International Journal of Speleology | 47 (2) | 127-135 | Tampa, FL (USA) | May 2018

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International Journal of Speleology
Official Journal of Union Internationale de Spéléologie

Moonmilk as a human and veterinary medicine: evidence of past artisan mining in caves of the Austrian Alps

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Abstract: The use of moonmilk for medical and other purposes in the Alps is documented since the 16th century. This article reviews speleological reports and sparse historical accounts about the extraction of moonmilk from 18 caves in the Eastern Alps of Austria in an artisan mining style. One such example from a cave in Tyrol is documented in detail, where moonmilk was mined until the beginning of the 20th century and which, due to its remote location, uniquely preserved traces of both the mining and processing style.

Keywords: speleothem, moonmilk, mining, medical use, history, Alps, Austria

Received 8 January 2018; Revised 26 March 2018; Accepted 27 March 2018

Citation: Spötl C., 2018. Moonmilk as a human and veterinary medicine: evidence of past artisan mining in caves of the Austrian Alps. International Journal of Speleology, 47 (2), 127-135. Tampa, FL (USA) ISSN 0392-6672 https://doi.org/10.5038/1827-806X.47.2.2174

INTRODUCTION

One of the most widespread types of speleothems in caves worldwide is moonmilk. This white, water-rich material can be mineralogically complex (Hill & Forti, 1997), but mostly consists of microscopic fibres of calcite (e.g., Borsato et al., 2000; Richter et al., 2008; Cailleau et al., 2009). Recent studies have shown that moonmilk contains a wide variety of microorganisms including bacteria, fungi and archaea (e.g., Barton & Jurado, 2007; Engel et al., 2013; Reitschuler et al., 2015, 2016; Maciejewska et al., 2016). These microbial communities are thought to play a key role in carbonate precipitation (Blyth & Frisia, 2008; Maciejewska et al., 2017).

Another aspect that sets moonmilk apart from other types of cave deposits is its use as a veterinary and human medicine in former centuries. One of the oldest historical documents is Konrad Gesner´s report (1555) about Montmilchloch near Lucerne, Switzerland, where moonmilk was extracted by locals and used as a remedy. Scattered reports exist about this practice in other regions of Central Europe and in particular in the Alps (e.g., Shaw, 1992). Moonmilk at that time was known as *Lac lunae* or *Nihilum album*, although dozens of other synonyms exist (Heller, 1966). *Nihilum album* is in fact the old pharmaceutical term of zinc oxide (e.g., Hahnemann, 1798; Richter, 1832; Moll, 1839). Its colour and powdery appearance are similar to (dehydrated) moonmilk. Zinc oxide is known for its antibacterial and antifungal properties (e.g., Sawai et al., 1995; Sawai & Yoshikawa, 2004; Padmavathy & Vijayaraghavan, 2008) and, for hundreds of years, was widely used to treat a variety of skin conditions and eye diseases (e.g., Lonitzer, 1578) until the discovery of antibiotics in the first half of the 20th century. On the other hand, it is still unclear to what extent moonmilk has pharmaceutical effects. In fact, most previous authors have supposed that it has little or no such effect and was an intended or unintended substitute for zinc oxide (e.g., Kyrle, 1923; Binder, 1963; Trimmel, 1968; Reinbacher, 1994).

Interestingly, despite a large number of mostly concise reports mentioning the use (or abuse) of moonmilk, little systematic research has been done, the etymology of this peculiar term being a notable exception (Reinbacher, 1994, 1995). Here, I review the sparse accounts and hints about mining activities for moonmilk in caves of the Eastern Alps of Austria and document one such cave which, due to its difficult access, uniquely preserved traces of former moonmilk extraction including relics of the primitive tools and techniques used.

