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Guilhem Mauran[1,2], Lena Bassel[1], Catherine Ferrier[3], Delphine Lacanette[4], Bruno Bousquet[5], Rémy Chapoulie[1]
[1] IRAMAT-CRP2A UMR 5060 – CNRS-Université Bordeaux Montaigne, Maison de l'archéologie, Esplanade des Antilles, 33607 Pessac Cedex, France
[2] UMR 7194 - Histoire Naturelle de l'Homme Préhistorique (HNHP) - CNRS-MNHN-UPVD-SU, Musée de l'Homme, 17 Place du Trocadéro, 75116 Paris, France
[3] PACEA UMR 5199 – CNRS-Université de Bordeaux, Bâtiment B8, Allée Geoffroy Saint-Hilaire, CS 50023, 33615 Pessac Cedex, France
[4] I2M UMR 5295 – CNRS-Université de Bordeaux
[5] CELIA, Université de Bordeaux UMR 5107, 33400 Talence, France

ABSTRACT

Cave Art is a fragile testimony of past humans societies and the development of modern behaviours. In limestone caves, moonmilk commonly endanger the artworks. It is a calcite-deposit known to present a large variability of chemical composition and morphological structures, hosting numerous microbial communities. The possibility to characterize this deposit on the field would help to get a better understanding of the cave behaviour and set up proper conservation measures.

The present study analyses the variability of a moonmilk strip of metric size in the Leye Cave. This cave located in the Vézère valley (Dordogne, France) is not ornate, and has been selected to become a laboratory cave in which in-situ observations and micro-sampling can be carried out, before performing them into cavities hosting parietal artworks. SEM observations of twenty-four samples allowed investigating, for the first time, the variability of the moonmilk deposit over a same wall of few meters dimension. Our observations highlight low variability of moonmilk at the microscopic scale regarding the chemical composition and the morphological structures despite significant macroscopic diversity, thus providing insights to optimize the sampling strategy of moonmilk in ornate caves.

Keywords

Calcite, Moonmilk, SEM, Sampling strategy, Vézère Valley, Cave Art

Introduction

Cave art is a unique testimony of the development of complex behaviours among modern humans societies, exposed to various alterations threatening its preservation. Henri Breuil (1952) and Philippe Renault (1983) initiated, through large-scale studies on the condition of the walls supporting parietal representations as well as on the art conservation (Renault 1983, 1987, 1989), the awareness of the parietal representations conservation. The appearance of the "green and white diseases" in Lascaux Cave (Dordogne, France) lead rock art specialists (Lorblanchet et al. 1973, Lorblanchet 1979) to further develop their work, resulting in the implementation of preservation measures such as access restriction (Schoeller 1967; Brunet 1992; Malaurent et al. 1992). Since then, numerous investigations focused on the field and covered various topics: visitors-induced wall-corrosion (Sanchez-Moral et al. 1999), characterization of specific artworks concretions (Sanchez-Moral et al. 1999; Cañaveras et al. 2001; Cuezva et al. 2009), microbiology from caves containing artworks (Cañaveras et al. 1999, 2001; Cuezva et al. 2009, 2012; Sanchez-Moral et al. 2003, 2012), influence of surface's pollution on the conservation of artworks (Arroyo et al. 1997).

Although anthropic actions were to blame for cave art degradation, it was also shown that non-anthropological chemical and physical mechanisms alter cave walls integrity and therefore the art they support (Lorblanchet et al. 1973; Renault 1983; Aujoulat 2002). Paving the way for current conservation concerns, these studies highlighted the large diversity of alteration processes.

Among the various deteriorations cave walls encounter, carbonate-calcite moonmilk is a common deposit in limestone caves. It is a microcrystalline aggregate with a high porosity and water content structured by small needle-fibers calcite (Bernasconi 1975; Hill and Forti 1997; Cañaveras et al. 1999, 2001, 2006; Borsato et al. 2000; Northup and Lavoie 2001; Chirienco 2002; Lacelle et al. 2004; Perrone-Vogt and Giles 2006; Richter et al. 2008; Curry et al. 2009; Baskar et al. 2011; Sanchez-Moral et al. 2012). Found in caves hosting parietal artworks, e.g., Altamira (Cañaveras et al. 1999, 2001, 2006; Sanchez-Moral et al. 2012), Tito Bustillo (Cañaveras et al. 2001), Lascaux (Berrouet 2009), Les Combarelles, Gargas (Berrouet 2009), Cosquer (Clottes et al. 2005), Kapova (Chervyatsova et al. 2014), moonmilk constitutes either the support of the representations, or deposit forming either close or over them threatening their long-term preservation. For these reasons, relative dating of moonmilk formation can be carried out. Paleolithic cave paintings covered by moonmilk are particularly reported on the ceiling of the Polychromes Hall in Altamira Cave or on the west wall of the Chamber of Signs in Kapova Cave (Cañaveras et al. 1999; Chervyatsova et al. 2014). Moreover, as moonmilk altered the support developing films of several millimetres of thickness (Sanchez-Moral et al. 2003; Cañaveras et al. 2012), it also represents major threats into altering rock engravings representations. Finally, moonmilk hosts a large microbial diversity ranging from archaea to fungi, therefore representing a large potential risk for the artworks (Cañaveras et al. 2001; Cuezva et al. 2009; Rooney et al. 2010; Braissant et al. 2012).

