizhou (Chine) mettent en évidence un type d'altération de la roche calcaire et de recristallisation quasi *in situ*, localisé dans la zone de condensation éclairée. Les observations micromorphologiques montrent : 1/ un contact de corrosion net entre le substrat (roche ou paléo-concrétion) et la concrétion, 2/ un front de corrosion qui pénètre la masse du substrat, 3/ la reprécipitation du CaCO<sub>3</sub> sous forme de micrite à structure grumeleuse, 4/ des bourgeons microrythmés (microstromatolites), 5/ des filaments algaires visibles dans la micrite et dans les faciès microrythmés. Le faciès microstromatolitique est attribué à une périodicité de la condensation (saison sèche / saison humide). Le faciès micritique grumeleux (ou thrombolites) est lié à la micritisation du CaCO<sub>3</sub> par les filaments algo-bactériens selon un processus classique dans la genèse des calcaires marins algaires. Le processus antagoniste biocorrosion / bioconstruction souligne le rôle de la microbiologie dans l'altération de la roche (« fantômisation ») et dans la genèse de certains spéléothèmes.

Mots-clés: Karst, phototropisme, biocorrosion, précipitation algaire, micrite, stromatolite, Chine.

#### 1. Introduction

Several terms have been used by scientists to name the concretions influenced by biological activity: phytokarst (Folk *et al.*, 1971, 1973), biokarst (Schneider, 1976), phytokarren, photokarren (Waltham & Brook, 1980), directed speleothems (Viles, 1984), aussen stalactiten (Viles, 2004), biothems (Cunningham *et al.*, 1995). In 1982, Bull & Laverty have summarised the various studies already made and proposed a first typology. They gave their preference to the term phytokarst, as it was defined by Folk *et al.* (1971), rather than photokarren: "Phytokarst is herein defined as a landform produced by rock

solution in which boring plant filaments are the main agent of destruction, and the major morphological features are determined by the pecular nature of this mode of attack".

Viles (1984) criticizes the term phytokarst, which he believes is too simplistic. His typology reintroduces the word biokarst, defined as follows: "a landform produced largely by the direct biological erosion and/or deposition of calcium carbonate".

The cave entrances sometimes show very particular concretions, oriented towards the daylight (*directed speleothems* of Viles, 1984). Such concretions are not very frequent in the temperate zone, with some examples mentioned for example in Ireland (Simms, 1990); but

they are numerous in the tropical and subtropical areas (Jones, 1989), where they are described as oriented tuf stalactites (Viles, 2004) and as topic aciform facies (Bull & Laverty, 1982). In South and South West China, these speleothems develop at most of the cave entrances and were described as phytokarstic concretions (Zhang Shouyue, 1988; Maire, 1991).

With reference to the accepted terms of speleothems and biothems, we hereby propose the expression "phototropic biospeleothem" to highlight the role of the biological genesis (photosynthesis) and the daylight (phototropism). In the present article, we will study:

- the speleothems directed towards the daylight (rod-like phytokarst of Bull & Laverty, 1982) in the Hujiadong cave. Such kind of concretions can also be observed in Poland, in the Tatras Range (P. Audra, oral information) (Czarna cave, Gradzinski & Kicinska, 2002);
- the oriented concretions in the Gebihe system;
- the honeycomb alteration in the Tianshenqiao system (Panxian, Guizhou), somehow similar to the "pits forming depressions 5 to 30 mm deep" described by Danin & Garty (1983). Further alteration leads to the mondmilch structure (Caumartin & Renault, 1958; Pochon et al., 1964); at the ultimate stage, concretions crumble into dust.