MOONMILK CAVES IN THE ALPS

There are hundreds if not thousands of caves in the Alps containing moonmilk, either as an actively forming, i.e. soft deposit, and/or as (partly) dehydrated, hard or crumbly crusts coating cave floors, walls and ceilings or other speleothems. Moonmilk deposits are commonly between a few millimetres and several centimetres thick, but reach up to about 1 m in places (Pavuza, pers. comm., 2018). These formations occur

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in a variety of geometries, from planar deposits to mammillary and stalactitic forms. The vast majority of these deposits consists of calcite. A systematic study in the Southern Alps (Borsato, 1996) showed that moonmilk is most abundant in caves between about 1,400 m a.s.l. and the upper limit of the timberline (i.e., close to 2,000 m a.s.l.). Moonmilk is rare in the twilight zone close to the entrance, and locally also forms subaqueously in shallow pools (so-called cottonballs).

The German expression for moonmilk in the western part of the Alps (mainly Switzerland) is Montmilch, while the term Bergmilch is common in the eastern part (Austria). The latter term is etymologically rather young and first appeared at the end of the 18th century (Heller, 1966, p. 56; Reinbacher, 1995, p. 19). In previous centuries, the synonym Nix was widely used and is still in use in Austria. This word is derived from *Nihilum album* and appears in historical accounts since the 17th century. The oldest mention to my knowledge is in a report from AD 1650 by the administrator at the guardianship court in Werfen (Pflegsverwalter in German), Kaspar Glück, about Scheukofen, a cave in the province of Salzburg, where moonmilk was mined by locals (see below). The word Nix is part of common cave names, e.g., Nixloch, Nixhöhle or Nixofen. Another German name indicative of moonmilk deposits is Galmei (e.g., Galmeiloch, Galmeihöhle). Galmei is the old miners' term for zinc oxide found associated with ore deposits and points to the already mentioned confusion between moonmilk and this oxide mineral that was used as a pharmaceutical. Other German synonyms for moonmilk used in the Eastern Alps are Kreide (e.g., Kreidelucke) and Schotten (e.g., Schottenloch).

HISTORICAL REPORTS ABOUT MOONMILK MINING IN AUSTRIAN CAVES

Figure 1 provides an overview of caves in the Austrian Alps whose (German) names indicate the presence of moonmilk. Highlighted are those sites where either written reports or in-situ observations of moonmilk mining exist. Below I summarize the available information about those caves where mining evidence is rather compelling, starting with the sites in the west and grouped according to the Austrian provinces, whereby the westernmost site and the only one in the province of Tyrol (Nixofen, 1264/9) will be discussed separately in the next section. The number in parentheses behind the cave name is the cave number based on the Austrian cave register.

Salzburg

Nixloch (1331/17) is a small, 32 m-long cave near Weißbach bei Lofer, whose entrance lies at 800 m a.s.l. Czoernig-Czernhausen (1926, p. 126), Waldner (1942, p. 3) and Klappacher & Knapczyk (1977, p. 181) reported that the moonmilk deposits from this cave were used by locals as animal medicine.

Scheukofen (1335/4), a 1,400 m-long cave that opens at 740 m a.s.l. in the Salzach Valley on the eastern flank of Hagengebirge, is an important site where moonmilk, present in the side chambers of the large entrance hall, was mined until the 19th century (Klappacher & Knapczyk, 1979, p. 143). The report from AD 1650 by the administrator at the guardianship court in Werfen mentioned above is not just the oldest known official document about primitive mining of moonmilk in the Eastern Alps; in spite of its shortness, it also gives some hints