The acicular calcite composing moonmilk is also found in soils (Riche et al. 1982; Butel and Ducloux 1984; Verrecchia and Verrecchia 1994; Borsato et al. 2000; Lacelle et al. 2004; Bajnóczi and Kovacs-Kis 2006; Perrone-Vogt and Giles 2006; Richter et al. 2008; Cailleau et al. 2009b; Millière et al. 2011b; Sanchez-Moral et al. 2012; Bindschedler et al. 2014), making it a large spread habitus of yet uncertain origin. Abiotic (Borsato et al. 2000; Lacelle et al. 2004), biotic (Bajnóczi and Kovacs-Kis 2006; Cañaveras et al. 2006; Cailleau et al. 2009b; Baskar et al. 2011; Millière et al. 2011a, 2011b; Zammit et al. 2011; Braissant et al. 2012; Sanchez-Moral et al. 2012) and simultaneously biotic and abiotic (Braissant et al. 2012; Sanchez-Moral et al. 2012) processes have been postulated to explain genesis and growing of moonmilk. On the contrary, the kinetic of moonmilk formation remains largely unknown and understudied. To our knowledge, only one reference mentions a time scale of around 50 years leading to the formation of a moonmilk deposit over an artificial wall of Altamira Cave (Cañaveras et al. 1999). The kinetic and time of formation of these deposits are still questions of interrogation that should be investigated in forthcoming studies.

The issue of the origin of the acicular calcite is partially due to the variability of the materials it refers to. During a long time, the expression « needle-fiber calcite » was used to describe three different features, each supposed to have a different origin. In the present study « needle-fiber calcite » refers to the smooth and usually paired needles forming cross section shaped as an eight, or an X, or other complex forms, while « epitaxial needles » refers to the needle-calcite features with serrated edges. Finally, « nanofibers » is the term used for microrods of a few micrometres long (Verrecchia and Verrecchia 1994; Bajnóczi and Kovacs-Kis 2006; Cailleau et al. 2009b).

While needle-fiber calcite in soils is claimed to be of fungal origin (Cailleau et al. 2009a, 2009b; Bindschedler et al. 2010, 2012; Milliere et al. 2011a, 2011b), the absence of fungal residues in caves suggests that biomineralization by actinobacteria might be an alternative to moonmilk development (Cañaveras et al. 2006; Zammit et al. 2011; Braissant et al. 2012; Sanchez-Moral et al. 2012). The epitaxial needles correspond to calcite needle-fibers that have evolved with some epitaxial growths on it. Its origin is thought to be mainly due to specific physico-chemical conditions, especially due to carbonate solubilisation and dissolution cycles. Nanofibers seem to be related to bacteria (Verrecchia and Verrecchia 1994) or actinobacteria (Cañaveras et al. 2006; Zammit et al. 2011).

As moonmilk is present in numerous caves hosting cave art, overlying multiple panels and representations, studying its origin and possible consequences on rock paintings is crucial. Since various parameters occur at distinct rates and distinct parts of the cave, the kinetic and impact of the alteration processes they induce might highly differ from one scale to another, ranging from microscopic to regional scales. Consequently, it is of tremendous importance to understand the various processes from their origin to their consequences and propose appropriate preservation strategies. Such a scope can only be reached through its analyses at the distinct scales of the karst, the cave, the room, the wall, the panel, the parietal representation and further down, it thus requires long-term investigations with various complementary sampling procedures.

Cave Art value and uniqueness prevent large sampling procedure, though not local ones performed in the vicinity of the representations after ensuring their representativeness. Therefore, evaluating the variability of cave walls alterations is of first consideration to ensure the feasibility and utility of such a tool for cave curators. Moonmilk is largely spread in karstic environments and assessing its variability over the scale of a panel provides first insights into the sampling procedures to use for future work on cave walls alterations.

The aim of the present work is to study the physico-chemical variability of a moonmilk deposit over an entire wall. It provides key insights to reduce the extent of invasive actions and to set up appropriate monitoring activities and sampling strategies to understand the development of moonmilk in the Leye Cave (Dordogne, France). Enhancing procedures and knowledge about this laboratory cave will later be serving the conservation on ornate contexts.

METHODOLOGY

Materials

The Leye Cave is located in the Vézère Valley, an area riche in ornate caves, and has been selected as a laboratory cave based on its numerous similarities with the surrounding ones hosting parietal artworks (Lacanette et al. 2013). The Leye Cave lies between 4 and 12 m under the ground surface and has a length of 50 m. White minerals deposits were observed inside the Leye Cave, overlying different substrates, including limestone host-rock, altered limestone, calcite, grey bacterial spots and clays. Inside Leye Cave, in a small room called the Throne Room (Fig. 1), calcite moonmilk and coralloids, two distinct facies, coexist. Each of them spreads on a different wall separated from less than two meters one from another. While coralloids cover the south wall (Bassel et al. 2016; Chapoulie et al. 2017), moonmilk strip largely covers the north wall (Fig. 1). This peculiar distribution will be investigated in the future. The present study focuses on the moonmilk variability found on the north wall of the Throne Room of the Leye Cave to better implement monitoring activities (humidity, temperature…) to understand the origin of this calcitic facies. In the Throne Room, moonmilk exhibits a large macroscopic variability ranging from a thick white film to a pellicular yellowish one.

Three samples (not shown here), were first taken in order to investigate the influence of the storage conditions on their microscopic morphology. One additional sample of calcite was collected in Leye Cave on the temperature station, namely a metallic box located in the Draperies Gallery. As its development is clearly due to water leakage on this box, this sample is considered as a local calcite reference.

In order to study the variability from a morphological and physico-chemical point of view, twenty-four samples of moonmilk-like deposits were collected with a sterile scalpel from the rock surface of the north wall of the Throne Room (Table 1 and Fig. 1). Sampling was performed after close observations of the wall and its deposits, ensuring the representativeness of the samples towards the macroscopic variability of the moonmilk in both its vertical and lateral extension. Sampling procedure was carefully documented through photos and description of the sampled areas. Storage of the samples was thence performed in sterile microplates at around 21°C (average annual temperature, recorded with an in-situ detector) until laboratory procedures, according to the previously observations made of the three samples and not shown in this article.