#### 2. Geoclimatic context and methods

#### 2.1 Geoclimatic context

The studied sites are located in the Guizhou province, China (Fig. 1), in an environment of subtropical conic karst of middle mountain (1500 m). The annual rainfalls, typical of the monsoon climate, reach 1100 up to 1400 mm, with 80-85 % concentrated from May to October. The annual mean temperature is between 14 and 18°C. The studied caves belong to the geotectonic unit of the Yangtse platform. The carbonate series, several thousand meters thick, cover a period spreading from the Precambrian (Sinian) to the Mesozoic (Trias); detrital and volcanic layers interbedded in the carbonated series are related to the numerous tectonic phases from Caledonian to Indosinian movements. During the Tertiary and Quaternary periods, the last phase of the Himalayan orogenesis led to the uplift of the platform. Such tectonic activity is also responsible for the erosion of the sedimentary layers (especially the upper Permian basalts) and for the active karstification. When they cross a limestone/dolomite area, the surficial rivers cause canyons and/or large through caves like Gebihe, Gesohe or Liuchonghe, often with stepped and dry cave levels (Maire et al., 2004).

#### 2.2. Methods

We sample concretions in active or dry caves, on rock (speleothems or nodules directed towards the daylight) or on altered concretions (honeycomb structures). We used microscopic observation:

- on polished sections and thin sections for micromorphological analyses;
- under epifluorescence with a mercury vapor lamp with UV (365 nm), blue (450-490 nm) and green (546 nm) filters. This observation under optical microscope underlines some micromorphological structures (calcite is slightly luminescent, aragonite is intensely luminescent) and also the role of the organic and/or biological action.

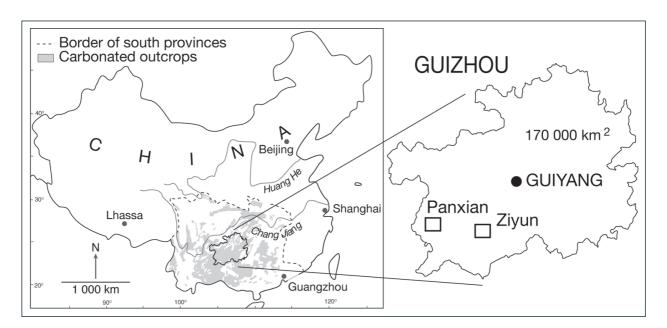


Figure 1- All the studied zones are located between latitude 25° and 28° N (Guizhou, China).

#### 3. Samples description and results

This part focuses on the oriented concretions and deteriorations of paleo-concretions located inside the caves, but in an area still influenced by the daylight (Maire & Vanara, 2004).

## 3.1. Hujiadong phototropic biospeleothems: needle structures

Hujiadong is a dry cave, 800 m long, located in Panxian district. It develops in the Triassic stratified limestones at an altitude of 1650 m (Fig. 2A). The entrance gallery is a 25° slope following the dip. 70 m after the entrance, the eastern wall is covered by numerous grayish needles, 3 to 7 cm long, oriented towards the daylight (Fig. 2B, C).

#### 3.1.1. Micromorphological study

On a polished longitudinal section, the general organization is clear (Pl. 1A). The grey concretion is organized roughly, with grey areas and some finely rythmic zones. The area in contact with the limestone substratum is irregular and includes small dissolving gulfs and sometimes residues of limestone hanging in the mass of the grey cryptocrystalline calcite.

Under microscopic observation on thin sections, the contact between the limestone and the deposit appears as a

alteration front. The epifluorescence examination shows a clear contrast between the micrite (grey cryptocrystalline calcite), which is very luminescent due to the organic material and a light-coloured calcite itself not luminescent (host rock) (Pl. 1B). Micrite is made of a very fine calcite whose crystals are smaller than 1 or 2  $\mu m$ . Laminar areas have a shape of long nodules (Pl. 1D). Growing lamina are 15 to 75 µm thick. Laminae also include doublets (Pl. 1E), each of them being made of a grey highly luminescent lamina and a bright non luminescent lamina (Pl. 1F). The highly luminescent laminae are 1 to 3-4 µm thick. Microdoublets can be seen in some sequences: they are  $2-3 \mu m$  thick and spaced out by  $1 \mu m$  highly luminescent microlaminae. Some blackish filaments, from 10 to 100 μm long and a few μm in diameter, spread across laminar areas (Pl. 1C).

