Petrological Study as a Tool to Evaluate the Degradation of Speleothems in Touristic Caves, Castañar de Ibor Cave, Cáceres, Spain

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Abstract In Castañar cave the surface of most of the speleothems present dissolution and corrosion features. In touristic caves, this process has usually been related to the acidification of the atmospheric moisture caused by CO_2 from the breath of visitors. However, in Castañar cave the process of corrosion has been also observed in rooms that are not visited by tourists. Petrological studies were carried out in the speleothems affected by surface corrosion in Castañar cave. The results indicate that this process occurs not only at present time, but over a period of thousands of years, as evidenced by the presence of corrosion lines inside and on the surface of the speleothems. All this and the fact that Castañar cave recovers very quickly from changes in the environmental parameters, indicates that the dissolution–corrosion process is slow and hence it is not related to the presence of visitors.

1 Introduction

The study of degradation processes in caves is a widely studied phenomenom. In touristic caves such studies have been focused on the impact of the visitors and the cave improvements (such as the lighting) over the cave environment and the speleothems. But there are also natural degradation processes, observed in touristic and non-touristic caves that are inherent to the dynamics of the cave systems.

In this contribution a case study is presented from Castañar de Ibor speleothems, in which degradation processes can be observed not only in the outer parts of the speleothems, but at different stages of their formation. In doing so, the processes that cause the alteration that change the surface appearance of the speleothems are envisioned.

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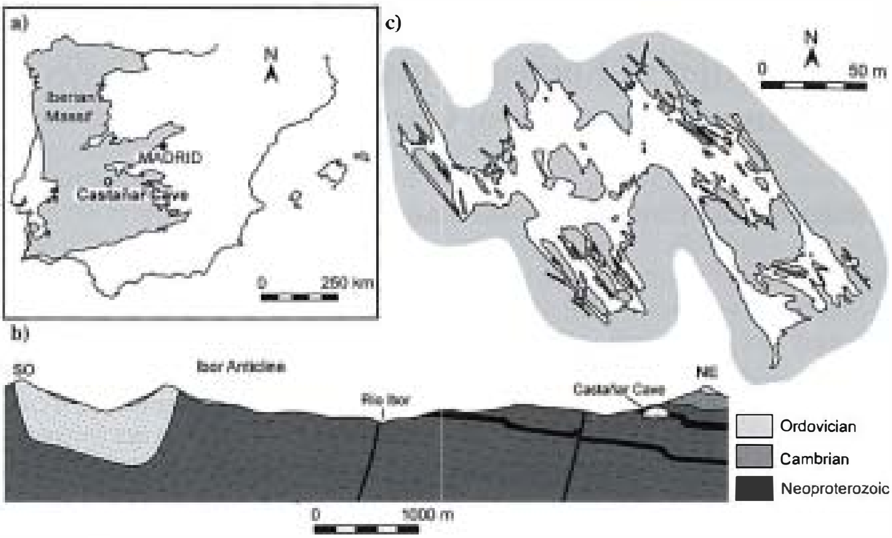

Fig. 1 **a** Geographical setting of Castañar Cave within the Iberian Peninsula. The *gray zone* corresponds to the Iberian Massif. **b** Map of Castañar Cave. **c** Geological section through the Ibor anticline. The cave is developed in the dolomitic layers of the Neoproterozoic series (*black lines*)

2 Geological Setting

Castañar cave is on the SE part or the Iberian Massif (Fig. 1a). The area where it has been developed is mainly siliciclastic, consisting of shales and greywackes with a few interbedded dolomite and magnesite layers (Fig. 1b), all of Neoproterozoic age (Díez-Balda et al. 1990). The formation of the cave is due to the dissolution of the carbonates and the later collapse of the siliciclastic materials.

The development of the cave is horizontal (Fig. 1c) and it has just one entrance that is opened only during the visits, so there is little interchange with the surface atmosphere. The enviromental parameters inside the cave are constant throughout the year: 17°C temperature, and humidity close to 100%. The nature of the host rock determines the composition of the infiltration cave waters, which have a Ca/Mg ratio of 0.5 to 0.1 and are usually saturated with respect to calcite, aragonite and dolomite (Sánchez-Moral et al. 2006). There is another source of water in the condensation of moisture. This moisture is undersaturated in all minerals and it is usually acidic.