METHODS

Influence of storage conditions

Before carrying out the extensive sampling campaign on the north wall of the Throne Room, three samples of moonmilk from the Leye Cave were studied during several months to know more about their temporal evolution under three distinct storage conditions. The first sample was stored in the laboratory (average temperature on 22 months: 23±4 °C), the second one in the basement of the laboratory building (average annual temperature: 18±7 °C), and the third one in an old subterranean quarry hosting biominerals alike the one observed in the Leye Cave (average annual temperature: 14±6 °C). The temperatures of storage were recorded continuously over time (every 30 minutes), thanks to in-situ sensors. The samples were observed under SEM daily during a first period of 14 days, then weekly for one month and since no temporal evolution was observed, they were finally monitored once a month for one year. Observations of the samples investigated the possible evolution of the organic contents and of the microstructure of the moonmilk at the microscopic scale. Both were assessed thanks to macroscopic and SEM observations.

At the end of this full year of monitoring, no evolution over time has been observed on the sample stored in the laboratory or its basement, while organic contents changed into the one stored in the quarry. As no organic content developed and the micro needles structure did not collapse nor evolve, and for convenience, it was decided to store the moonmilk samples dedicated to SEM-EDS observations inside sterilized boxes from the sampling in the cave, and then to put them in a locked closet in the laboratory at around 21°C until the analysis.

Digital microscope

The Hirox VCR 800 digital microscope was operated in the laboratory on samples from the Leye Cave in order to assess its use to achieve in-situ moonmilk identification. Several images acquired with the digital microscope with different magnification factors were stacked together with the Helicon Focus software (HeliSoft) to reconstruct the moonmilk 3D structure.

SEM

Micro-fragments collected from the cave wall were observed and analysed with a JEOL JSM-6460LV Scanning Electron Microscope (SEM) coupled to an Oxford Instrument X Max Energy Dispersive Spectrometer (EDS). Samples were first observed in the Low vacuum mode without any preparation, at a pressure of 20 Pa, with a tension of 20kV, and a working distance around 8 mm.

Two samples from the Leye Cave, chosen on the basis of their high diversity of needle fiber calcite shapes, were gold-coated (Emscope SC500) during 180 s, at 25 mA, and finally observed in the High vacuum mode.

To study the moonmilk-substrate interfaces, four petrographic thin sections were made from four different samples, clay being the substrate for two of them and calcite for the two others. The thin sections were prepared with a diamond blade of 150 nm height. They were observed in the Low Vacuum mode of the SEM-EDS instrument.

RESULTS

Spatial variability

White concretions are largely spread on the north wall of the Throne Room, where it is organized into a large band horizontally elongated of around 60 cm large and 4 m long. Its thickness, measured on the microsamples, varies significantly from pellicular (less than 1 mm) to more than 5 mm (Table 1). The thickest layers are located on the edges of the median strip, while its centre is presenting thinner layers. The sundry observations mentioned in Table 1 were collected thanks to both macro observation on the field in order to describe the criteria such as color, morphology and support as well as SEM observations of the micro samples to determine the present generations and the occurrence of epitaxial needles and NFC.
Moonmilk aspect varies in the nature of the macrostructures it forms (buds to irregular films), in their size (small to big buds) and in colours (white-beige to grey). This variability is not imputable to the substrate, despite its own variability (Table 1). Indeed, moonmilk covers two types of substrates: a loamy-sandy sediment heritage of an ancient alluvial filling, almost entirely eroded which subsists as thick inlays and very thin films, and greyish calcite, less frequently found and present beneath as well as above the median strip. Moonmilk is thus able to similarly form and develop on both loamy-sandy sediment and calcite supports.

Despite the clear macroscopic differences observed on the moonmilk developing on the north wall of the Throne Room, all the samples seemed to present a similar mesoscopic structure made of acicular calcite crystals, confirming the presence of moonmilk. Laboratory tests conducted later on confirmed the identification of moonmilk by the observation of needle-fiber calcite using stacked digital microscope pictures.

Variability of facies

The SEM observations of the 24 various samples enabled a better insight into the microscopic structure of Leye Cave's moonmilk. At the microscopic scale, large variability was observed on the calcite needles morphology and organic content of the different samples (Fig. 2 and Fig. 3).

Three distinct facies were spotted: needle-fiber calcite (Fig. 2.A), nanofibers (Fig. 2.B) and epitaxial needles (Fig. 2.C). These three kinds of needles observed corresponds to the morphologies already reported by Cailleau et al. (2009b).

Needle-fiber calcite (NFC) found in Leye, namely the long monocrystalline needles of calcite, displayed on Fig. 2.A are crystalline structures of 1 to 5 microns wide and 100 to 200 microns long. They are smooth and are most of the time paired forming various cross-sections. Epitaxial needles shown on Fig. 2.C have a similar shape than the NFC, though they exhibit signs of epitaxial growths, which lead to altering their shape and edges. Their diameter is similar to the NFC and varies between 0.5 to 5 microns, though presenting smaller length, ranging from 5 to 150 microns. Nanofibers displayed on Fig. 2.B are much smaller than the NFC and correspond to microrods of typically 0.5 µm diameter and 2 µm length. They usually connect the NFC between them. Sometimes bacterial communities develop on those nanofibers (Fig. 3.C and Fig. 3.D).