#### 3.1.2. Interpretation

The oriented morphology and the petrographic examination provide evidence that the concretions are sensitive to the daylight, thus to photosynthesic process. We interpret the filaments found in the samples as cyanobacteria and/or filamentous algae which altered the limestone and then precipitated the CaCO<sub>3</sub> towards the daylight (role of the chloroplasts) in the forme of either micritic structures, more or less lumpy, or of finely oriented nodules corresponding to microstromatolitic structures.

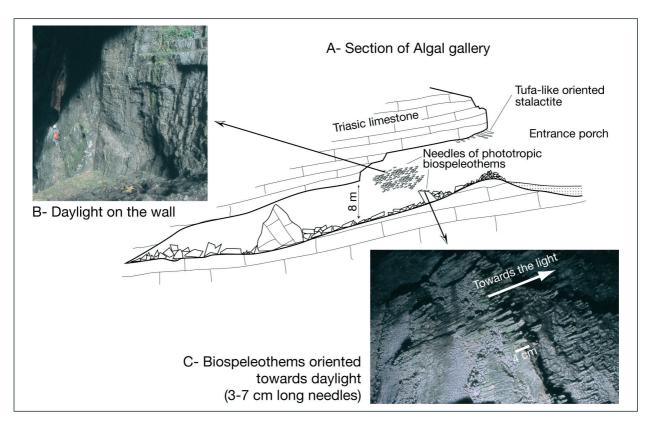


Figure 2: - Hujiadong phototropic biospeleothems.

The high fluorescence of the grey calcite demonstrates the presence of organic matter constituted by the algae-bacteria reticulum. We can deduce from these observations that photosynthesis simultaneously causes a bioerosion of the rock facing the daylight (role of condensation water in the entrance galleries) and a bioconstruction of phototropic calcite.

The laminar sequences are of particular interest. It is possible to interpret the 15 to 75  $\mu$ m doublets by the alternation of the seasons. Moreover, repetitive sequences inside a single season are suggested by the observation of exceptionally sharp microdoublets subdivisions (1  $\mu$ m microlaminae). A succession of phases of rain, condensation... are underlined by the organic matter successively brought to the gel evidenced by the epifluorescence.

## 3.2. Gebihe phototropic biospeleothem: cauliflower structures

Samples from the Gebihe huge tunnel-cave, come from the lower part of the 370 m deep well, which opens through the ceiling of the entrance gallery (Fig. 3A, B). Deposits display small cauliflowers structures, much different from the Hujiadong needles (Fig. 3C).

#### 3.2.1. Micromorphology

The most typical sample shows, on a polished section, a pale blue calcareous substratum with Carboniferous foraminifera (biomicrosparite) and a sedimentary dark area without orientation (Pl. 2A). This plasmic part shows a very fine micritic fabric looking curled, that we have quali-

fied as "pelote" (in comparison with a wool ball) (Maire, 1991). We observe rare remains of prosobranchiate or pulmonate gastropods (Mr Wienin, oral information) seized in the mass and caught during concretioning (Pl. 2B). The rock/concretion boundary shows an irregular surface with corrosion gaps and peduncles and some elements of eroded rocks fragments floating inside the micritized mass (Pl. 2C).

Another sample given for comparison shows a similar fabric but where the micritic brown deposit replaces a primitive grey-beige microstromatolitic facies (Pl. 3A, B, B', C) made of buds (1 mm large and 3 mm long) of needle-shaped crystals (Pl. 3D). The dark plasmic coating has no orientation; a piece of gastropod shell of the same age is also stuck in the plasmic mass. A white sparitic calcite fills interplasmic cracks and gaps between micritic calcite and paleodeposit (Pl. 3E).

#### 3.2.2. Interpretation

The irregular corrosion front with stranger elements confirms the occurence of allochtonous material within the corrosion front. There is actually a corrosion of the substratum followed by a micritic precipitation more or less curled. Corrosion processed by invading the limestone through its microporous network (Pl. 2D, E). The "digested" rock turns first to grey, then to brown during the micritization. The progress of the biochemical front allowed incorporation of rocks particles, not completely dissolved, inside the micrite. When the corrosion front is inactive, retraction fissures and dissolution gaps are filled with secondary calcite of a sparitic type.