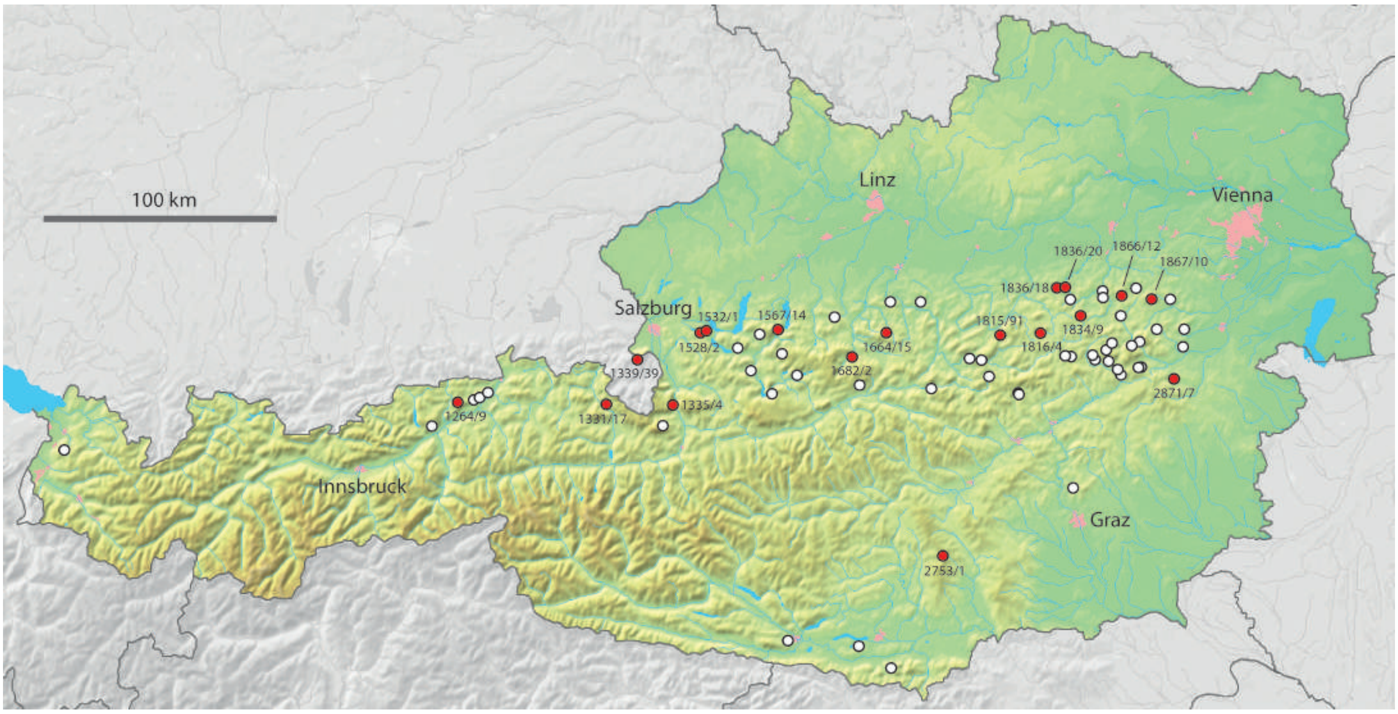

Fig. 1. Map of Austria showing caves whose names contain the German word Bergmilch, Nix, Kreide, Galmei or Schotten and hence indicate the presence of moonmilk (white dots). Many more caves in this country contain moonmilk but not as part of their name. Sites with evidence of former mining of moonmilk based on historical accounts or in-situ observations are shown by red dots including their cave register number. Nixloch bei Hallthurm (1339/39) is located in Bavaria close to the Austrian border. Nixofen (1264/9), discussed in detail in this article, is the only currently known moonmilk mine in the western part of Austria. Cave data based on Spelix database (https://www.spelix.at). Basemap: https://commons.wikimedia.org/wiki/File%3AAustria_topographic_map.png.

about the style of these activities. Importantly, the cave and its moonmilk deposits were apparently unknown to the authorities who became suspicious as a result of folk stories, e.g. about treasures in this cave guarded by mountain trolls. On behalf of the archiepiscopal counsellor, the administrator made inquiries about this cave. He learned that crowds of people, both citizens and foreigners, knew about the cave and had entered it (some of them secretly). They removed a white substance from the cave and sold it to the local pharmacist (Vierthaler, 1816, p. 181). The document even reports how much money these people made per sold pound: the pound moonmilk was sold for 4 Kreuzer. A common way to compare historical prices to present-day currencies is to take a common commodity for which there are records of prices over the centuries. E.g. in 1650 the price for one pound (half a kilogram) of beef in Vienna was about 3 Kreuzer (http://www.habsburger.net/en/glossary/what-could-viennese-buy-their-kreuzer-and-gulden). In the 17th century 1.4 litres of wine costed between 10 and 16 Kreuzer in Linz (Rumpl, 1962, p. 339).