Moonmilk chemistry and structure

SEM-EDS analyses provided some information on the elemental composition of Leye Cave's moonmilk. Figure 4 presents different SEM-EDS spectra ranging from the reference calcite collected in the Draperies Gallery to the spectra related to a microbial structure spotted in one of the samples from the Throne Room. The spectrum of the calcite needles composing the moonmilk without any microbial contamination is also shown (Fig. 4.B). Since this latter corresponds to a very local analysis designed by the x mark in the image B, an "average" spectrum is also presented (Fig. 4.C), comparable to a typical moonmilk spectrum.

Thin-sections together with the samples SEM observations highlighted the presence of three distinct areas structuring the moonmilk sampled in the Throne Room of the Leye Cave (Fig. 5).

The most external part (Fig. 5.A) is the visible one on the field: it is mainly composed of low-altered white and superficial NFC. These NFC present less alteration phases than the ones found inside the moonmilk microstructure.

The middle area (Fig. 5.B) is the interface between the NFC and the substrate (whether clay, limestone or calcite). It is rich in clay phases, does not depend on the substrate and presents a high porosity. The NFC in this area are lying on the substrate, exhibiting numerous evidences of mechanical and chemical alterations, and entangling together with some clayish fractions forming a beige-brownish crust clearly visible on the sample cross section.

The most internal part (Fig. 5.C) is the substrate which presents a considerable variability. It seems that clay and epitaxial needles assure the cohesion between the middle area and the internal part. Indeed, although it was not always observed on the field, and therefore, not reported in Table 1, all the samples analysed in the frame of this work presented at least a thin layer ensuring the binding of the moonmilk with the host-rock composed of calcite needles, both epitaxial and broken NFC, entangled with minor clay fraction possibly deposed by water leaking over the wall.

DISCUSSION

Identification

The moonmilk covering the north wall of the Throne Room in Leye Cave presents a large macroscopic variability which makes the identification on the field difficult by only relying on observations at this scale. Being able to establish a first in-situ diagnosis is primordial to identify easily the presence of moonmilk and help to understand its origin and spread. The laboratory tests performed with the digital microscope are in this way crucial since such observations on the field without the need of sampling could suffice to confirm the diagnosis. Such a technique should consequently be implemented for in-situ sampling strategy and direct identification.

Moonmilks variability

The large macroscopic variability of the moonmilk could not be correlated to any microscopic variability in terms of features and characteristics. Indeed, although some diversity of the calcite needles forming the speleothem was spotted, all the samples studied are composed of NFC, epitaxial needles and nanofibers. The study mainly evidences the existence of two distinct phases of moonmilk development, strengthening the structure proposed by Cañaveras et al. (2006).

Based on this model, during the first stage of moonmilk formation, microorganisms fix themselves to the rock surface. As the microbial communities develop, they release metabolic products leading to the dissolution of the rock and calcification of various microbial features such as hyphae and extracellular polymeric substance. These calcified structures lead to a network that under further growth collapse due to mechanical effects, corresponding to the second phase of the model (Cañaveras et al. 2006). The final stage corresponds to the development of new microbial communities over the collapsed structure, cementing and leading to the formation of a crust from the collapsed calcite microstructure.

The internal areas (Fig. 5.B and C) correspond to the substrate and the earliest development of moonmilk. Most of the acicular needles are epitaxial ones entangled with clay and seem to be the direct connection between the moonmilk and the support. When connected to the low porosity of the material in this part, such an observation points out to a collapsed moonmilk structure in which the NFC greatly suffered from various alteration processes imputable to water leaching and mechanical breakdown. The most external part (Fig. 5.A) suggests the existence of a second phase of moonmilk development over the initial acicular calcite structure.

Variability and sampling strategy

Regarding sampling strategies, the microscopic and mesoscopic structures of the various samples indicate a general homogeneity over the whole north wall of the Throne Room of Leye Cave, despite some minor discrepancies. Indeed, the macroscopic differences are not related to any microscopic or mesoscopic specificities. The only differences spotted at the microscopic level such as the presence of microorganisms (Fig. 3), could not be considered as relevant when considering the moonmilk itself. From a microbiological point of view, it is well-known that moonmilk hosts a large diversity of microorganisms. Although it is acknowledged that microbial activity mediates moonmilk genesis (Cañaveras et al., 1999, 2006; Bindschedler et al. 2010, 2014; Portillo and Gonzalez 2011), a large number of the organisms thriving on this kind of speleothem do not play any role in its formation and only benefit from the unique ecosystems it provides: high water content and nutrients trap thanks to the porous structure formed by the acicular needles. The various microorganisms observed are testimonies of the microbial activity thriving on the moonmilk and triggered some microbial analyses (Ferrier et al. 2015). Discussion about the microbial diversity existing on Leye Cave's moonmilk is of uttermost importance in understanding the speleothem formation and its possible consequences in rock art context, though it goes beyond the scopes of the present work solely assessing the structural and physico-chemical diversity of the moonmilk at the scale of an entire wall.

SEM analyses highlight the high content in calcium within the moonmilk, with some minor content of silicium and aluminium imputable to trapped clays. As no significant variation in the chemical composition of the moonmilk was spotted, it seems that moonmilk development, although spread space, should be considered as homogeneous, at least for samples of the same generation.
If this characteristic is to be confirmed in the other parts of Leye Cave and in other caves from the Vézère Valley hosting moonmilk, it would then be possible to considerably reduce the sampling procedure to study its variability. Indeed, it would be possible to perform a first diagnostic through macroscopic observation coupled with digital microscope observations to state the extent of the moonmilk development.
The in-situ identification would provide an overview of the macroscopic speleothem structure, help to the identification of the concretions and lead to the proposition of an appropriate sampling strategy by provinding a proper connection and representativeness of the samples. As misidentification of the facies can still occur, in order to assess correctly the presence of moonmilk, it remains necessary to confirm this diagnostic thanks to microsamples analyses. Nonetheless, the present study proves the low variability of a monnmilk deposit at the scale of a wall, thus inferring that the analysis of one sample is enough to confirm the presence of moonmilk over an entire wall. At this point, the implementation of a database about cave walls concretions and alterations would greatly help, as it would provide key information about the various speleothems encountered in karstic environments. Naturally, the use of a local database with cavities of the same region would ensure a better understanding of the alterations one could find in a cave.