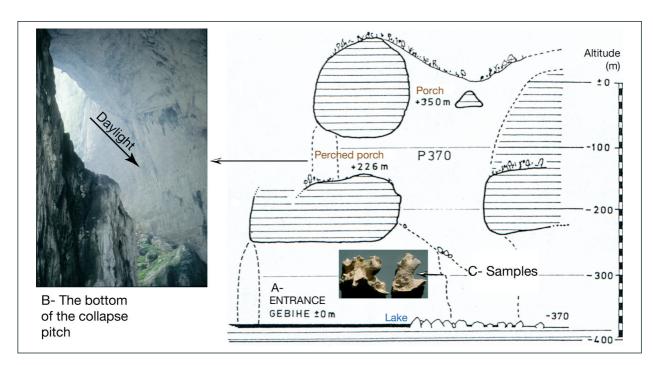


Figure 3: Gebihe phototropic biospeleothems.

# 3.3. Example of biocorrosion in a dry cave: Tianshengqiao

Tianshengqiao is a dry through cave located North of Panxian district. It is the former Gedahe underground river now situated 100 m above the present subterranean river, due to tectonic uplift (Fig. 4). Erosion of the plateau caused two breakdowns (avens) with a natural bridge between them (Fig. 4A). Inside the gallery, 40 m upstream the bridge, one can see a whitish and old stalagmite, 3 m high, at the base of the south wall (Fig. 4B).

#### 3.3.1. Description

Weathered concretion shows a honeycomb morphology. The site of sampling is influenced by daylight coming from the first aven, 20 m diameter. An alteration front (Pl. 4A, B) is observed between a white fibrous calcite, little or not altered, and a mixed calcite made of irregular masses of cryptocrystalline grey calcite and of nodular micrite separated by areas of sparitic calcite (Pl. 4C, D). At high magnification, biologic filaments are visible into the white calcite. The presence of organic matter is attested by high luminescence in blue and green light (Pl. 4E).

#### 3.3.2. Interpretation

The case described above is a typical example of bio-alteration by algae growing under daylight. Here, corrosion of the columnar calcite followed by its precipitation into micritic calcite has not created phototropic concretion as observed in the Gebihe site. The active bio-recrystal-lization by microorganisms in a photosyntetic context leads to micritization. Sparitic calcite (or mosaic calcite) subsequently grew the biomicritic heaps. So the process can be summerized in a two steps sequence: a bio-dissolution at the surface of the paleoconcretion followed by biological reprecipitation of CaCO<sub>3</sub>.

## 4. Discussion: biochemical alteration of limestone

#### 4.1. Micromorphology

The petrographic examinations made on Guizhou biospeleothems show:

- a very clear corrosion contact between the rock (or old concretion) and the concretion itself;
- a corrosion front into the rock;
- the precipitation of CaCO<sub>3</sub> into micrite calcite, with a more or less clotted structure;
- some microstromatolites into micrite calcite;
- algal/bacterial filaments both into micrite and microstromatolites;
- concretions growing towards the daylight, fed by the rock alteration.

#### 4.2. Corrosion/precipitation in situ

Phototropic biospeleothems are found in an intermediary underground area, hit by the daylight with condensation

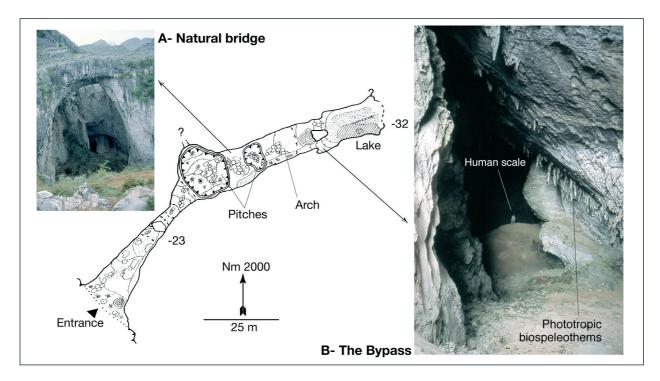
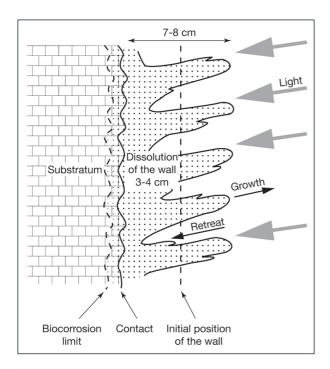


Figure 4: Cave of Tianshengqiao.