While no details are given about the style of mining in Scheukofen, it is interesting that the administrator had trouble finding people who were ready to provide information about the cave and its location. Several witnesses disappeared or pretended not to know the whereabouts of this cave (Klappacher & Knapczyk, 1979, p. 147). Only an old miner told the administrator that the last time he visited the cave was some fifty years ago, when he searched for ore but only found two skulls. The overall impression this report from the 17th century conveys is that several people knew about the cave and its moonmilk but that this information was kept secret.

Schotterloch (1528/2) is a short, only 12 m-long cave at 830 m a.s.l. east of Fuschl. Waldner (1942, p. 8) reported that locals were still visiting this cave to obtain moonmilk in the 1940s, which was being used by farmers to cure intestinal diseases in cattle. Interestingly, there is no mention of these activities in other speleological accounts, e.g. Czoernig-Czernhausen (1926, p. 47) or Klappacher (1992, p. 338).

Another moonmilk-bearing cave is Nixloch (1532/1) located 2.5 km northeast of Schotterloch on the Drachenwand (1,100 m a.s.l.). While neither Czoernig-Czernhausen (1926, p. 45-46) nor Waldner (1942, p. 3) mentioned traces of mining, Klappacher (1992, p. 346) stated that moonmilk was extracted from this cave for centuries.

Upper Austria

Nixlucke im Annerlgraben (1567/14) is a 150 m-long cave located west of Ebensee, whose entrance opens at 755 m a.s.l. Franz Kraus, an eminent Austrian speleologist and author of the first book on cave science published in German (Kraus, 1894), visited this cave in 1879 guided by an old man whom he referred to as *Nixgräber* ("moonmilk digger"). Three other men joined them; one of them was a licenced local mountain guide. It is telling that this person had heard about the cave but did not know its location. Kraus described the difficult access to this cave, its narrow entrance and the presence of a wooden ladder which was installed by the *Nixgräber* seven years earlier (Kraus, 1880, p. 79).

Kreidelucke (1682/2) is a well-known cave rich in moonmilk, located near Hinterstoder. It has a total length of 1,042 m and opens at 580 m a.s.l. Hauenschild (1866, p. 361-362) organised an expedition into the cave and described traces of moonmilk extraction, including deep holes left by mining, steps carved into the moonmilk, and old wooden ladders and inscriptions. He mentioned that moonmilk was sold also to cattle dealers who added it to the forage to make farm animals, in particular horses, look stronger. Gressel et al. (1951) studied the cave and its sediments and noticed clear traces of moonmilk mining. They were told by an informant that moonmilk was used until recent times as a raw material for the production of chamotte.

Nixlucke (1664/15) is a cave on the northern side of Sengsengebirge that opens at 1,470 m a.s.l. The walls of this 36 m-long cave are partly covered by moonmilk and show clear cut marks that were created during the former extraction of this material (Weichenberger, 2000, p. 134).

Lower Austria

Southeast of Göstling, Krähenloch (1815/91) opens at 760 m a.s.l. Hartmann & Hartmann (1985, p. 125) reported traces of moonmilk extraction in this 100 m-long cave.

Galmeiloch (1816/4), 226 m long and located at 1,346 m a.s.l. WNW of Mariazell was also visited in former times in order to extract moonmilk. Waldner (1942, p. 5-6) reported that this cave was still being visited by people looking for moonmilk and locals told him that moonmilk was commonly used to clean cutlery. Hartmann & Hartmann (1985, p. 172) mentioned the presence of wooden ladders as evidence of the primitive mining activity.

WSW of Frankenfels is another former *Nixbergwerk* ("moonmilk mine"), Mariannenhöhle (1836/18, 437 m, 636 m a.s.l.). In addition to clear traces of moonmilk extraction, Waldner (1942, p. 4) reported black characters made by the diggers using torches, whereby crossed strokes and scissors-like signs were the most common ones.