In the case of caves hosting some parietal representations, such a database could permit to provide curators with an efficient tool to confirm their diagnosis and help them to understand the evolution of the cave and the artworks it hosts. In case of doubts, a sampling procedure far from the paintings or engravings endangered by moonmilk development could then deliver information of the deposit. Indeed, as demonstrated in the case of the Throne Room of Leye Cave, the study of the microscopic features of the samples could be performed on samples collected on the same wall but far from the valuable part of the wall, reducing considerably the drawbacks of the intrusiveness of such techniques (Chapoulie et al. 2017). As moonmilk presents a large variability in its chemical and structural composition, local sampling would then complement the in-situ observations by providing chemical composition, morphologies of the calcitic needles, general structure and microbial content insights allowing to understand its development: continuous or not, existence of several growth phases, and coupling with other speleothems.
As correlation between dating measurements and environmental proxy revealed crucial data on the conditions of formation of the coralloids of the Leye Cave (Bassel 2017), dating the two generations of moonmilk is a crucial step to understand their developments. Although, arduous because of the size of the acicular calcite and the presence of impurities in the moonmilk structure, dating the two generations would be made easier thanks to their possible distinction by in-situ observations with the digital microscope. Moreover, thanks to the moonmilk microscopic similarity over the wall of the Leye Cave, dating could be performed on some specific locations and not all over the wall as it was done with the samples studied in this work.
If confirmed by dating, the low variability of the moonmilk observed in the Throne Room of Leye Cave could make moonmilk a good candidate to provide chronological data in connection with rock art thanks to samples taken far apart. Until now, to our knowledge, studies focused on dating or characterising calcite layers covering paintings focused on few areas or local points (Ruiz et al. 2012; Jones et al. 2017; Sanchidrián et al. 2017).

The spatial distribution in the various areas of the Leye Cave and on numerous distinct supports of the cave tend to show that moonmilk does not require very specific conditions to develop in karstic environments. It is supported by the literature considering moonmilk as the most abundant speleothem of limestone caves.

CONCLUSION

Our study presents the first analysis of moonmilk variability over an entire wall of 5 meters long. It highlights the low correlation of the macrospic variations with the physico-chemical microscopic properties of the moonmilk deposit. The present paper shows the existence of two different phases of development, reinforcing previous models of moonmilk formation. Despite the two generations, it evidences the low variability of this speleothem at the scale of the wall under study, underlining the possibility to reduce the number of samples in case of laboratory analysis.

Thanks to laboratory observations performed with a digital microscope, further investigations are being carried out to analyse the variability of the moonmilk at the scale of the cavity but also at the scale of the Vézère Valley. Indeed, field surveys have been performed to locate numerous cavities in which moonmilk is found. Analyses to study their variability will be performed to have a better insight on the variability of this calcite speleothem.

These analyses, implying new galleries of Leye Cave and other cavities of the region, will provide crucial information for the understanding of moonmilk development. The protocol developed during the study of the Throne Room of Leye Cave relying on in-situ observations at both macroscopic and microscopic scale, coupled with elemental analyses, microbial, water and organic contents analyses would help to understand this speleothem and to suggest strategies to preserve the fragile parietal artworks threatened by this specific alteration.

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FIGURE CAPTIONS

Figure 1: Localization of the studied samples on the north wall of the Throne Room with in insert the topological map of the Leye Cave.

Figure 2: Variability of the carbonate-calcite facies encoutered in the moonmilk samples of Leye. A: NFC with an eight (center) and an X (right) cross-section. B: Nanofiber of possibly microbial origin developed on NFC of different shapes. C: Epitaxial needle with distinct phases of growth. D: Calcite crystal.

Figure 3: Microbial evidences observed with SEM-EDS. A: Microbial structure imputable to fungal contamination. B: Bacterial communities embedded in extracellular polymeric substance structure. C: Spores with echinulate ornamentation. D: Commonly cave-found bacteria, shaped like beads-on-a-string, of unknown phylogenetic affiliation.

Figure 4: Moonmilk elemental composition. A) Observation of reference calcite and associated SEM-EDS spectra (investigated area corresponds to the black square). B) Observation of NFC and SEM-EDS measurement on a single NFC with associated SEM-EDS spectra (the spot is indicated by the cross). C) Observation of a structure of NFC and associated SEM-EDS spectra (investigated area corresponds to the black square). D) Observation of an organic structure close to NFC and associated SEM-EDS spectra (investigated area corresponds to the black square).

Figure 5: Moonmilk structure observed by SEM. A: The recent stage with low-altered NFC. B: The first stage of collapsed NFC entangled with clay. C: The link between the moonmilk speleothem and the clayish support on which it is lying. The insert (down, left) shows a larger view with optical microscopy of this complex superposition.

TABLE CAPTION

Table 1: Observations of the moonmilk variability from macroscopic to microscopic scale.