**Figure 5:** Biochemical alteration of the limestone and reprecipitation *in situ*.

phenomena, whereas the tufaceous speleothems with green algae are located at the very entrance of the cave. Periodical underground dew (dry/wet season) enables the biocorrosion process. The presence of small gastropods recently trapped in the speleothems confirms the subsequent growth of the concretion towards the daylight, but fed by the dissolution of limestone. For most of the speleothems formed by percolating water, gravity is the dominant parameter. For the studied biospeleothems, this parameter is daylight. Biocorrosion of the carbonate with subsequent calcite reprecipitation is a kind of epigenesis with material migrating over several mm or cm. No material is actually removed away from the system in opposition to pedologic and isovolumetric alteration processes (called « phantomization »), where some material disappears, e.g. decarbonatation (Vergari & Quinif, 1997; Vergari, 1998) or desilicification (Willems, 2000), algal corrosion leads to precipitation of the calcite dissolved nearby (Fig. 5).

#### 4.3. Role played by microorganisms

The algal micritization process and its role in the sea limestone genesis have been studied since a long time (Monty, 1973; Castagnier, 1987). Three main types of sea concretions have been identified 1/ rhythmic: stromatolites, oncolites... and non rhythmic: thrombolites, 2/ algal carbonated deposits... and 3/ algal tufa on cornices and platforms. In fresh waters of continental areas, the main algal concretions are tufa, riverbed nodules, lake concretions (Adolphe, 1981; Casanova, 1986). Other studies have focused on the role of microorganisms in

the genesis of other speleothems, such as pool concretions (Adolphe *et al.*, 1991).

The two main phototropic biospeleothems can be compared to the two most typical algal sea limestones: stromatolites and thrombolites. In the case of the Gebihe microstromatolites as well as for sea stromatolites, the origin of laminites and microlamines seems to be linked to a periodic process: day/light or dry/wet seasons. The micrite clotted fabric, which is the most common, can be compared to those observed in lower subtidal and intertidal environments, next to sea channels (Aitken, 1967). Our study did not focus on algal identification, yet we can state that they belong to the cyanobacteria family (Taborosi & Hirakawa, 2005) and/or chlorophyceous, which are capable of microboring (Peyrot-Clausade et al., 1995). The bioprecipitation mechanism was successfully produced under laboratory conditions (Adolphe & Billy, 1974). Other studies have also evidenced the perforating metabolism of bacteria and alga: calcium comes through the cell and mineralizes it (Adolphe, 1981; Adolphe et al., 1991; Castagnier, 1987).

#### 5. Conclusion

Phototropic biospeleothems are of great interest as they are an illustration of a new kind of limestone microbiological alteration and of micrite precipitation in a specific continental environment. Petrographic examination highlights the alteration process through algal/bacterial corrosion and precipitation. Then photosynthesis due to microbiological activity causes calcite recrystallization in the form of thrombolites and microstromatolites. The study of such type of biological alteration/precipitation processes may shed new light on the process of "phantomization" and "microphantomization", still under investigation (Quinif, 1999; Vergari, 1998). It is another illustration of the active role played by the biochemical activity of algae-bacteria in the alteration of low carbonate platforms and probably also in landscape genesis by differential erosion during the geological times.