The main minerals in Castañar cave are carbonates, mainly calcite and aragonite, but due to the high concentrations of Mg in the cave waters, Mg-carbonates such as dolomite and huntite are also found (Alonso-Zarza and Martín-Pérez 2008).

3 Materials and Methods

Conventional optical petrography studies were performed on corroded speleothems. Thin sections were taken from different forms, including stalactites, stalagmites, and draperies. To make the thin sections the samples were immersed in a resin containing Epofer EX 401 and Epofer E 432 in a vacuum system before cutting and polishing. Scanning electron microscopy observations were performed on gold-coated samples using a JEOL 6400 electron microscope working at 20 kV and with a resolution of 35 Å.

4 Characterization of the Corrosion Process in Speleothems

The process of surface corrosion on speleothems is a common process in caves. It has been described all over the world in touristic and non-touristic caves (Sarbu and Lascu 1997; Dublyansky and Dublyansky 1998; Tarhule-Lips and Ford 1998; Zupan-Hajna 2002; Auler and Smart 2004; de Freitas and Schmekal 2006; Martín-García et al. 2009).

The corrosion occurs when undersaturated or acidic waters (with high concentrations of CO_2 or H_2S) contact the surface of the bedrock and speleothems dissolving them. There are different mechanisms of corrosion; the most common is the condensation-corrosion that consists in the presence of aggressive condensed moisture over the rocks.

When a speleothem is corroded, the surface appears as a white matt powdery wrap making the speleothems appear chalky (Fig. 2). If the corrosion layer is thick enough, it usually falls off so the inner fresh part of the speleothems can be seen (Fig. 2a).

When polishing the samples, the thickness of the corrosion layer can be measured. Thinner lines of the same kind appear in the inner zones (Fig. 3a), all of which are concentric and appear between layers of fresh clean crystals (Fig. 3b,c). The thinner lines sometimes are invisible to the naked eye, but are visible under the

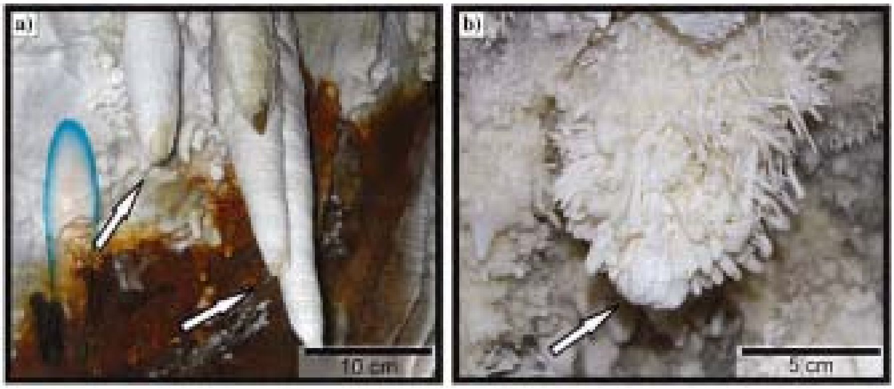

Fig. 2a,b Two examples of corroded speleothems in Castañar cave. The overall aspect is chalky and matt. **a** Calcitic stalactites. The tips of these stalactites have lost their chalky coating (*white arrows*). **b** Aragonitic anthodites corroded specially on the tips (*white arrows*)