Figure 1

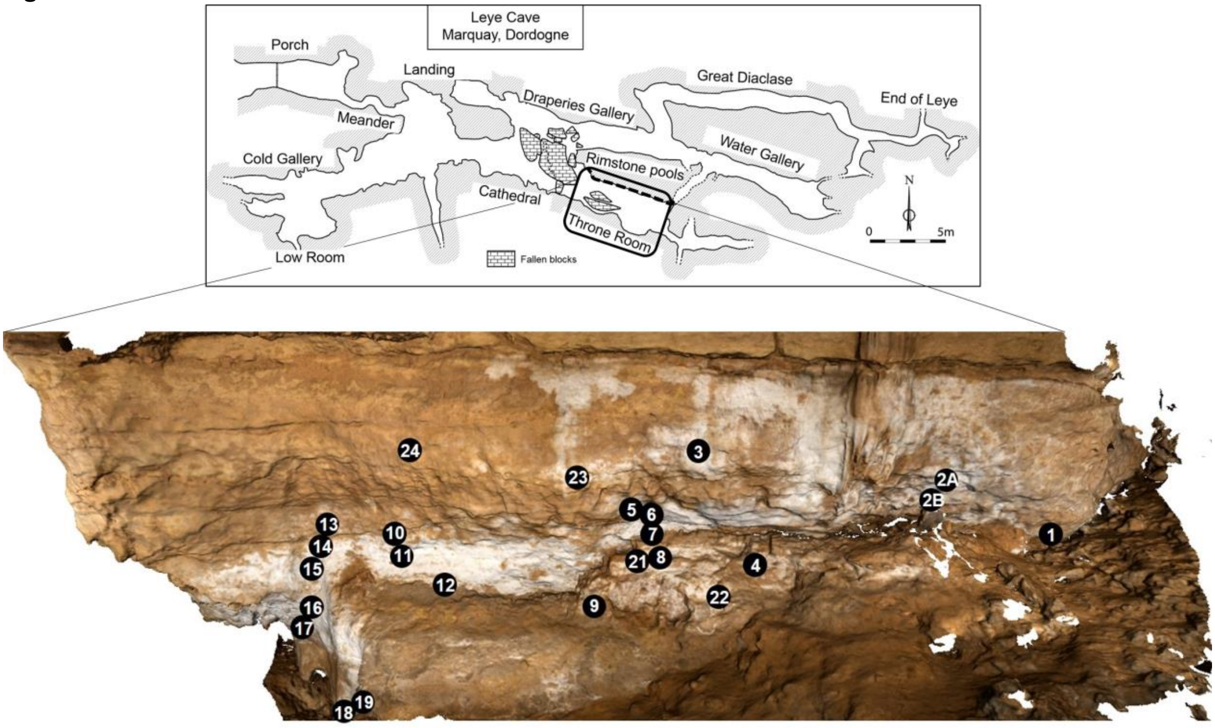
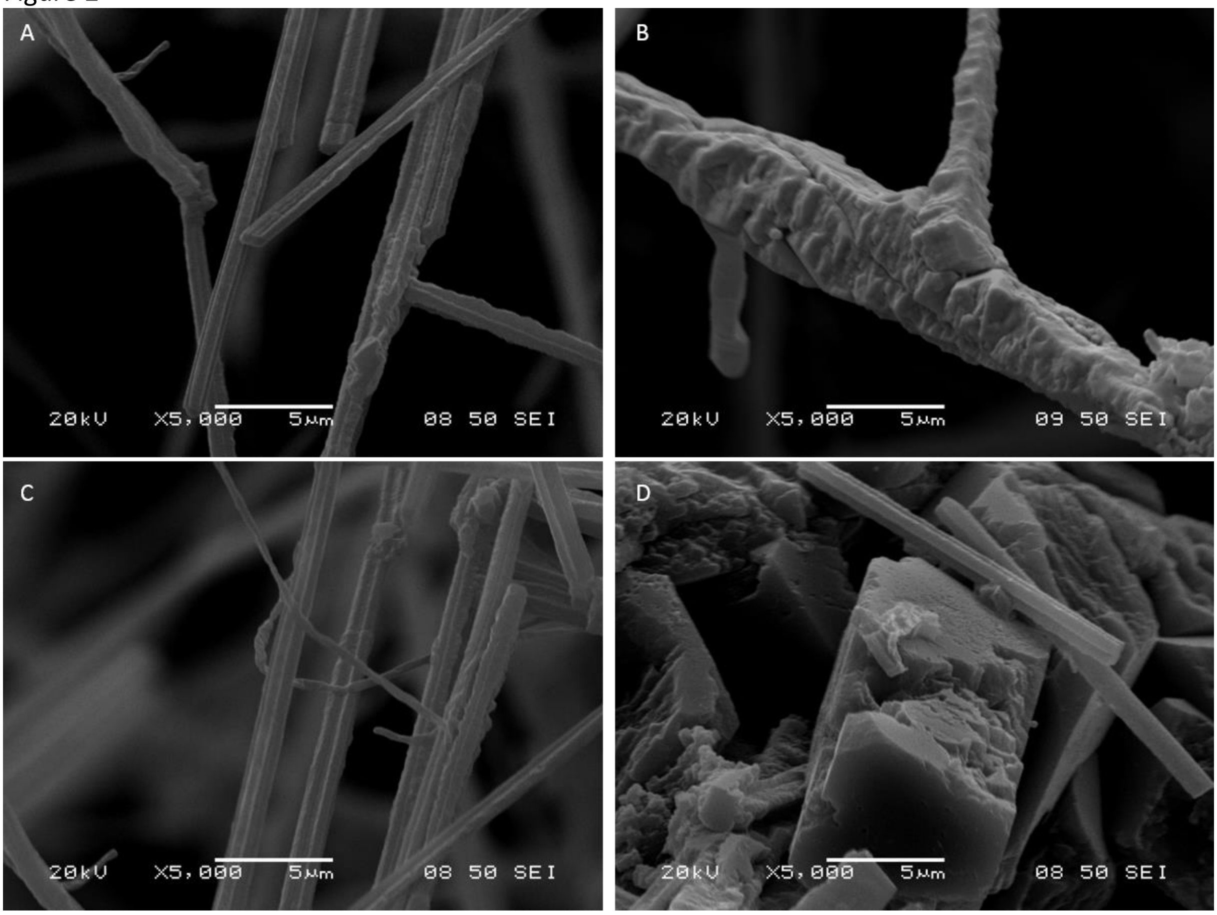


