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Relationships between colour and diagenesis in the aragonite-calcite speleothems in Basajaún Etxea cave, Spain

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ABSTRACT

Basajaún Etxea Cave, North Spain, contains a wide morphological and colour variety of speleothems. Most of them are composed of aragonite, but calcite speleothems are also found. Their most common colour is white, but there are also pink, green and turquoise speleothems, in different areas of the cave. Mg-rich dissolution waters from the cave's crystalline dolostone and magnesite host rock favour aragonite precipitation and drive important diagenetic changes. In this paper we will discuss how diagenesis modifies speleothem texture, mineralogy and geochemistry, causing significant changes in the colour. We also discuss how speleothems that have undergone diagenesis may also be useful indictors of paleoclimatic conditions. Our work shows that diagenesis changes the colour of the speleothems because of the mobility of the chromophore elements during this process. Along with this elemental alteration comes the loss of the primary isotopic signals of speleothems. Detailed petrological studies of speleothems should precede their analysis for palaeoclimatic reconstruction so that influence of areas affected by diagenesis can be eliminated. In addition, diagenetic signals also contain valuable information on the changes of the waters within the cave, and the overall evolution of speleothems and the cave itself.

1. Introduction

The study of petrology and diagenesis of speleothems, recently an interesting area of research, continues that of only a few papers dealing with it before the 1980's (Folk and Assereto, 1976; Kendall and Broughton, 1977, 1978; Cabrol, 1978). More recent studies dealing with speleothem diagenesis (Frisia, 1996; Frisia et al., 2002; Woo and Choi, 2006; Woo et al., 2008; Hopley et al., 2009; Aramburu Artano et al., 2010; Pagliara et al., 2010; Perrin et al., 2014; Zhang et al., 2014) have shown that diagenetic processes: 1) change the geochemical signals used for dating and/or paleoclimatic studies (Martín-García et al., 2009; Frisia and Borsato, 2010); 2) driven by environmental changes, are also archives of paleoenvironmental conditions (Cabrol and Coudray, 1982; Frisia et al., 2002); 3) especially in aragonite speleothems (where the driving mechanisms are less well-known than those of their marine counterparts), can produce similar features to those observed in marine aragonite deposits like micrite, cements and aragonite to calcite transformation (Woo and Choi, 2006; Martín-García et al., 2009; Martín-Pérez et al., 2012; Perrin et al., 2014; Zhang et al., 2014); 4) can change the aspect, shine and colour of speleothems, modifying their impression on visitors (in case of tourist-attraction caves). Diagenetic processes affect mostly aragonite speleothems, due to their unstable nature under surface conditions, transforming them to calcite, the stable polymorph (Hill and Forti, 1997; Rowling, 2004). Aragonite is an unstable polymorph of $CaCO_3$ due to its structure, in which the space for the Ca ion is larger than in the calcite (Klein and Hurlbut, 1993). However other carbonate cave minerals, such as calcite or huntite, also undergo such diagenetic processes as dissolution, recrystallization, micritization or even dolomitization (Alonso-Zarza and Martín-Pérez, 2008; Jones, 2010; Melim and Spilde, 2011). Diagenetic processes in speleothems have been unequivocally recognized (Railsback et al., 2002; Ortega et al., 2005; Melim and Spilde, 2011; Devès et al., 2012; Lachniet et al., 2012; Martín-Pérez et al., 2012), driven by the differences in chemistry through time of the waters within the cave and by kinetics.

However detailed petrological and geochemical studies are critical to distinguish between the primary signals and those imprinted by

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diagenesis (Cabrol, 1978; Bar-Matthews et al., 1991; Frisia et al., 2002; Woo and Choi, 2006). Usually carbonate speleothems lack very distinctive colours, this is not the case with those found in some caves, such as for example Cliefden, Australia (Turner, 2002), the Blue Cave, France (Cabrol, 1997), Crovassa Azzurra Cave, Sardinia (Caddeo et al., 2011) or the Basajaún Etxea Cave studied in this paper, all of them showing blue to turquoise speleothems. The colour of speleothems has formerly been related to the presence of Mn, Co, Cu (White, 1997) or humic compounds (James, 2003).

This paper analyses mostly aragonitic speleothems from Basajaún Etxea Cave, Navarra (Spain), which have undergone different diagenetic processes. Some of the speleothems show very distinctive green, turquoise or pink colour. The aims of our paper are to: 1) characterize the diagenetic processes that the speleothems have undergone, describing the mineralogical, textural and geochemical changes occurring during diagenesis; 2) discuss the causes of the diagenetic processes and their possible environmental significance and, 3) elucidate what element likely correlates with the colour of speleothems and the possible variation of colour and trace element content during diagenesis. In doing so we intend to offer clear criteria for the recognition of diagenetic processes in speleothems and contribute to a better understanding of the study of early diagenesis in caves.

2. Case setting

2.1. Regional geology and climate

Basajaún Etxea cave (also called Ayerdi III) is part of a group of caves located on the northern slope of Mount Ayerdi (815 m a.s.l.), 2.5 km to the north of Lantz, Navarra (Spain) (Fig. 1), within the South Pyrenees. These caves are located within and area used by the Romans for Cu-mining in the 1st and 2nd centuries (Mezquíriz, 1973).