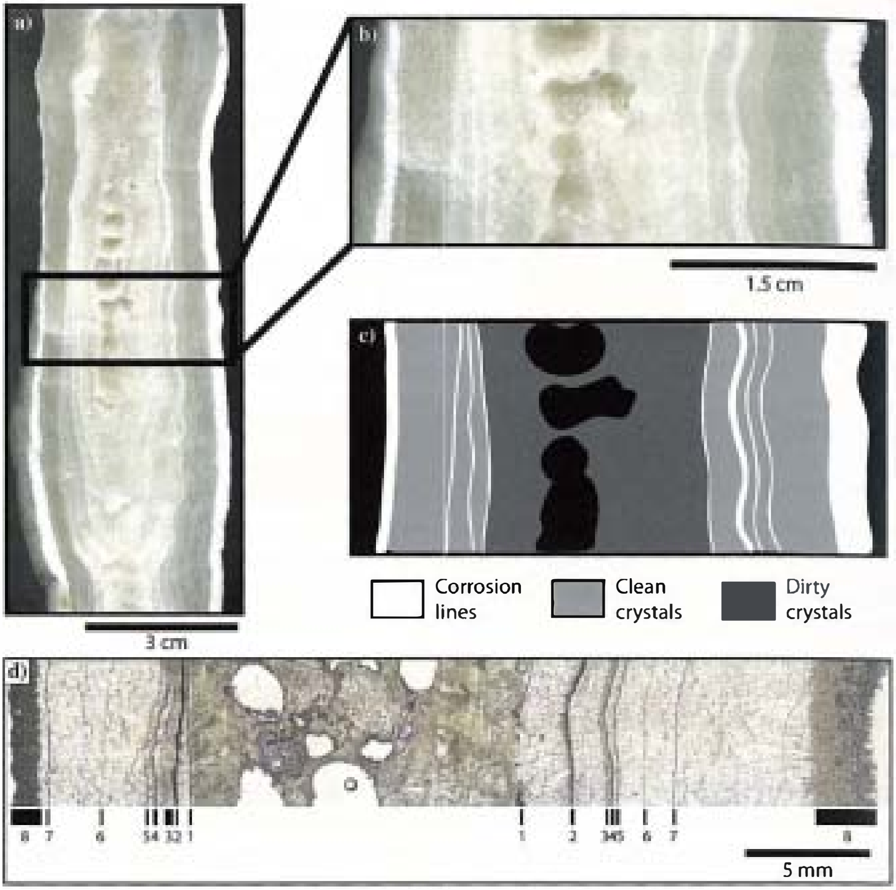

Fig. 3 **a** Polished sample of a stalactite. **b** Detailed view of a. From the surface to the inner zone it shows: a superficial corrosion layer (*white*), clean crystals (*gray*) and a wide whitish zone that contains concentric *white corrosion lines* of different thickness. The *holes in the middle* are the relics of the central channel that has been partially cemented. **c** Sketch based on b. **d** Microphotograph with plain polarised light. The *white lines* in hand sample here correspond to the *darker ones*. The number of corrosion lines observed under the microscope is larger than the observed in the hand sample. Also, the number of lines at each side of the central channel is the same

microscope (Fig. 3d). At both sides of the central channel the number of lines is the same but the distance between them, that represent growing stages, is different.

Under the microscope, the white layers look like a dark opaque structureless mass (Fig. 4a). This mass is constituted by small crystals formed by the dissolution of the larger ones that form the body of the speleothems (Martín-García el al. 2009) leading to micrite formation (Jones and Kahle 1995). In an initial stage previous stage of corrosion, when the small crystals are still not formed, the surfaces of the crystals appear partially dissolved and etched (Fig. 4b). The contact of this micritic mass with the fresh crystals is usually the crystal boundary, but if the corrosion is

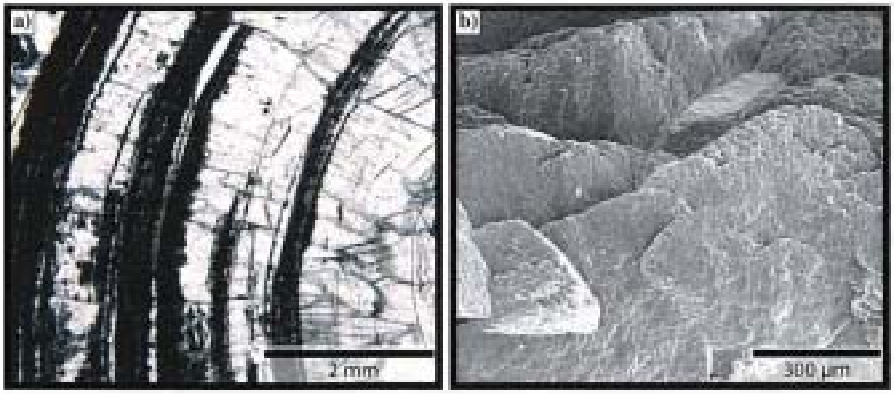

Fig. 4 **a** Microphotograph showing concentric corrosion lines between the crystal boundaries of the same growth band. Plane polarised light. **b** SEM image of calcite crystals showing etched surfaces

very aggressive the contact does not follow any boundary but they cut across the crystals.