Figure 2



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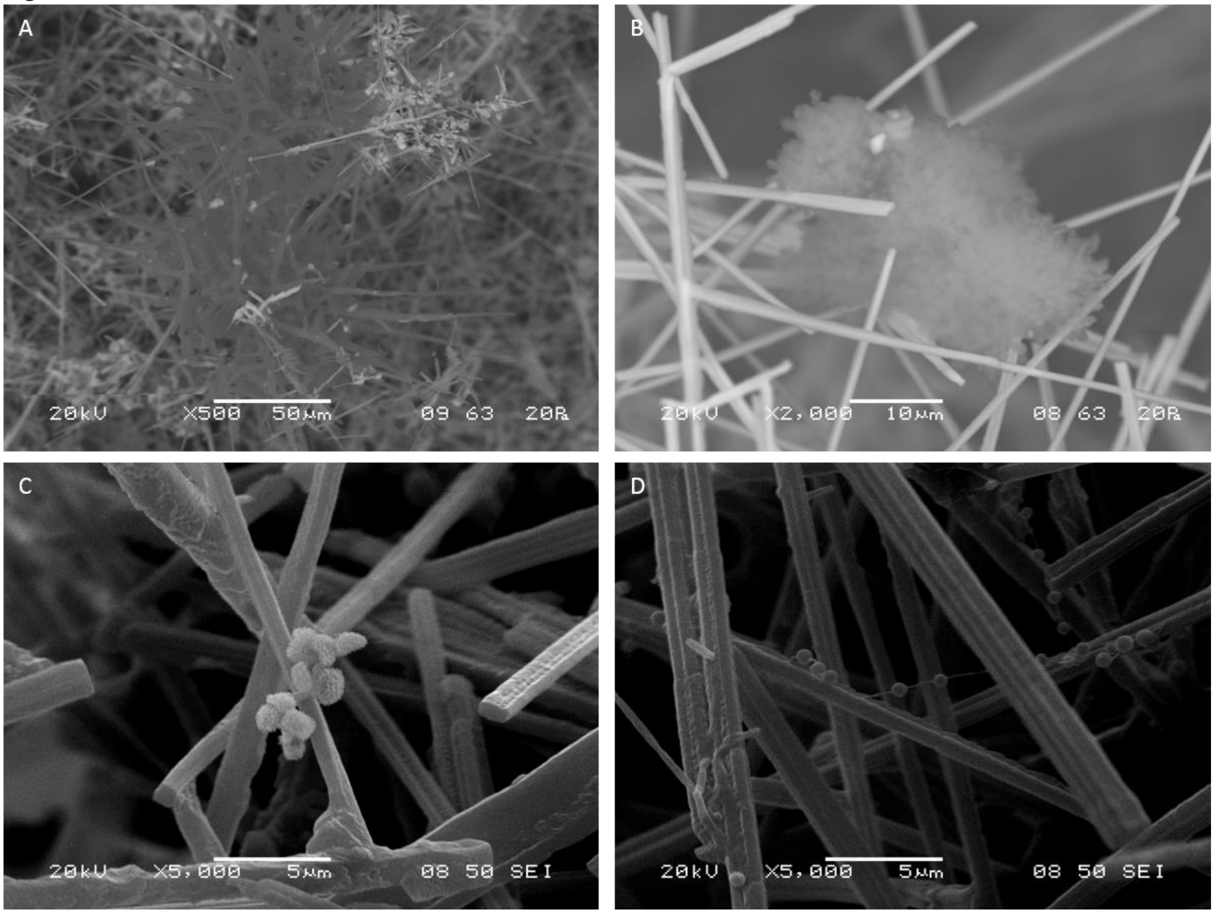