Nixhöhle (1836/20) is a show cave located WSW of Frankenfels that is 1,410 m long and opens at 556 m a.s.l. According to locals this cave was visited by "moonmilk diggers" who carried the material to Mariazell and probably sold it there (Waldner, 1942, p. 4). Hartmann & Hartmann (1982, p. 74) also mentioned traces of moonmilk mining, and the up to 1 m deep cuts in the moonmilk deposit were later made in the course of the development to a show cave (Pavuza, pers. comm., 2018).

The eponymous Nixhöhle (1834/9, 73 m long, 695 m a.s.l.) SSW of Türnitz was a moonmilk mine whose thick deposits show clear traces of extraction of this material (Waldner, 1942, p. 4; Hartmann & Hartmann, 1982, p. 37).

Stadelbauernhöhle (1866/12) is 70 m long and its entrance opens at 860 m a.s.l. south of the village

Traisen. Waldner (1942, p. 5) reported abundant traces of mining activity and found remnants of old mining tools on the floor. Interestingly, the local farmers did not know about this cave and its moonmilk deposits, and nobody was able to provide information about the cave. Waldner did not report the name of the cave, but it is undoubtedly Stadelbauernhöhle (cf. Hartmann & Hartmann, 1982, p. 129).

Another cave where moonmilk was found and used in the past is Nixofen (1867/10), a 34 m-long cave located at 840 m a.s.l., NNW of Gutenstein. Hartmann & Hartmann (1982, p. 160) referred to it as an old *Nixbergwerk*.

The easternmost cave with clear traces of moonmilk extraction is Hermannshöhle (2871/7) at Kirchberg am Wechsel. This 4.4 km-long labyrinth cave has long been known and opens at 620 m a.s.l. Jäger (1873, p. 250) reported that tests had shown that the dazzling white speleothems (which include moonmilk) can be used in the production of various things including soda water, paper and Gutta-percha. He quoted a price of 3 Gulden per 50 kg which is quite inexpensive when compared to other products and services at that time (Mrkos, 1997). Although there are traces of moonmilk mining at Weiße Kluft and near the Teich (Ilming, 1973) as well as above Dietrichshalle (Plan, pers. comm., 2018), the extracted volume was apparently small. Topitz (1974, p. 200) reported that local farmers used this moonmilk to prepare eyewashes.

Carinthia

The only site currently known in the southern part of Austria where moonmilk was extracted is Nixlucke (2753/1) near Klippitztörl. According to an old report, local farmers frequently went into this sub-horizontal 250 m-long cave, whose entrance is located at 1,545 m a.s.l., and obtained moonmilk that they used as veterinary medicine (Reiner, 1857, p.145). Several inscriptions can be found in the cave, some dating back to the 18th century. According to Waldner (1942, p. 3) this cave was visited more frequently in past centuries than in recent times.

Bavaria (Germany)

One site close to the Austrian border SSW of Salzburg is Nixloch bei Hallthurm (1339/39), which opens at 723 m a.s.l. and is 163 m long. According to Waldner (1942, p. 2), this cave was still visited by "moonmilk diggers" during the first half of the 20th century.

CASE STUDY: NIXOFEN

The only cave where moonmilk was extracted in the western part of Austria and probably one of the best-preserved sites in the Austrian Alps is Nixofen (1264/9) in Brandenberg in Tyrol (Fig. 1). It opens at 1,283 m a.s.l. on a steep north-facing slope (Fig. 2) that can only be accessed during snow- and ice-free conditions. Due to its remote location it is rarely visited, even by local cavers. The cave developed along the intersection of a fault and a bedding plane in thick-bedded Triassic limestone and has a simple, slanted geometry with the rear part being the highest (Fig. 3). Moonmilk is abundant in the middle and rear parts of the cave and comprises soft, sheet-like deposits typically 10-20 cm in thickness and moonmilk stalactites and columns that reach up to 2 m in length and up to about half a meter in diameter (Fig. 4A).

Fig. 2. Entrance to Nixofen (right), view towards East.