#### 6. Acknowledgments

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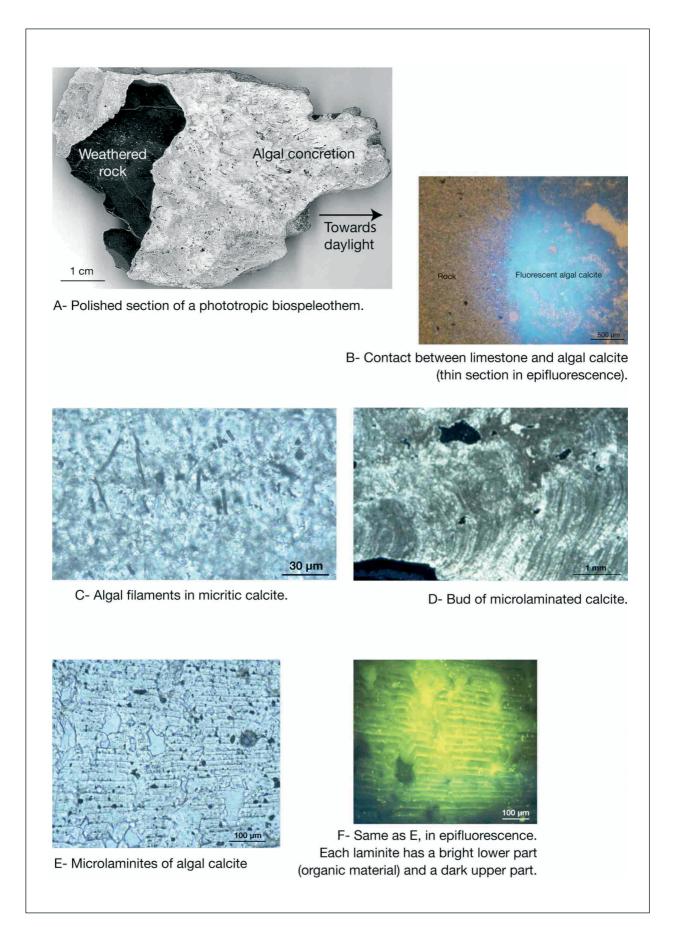


Plate 1: Micromorphological study of Hujiadong phototropic biospeleothems.

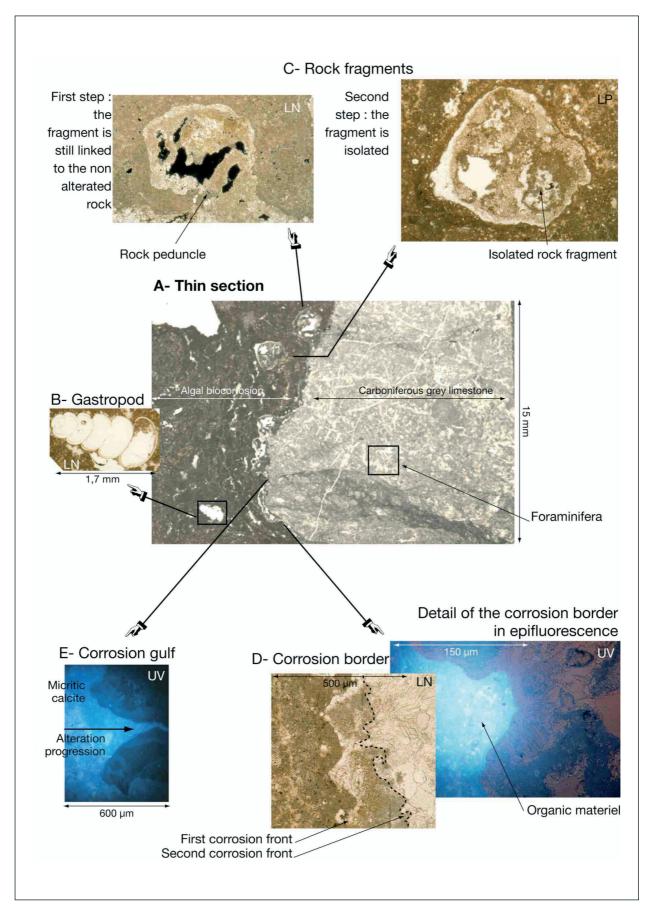


Plate 2: Micromorphological study of Gebihe phototropic biospeleothems: example 1.