Figure 4

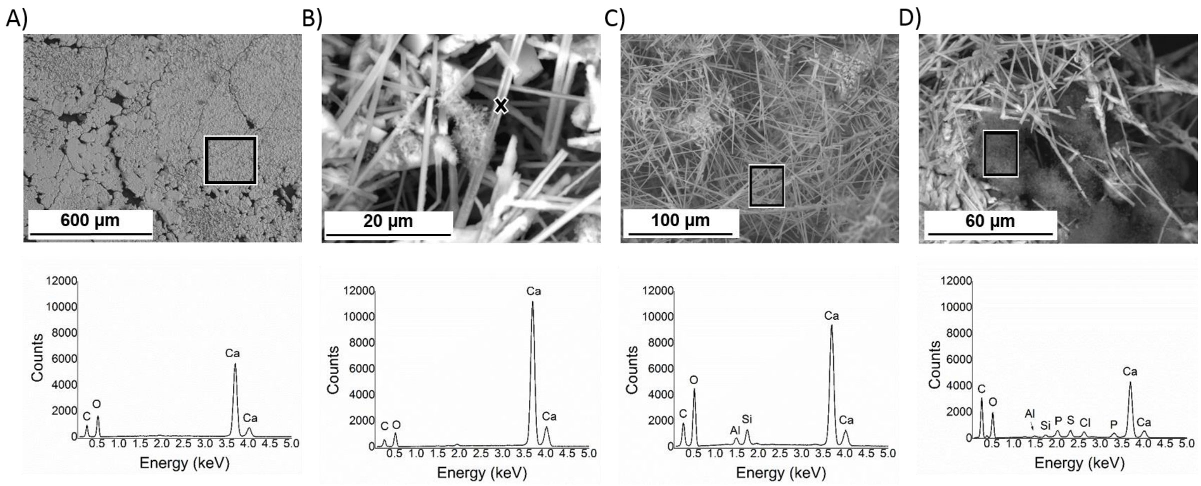

Figure 5

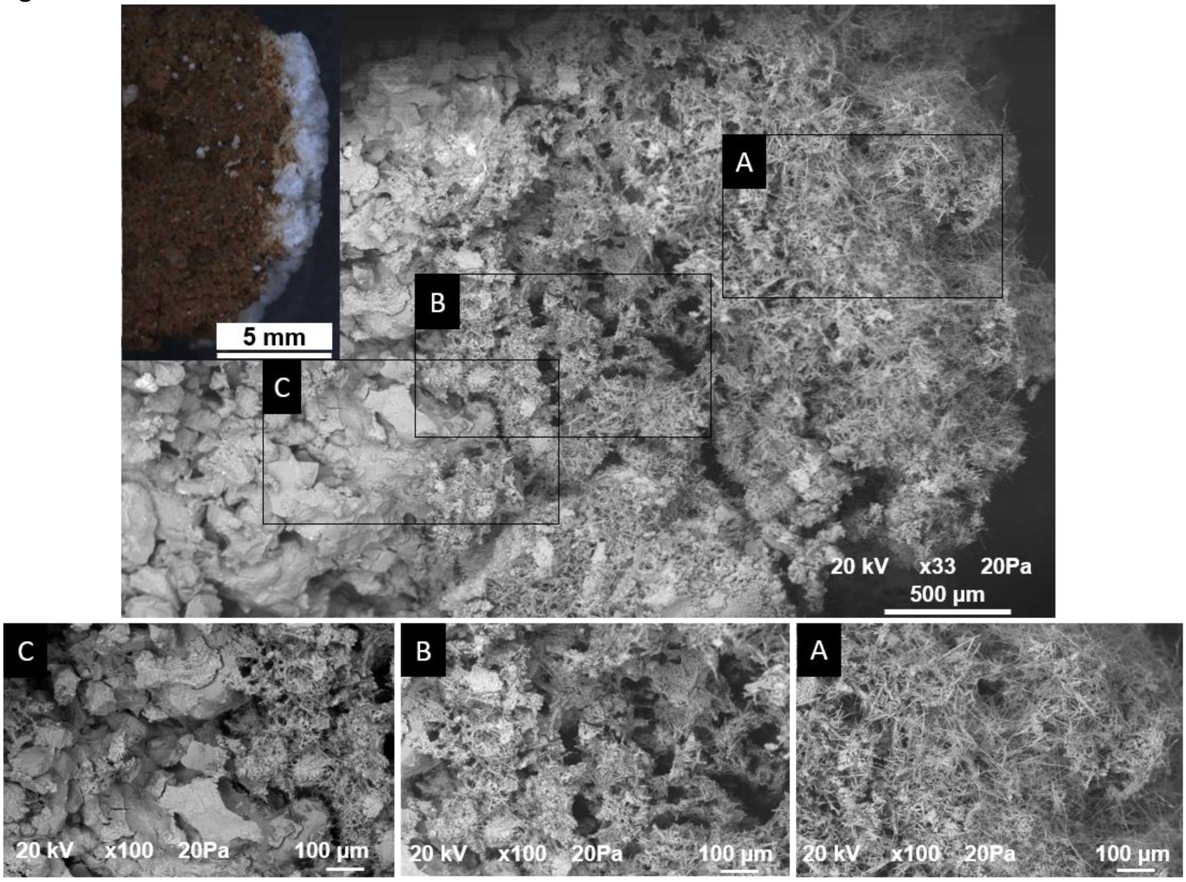

Table 1

Sample	Macroscopic description			Thickness (mm)	Present generation	Epitaxial occurrence	NFC occurrence
	Support	Color	Morphology				
1	Brown calcite	White	Small buds	1	2		+++
2A	Brown calcite	White	Buds	1	2		
2B	Brown calcite	White	Coalescing buds	1,5	2		
3	Calcite	White	Small buds	<1	2		+++
4	Alluvions	White	Smooth coalescing	<1	1 and 2	+++	+++
5	Brown calcite	White	Small buds	<1	2		+++
6	Brown calcite	White	Big buds	2	2		+++
7	Alluvions	White	Buds	>5	2		+++
8	Alluvions	White	Coalescing buds	<1	1 and 2		+++
9	Alluvions	White	Coalescing buds	<1	1 and 2		
10	Alluvions	White	Big craggy buds	5	2		+++
11	Alluvions	White	Coalescing buds	1	2		+++
12	Alluvions	White	Craggy minerals	2	1 and 2		
13	Alluvions	White	Small coalescing buds	2	2		+++
14	Alluvions	White	Small coalescing buds	2-3	2		+++
15	Alluvions	White	Coalescing buds	<1	1 and 2	+++	
16	Brown calcite	Beige	Small buds	<1	2		
17	Calcite	Grey	Small buds	<1	2		
18	Alluvions	White-beige	Craggy minerals	<1	2	+++	
19	Calcite	White	Craggy minerals	<1	2		
21	Alluvions	White	Craggy minerals	1	1 and 2		+++
22	Alluvions	Yellowish and white	Irregular veil under minerals	<1	1 and 2		
23	Alluvions	White	Smooth leaking	<1	1 and 2	+++	
24	Alluvions	White	Irregular mineral film	<1	2		