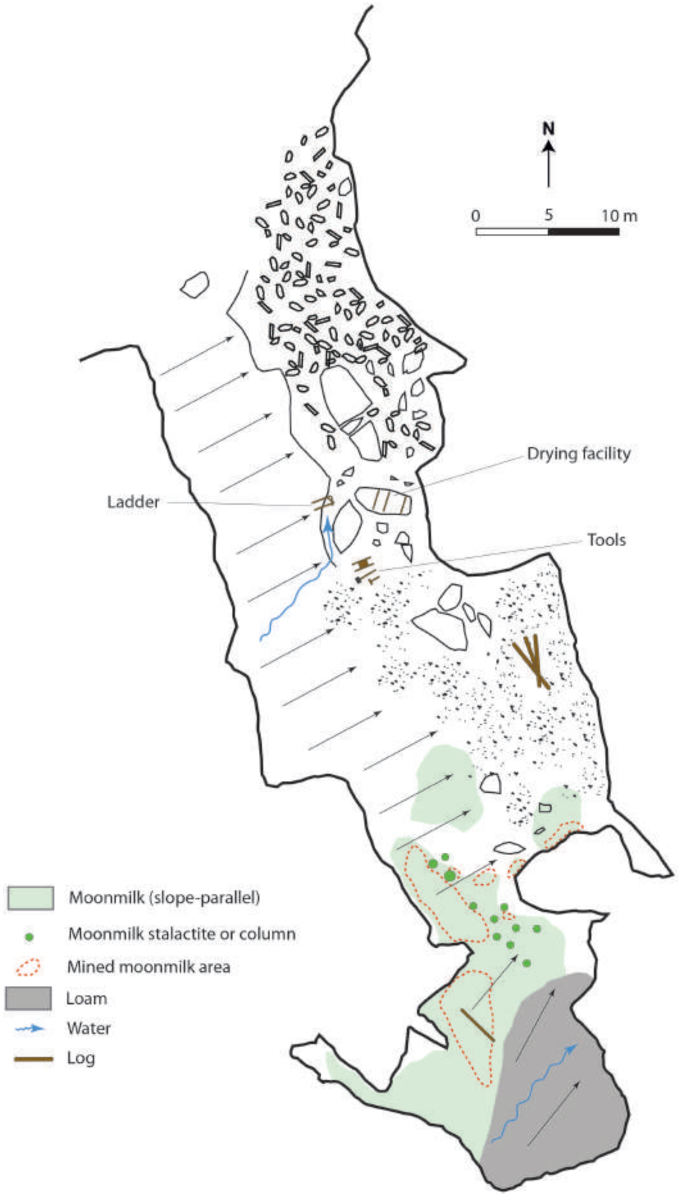

Fig. 3. Plan view of Nixofen showing the distribution of moonmilk both mined and still present.

This *Nixbergwerk* is unique in the sense that it contains well-preserved traces of moonmilk mining as well as the remnants of primitive tools and devices used for mining and processing of moonmilk. Mining traces are found primarily in the rear part of the cave and show short linear features indicating that some sort of hoe was used to chop off moonmilk (Figs. 4B-4D). The miners proceeded in a rather systematic manner and mined the moonmilk from below, working their way up the slope in the rear part of the cave. Close inspection of the hoe marks shows that they have since been overgrown by new moonmilk forming a layer up to about half a centimetre in thickness (Fig. 4E). The innermost part of the cave is still fairly pristine and contains white moonmilk up to 40 cm thick, indicating that the operation had ceased before all the moonmilk was extracted. The 10-20 cm thick moonmilk deposit on the inclined slope of the cave was the primary target of the miners, but at some places they also tried thick stalactites as shown by hoe marks (Fig. 4F). These moonmilk stalactites consist of partly dehydrated moonmilk that was apparently more difficult to mine than the soft variety. On the steep slope the miners made narrow horizontal terraces up to a few meters long in order to better access the moonmilk and because moonmilk-covered slopes are slippery.