The cave is located in the Alduides-Quinto Real Massif, one of the three Basque Massifs, of Palaeozoic age, between the Pamplona fault and the South Pyrenean Zone, in the Western Pyrenees (Fig. 1a).

The deformation is characterized by the presence of N-S and NNW-SSE oriented folds and E-W and ENE-WSW oriented faults. The most important structure is the thrust fault to the south of the Massif, which places the Palaeozoic materials over the Upper Cretaceous ones.

In the East sector of the Massif, Devonian to Carboniferous deposits are 2500–3000 m thick. The base is characterized by the presence of schists and sandstones of Devonian age, followed by an alternation of carbonates and schists of the Devonian–Carboniferous transition. Finally a thick Late-Carboniferous turbiditic succession crops out, pinching out onto shallow carbonate platforms (Olmedo et al., 1992).

These caves are hosted in crystalline dolostones and magnesites interbedded between sandstones and shales, all of Carboniferous age (Fig. 1b). Chalcopyrite mineralizations present in the dolostones have a hydrothermal origin and appear as veins with a N-S orientation (Trapote Redondo et al., 2006). Sandstones and shales occur in well-laminated decimetre-thick beds. These siliciclastic rocks are in places weathered, mainly by hydrolysis.

The climate of the area is temperate oceanic climate (Cfb according to the Köppen–Geiger climate classification (Peel et al., 2007). The nearest weather station is in Esteribar (8.93 km far, altitude 615 m a.s.l.) and it gives a high average precipitation (1200–2500 mm/year) distributed regularly throughout the year. The mean external annual temperature is between 6 and 8 °C.

2.2. Cave setting

Basajún Etxea Cave is a small sub-horizontal cave, is 900 m in length with interior temperature of about 8 °C and relative humidity of 99%, constant throughout the year (López-Acevedo Cornejo, 1976). The waters of the cave are slightly basic, with pH fluctuating from 7.7 to 8.2, and Mg/Ca molar ratio of 2.3 (López-Acevedo Cornejo, 1976).

Most of the speleothems in Basajaún Etxea cave are on the ceiling and walls, while scarce on the floors (stalagmites). Following the classification of Hill and Forti (1997), the morphologies of these speleothems are crusts, frostworks, helictites, stalactites, columns and draperies.

One of the most striking features of this cave is its green, turquoise and pink speleothem (mostly) crusts, helictites, and soda-straws which are distributed irregularly throughout the cave (Fig. 2).

The cave morphology is characterized by a network of galleries with a NW-SE orientation controlled by lithology and bedrock. Of its two levels, the lower is up to 30 m below the surface while the upper level is only 5 m below surface. Both levels are connected at two points; by a steep ramp at the end of the first upper-level room, and through a hole about 25 m deep at the end of the large

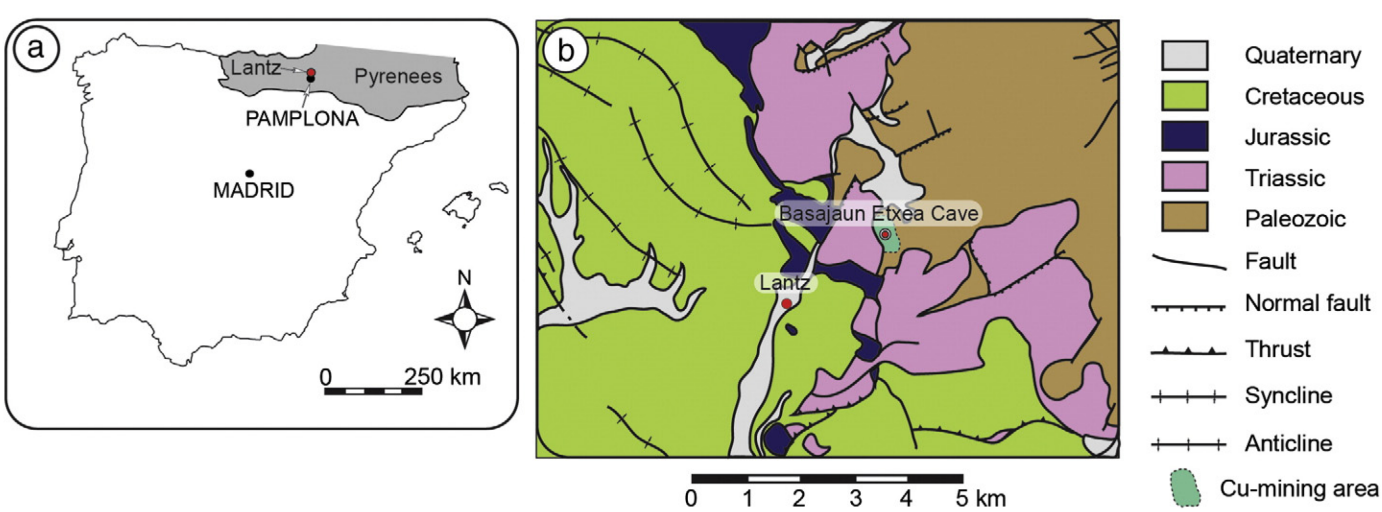

Fig. 1. Geological setting of Basajaun Etxea cave. a) Location of the area studied within the Iberian Peninsula. The grey zone corresponds to the Pyrenees. b) Simplified geological map of the region.
Modified from IGME (1975, 1978).