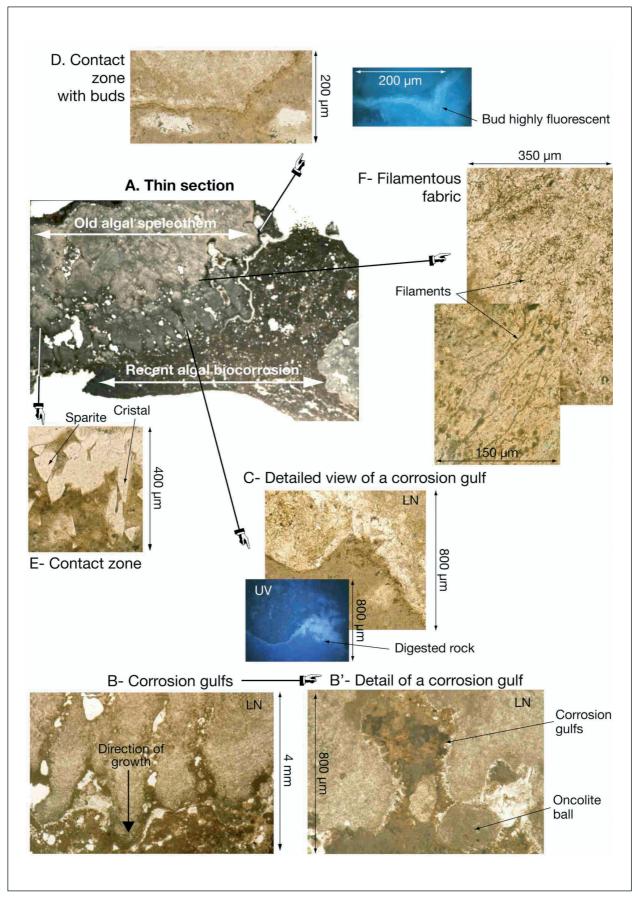


Plate 3: Micromorphological study of Gebihe phototropic biospeleothems: example 2.

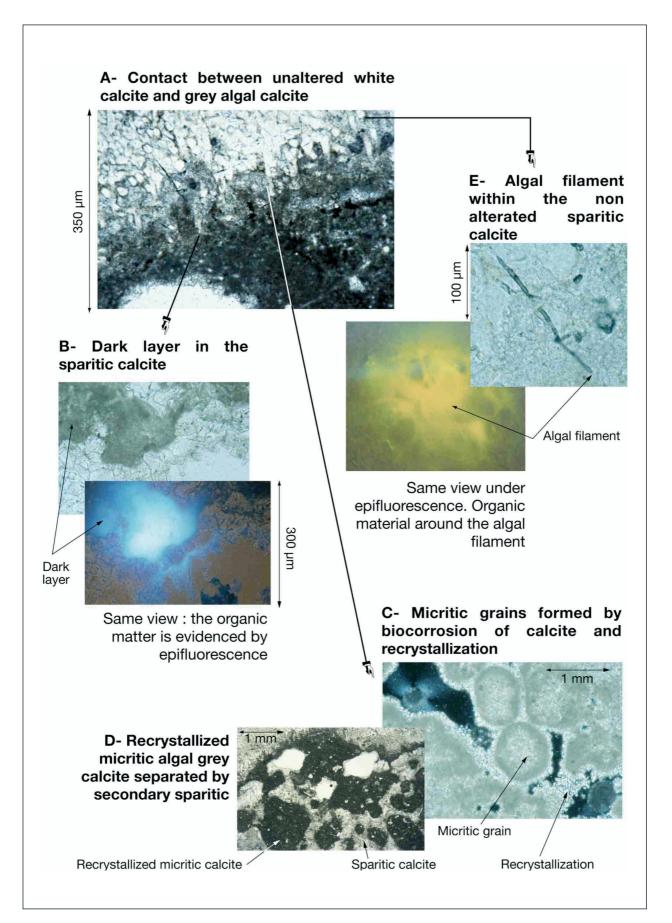


Plate 4: Biocorrosion in a dry cave: Tianshengqiao.