Wooden tools are still preserved in the middle part of the cave (Fig. 5A) and in two places there are also rotten logs and wooden sticks that were obviously transported into the cave. The tools comprise (a) a wooden barrow (mortar trough) to be carried by two people, which was apparently used to transport the wet moonmilk to the flat middle part of the cave where is was processed, (b) a wooden tray, again probably used to transport moonmilk (has meanwhile

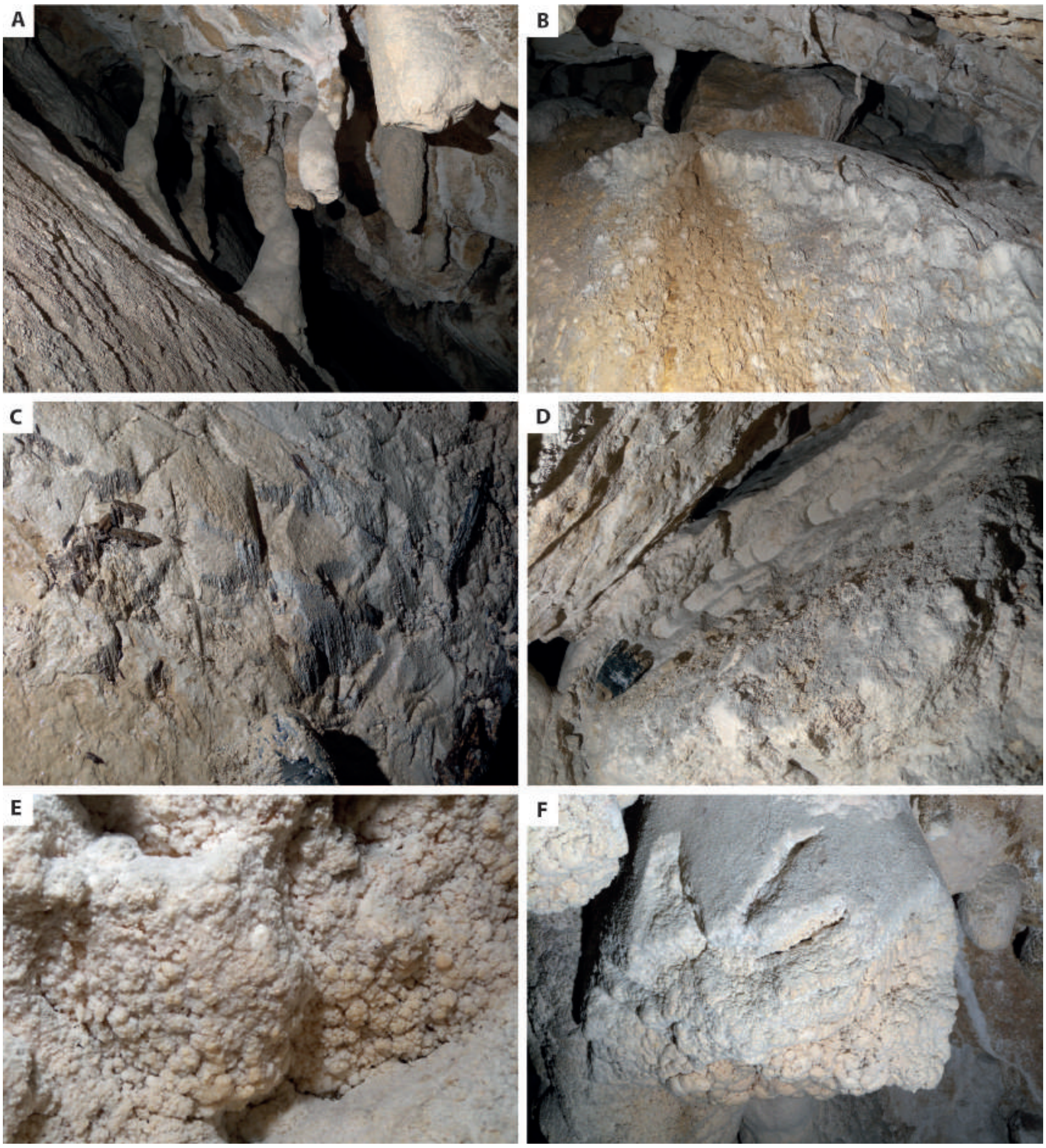

Fig. 4. A) Moonmilk columns and stalactites in the rear part of Nixofen. The column in the centre is almost 2 m tall; B) Sheet-like moonmilk (view upslope), which has largely been extracted except for the uppermost part. Width of image about 4 m; C) Close-up of slope just beneath (B) showing hoe marks at the base of the former moonmilk deposit and traces of old wood fragments. Width of image about 0.5 mm; D) Lateral hoe marks produced by a tool with a round edge. The entire deposit was mined exposing the bedrock underneath (white area in the foreground). Glove for scale; E) Close-up of (D) showing newly formed moonmilk covering the hoe marks. Width of image about 20 cm; F) Hoe marks at the base of a moonmilk stalactite partly overgrown by new moonmilk. Width of image about 0.7 m.