5 Discussion

This corrosion process occurs only on the surfaces of the speleothems, thus the inner lines may correspond to ancient surfaces. This may indicate that the process is episodic in the area and that corrosion and growth alternate rather than occurring at the same time within the same speleothem.

The relation between the visits and the chemical degradation of the speleothems is not clear. The acidification of the atmospheric moisture caused by human breath may amount to the same as the natural process, but the inner lines indicate that this process has been occurring for thousand of years, long before the cave was firstly discovered and visited.

The most probable mechanism of corrosion in the case of Castañar cave is the one explained by Palmer (2007) that is applicable to caves where little or no circulation of air and little running water are common features, as in the example of this study. The main idea of this model is that water condenses in the upper parts of the cave and then seeps down through the rock pores or over the rock surfaces dissolving the materials.

6 Conclusions

The corrosion of the speleothems is a natural process that occurs in touristic and non-touristic caves causing the loss of brightness and general disfigurement of the formations. It occurs only on the surface of the speleothems and the host rock and it is recorded in the speleothems during their formation providing information about the growing mechanisms.

The contribution of the visits to this degradation process is not clear, but is likely to be pronounced, as evidenced by the existence of old lines preserved.

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References

Alonso-Zarza AM, Martín-Pérez A (2008) Dolomite in caves: recent dolomite formation in oxic, non-sulfate environments. Castañar Cave, Spain. Sediment Geol 205:160–164.

Auler AS, Smart PL (2004) Rates of condensation corrosion in speleothems of semi-arid north-eastern Brazil. Speleogenesis and Evolution of Karst Aquifers, 2.

de Freitas CR, Schmekal A (2006) Studies of condensation/evaporation processes in the Glow-worm Cave, New Zealand. Int J Speleol 35:75–81.

Díez-Balda MA, Vegas R, González-Lodeiro F (1990) Central-Iberian Zone. Autochthonous Sequences: Structure. In: Dallmeyer RD, Martínez-García E (eds) Pre-Mesozoic Geology of Iberia. Springer-Verlag, Berlin.

Dublyansky VN, Dublyansky YV (1998) The problem of condensation in karst studies. J Cave Karst Stud 60:3–17.

Jones B, Kahle CF (1995) Origin of endogenetic micrite in karst terrains: a case study from the Cayman Islands. J Sediment Res A65:283–293.

Martín-García R, Alonso-Zarza AM, Martín-Pérez A (2009) Loss of primary texture and geochemical signatures in speleothems due to diagenesis: Evidences from Castañar Cave, Spain. Sediment Geol 221:141–149.

Palmer AN (2007) Cave Geology. Cave Books, Ohio.

Sánchez-Moral S, Cuezva S, Lario J et al (2006) Hydrochemistry of karstic waters in a low-energy cave (Castañar de Ibor, Spain). In: Durán JJ, Andreo D, Carrasco F (eds) Karst, cambio climático y aguas subterráneas. Hidrogeología y aguas subterráneas. IGME, Madrid.

Sarbu SM, Lascu C (1997) Condensation corrosion in Movile Cave, Romania. J Cave Karst Stud 59:99–102.

Tarhule-Lips RFA, Ford DC (1998) Condensation corrosion in caves of Cayman Brac and Isla de Mona. J Cave Karst Stud 60:84--95.

Zupan-Hajna N (2002) Chemical weathering of limestones and dolomites in a cave environment. In: Gabrovšek F (ed) Evolution of karst: from prekarst to cessation. Zalozba ZRC, Postojna-Ljubljana.