disappeared), (c) a spade, (d) a wooden mallet and (e) a wooden ladder (Fig. 5B). Previously, an old hobnail leather boot was also found there. Interestingly, the shoe was rather small (about European size 37, i.e. about 23 cm long: Krejci et al., 1982). Of particular interest are the remains of a primitive facility to process mined moonmilk. A breakdown block with a flat inclined surface was used to dry moonmilk formed into hand-sized balls. For this purpose, vertical holes were drilled into the rock in order for short wooden sticks to hold horizontal wooden sticks that acted as shelves. This wooden structure is still preserved in the cave and the fact that these sticks are not rotten demonstrates that this spot was well selected by the miners to dry moonmilk. A photograph taken in 1977 still shows several moonmilk balls on these shelves (Fig. 5C) indicating that the mine was abandoned in a somewhat disorganized manner. The moonmilk balls have since been removed by occasional visitors and a few can still be found in private collections (Fig. 5D).

No historical documents exist about this *Nixbergwerk* and it was apparently forgotten. Georg Mutschlechner, the doyen of the mining history in Tyrol who had searched for past mining activity in Brandenberg did not mention this cave (Mutschlechner, 1975). According to Georg Auer (Brandenberg, pers. comm., 2017), the critical information for the re-discovery came from an old local (Josef Hintner, born in 1887) who saw the cave at the age of 14, i.e. at the beginning of the 20th century, when it was still in operation. In his old days he still remembered how to reach the cave and in 1977 Georg Auer and four other locals found it after a long search and took the first photographs.

The style of moonmilk mining in Nixofen suggests a multi-annual operation restricted to the summer/fall season when this site could be accessed safely. Very few people probably knew about this activity and the authorities had no information about it. Due to the lack of written and oral documentation we can only speculate that the miners worked in this *Nixbergwerk* for short intervals, possibly slept in the cave, processed a batch of moonmilk balls and then left the cave with rucksacks full of dried moonmilk balls. The final product was most likely sold to a pharmacy. Back in the 19th century, the closest one was located in Rattenberg in the Inn Valley to the south of the cave, which is approximately a 20 km-long hike (depending on the route).

The amount of moonmilk extracted from Nixofen is difficult to assess. Using the conservative assumption of an average thickness of the deposit of 10-15 cm, the cave survey suggests that between 4 and 7 m^3 of wet moonmilk was mined in total. Given the small dimensions of the drying facility (and the unknown time required to dehydrate the moonmilk so that it could be transported and sold - likely months), this volume of mined moonmilk suggests that the *Nixbergwerk* was in (seasonal) operation for decades. The precise timing and reason for its abandonment are unknown, but the available information and in-situ observations point to an unplanned end early during the 20th century, possibly related to the fact that most men were drafted into the Austrian army during WWI and many never returned.

Fig. 5. A) View from the middle part of the cave towards the entrance. Wooden tools lean on the left slope and remains of the drying facility can be seen on the right side; B) Primitive tools left by the moonmilk miners; C) View of the drying facility showing a series of ball-shaped moonmilk chunks left by the miners. Width of image about 2 m. Photograph taken in 1977 (courtesy G. Auer); D) One of the very few remaining (and meanwhile completely dehydrated) original moonmilk balls.

DISCUSSION AND CONCLUSIONS

The picture that emerged from the study of Nixofen is in many ways consistent with the scattered and scarce information available from other sites in Austria:

- Extraction of moonmilk was common practice and the majority of these *Nixbergwerke* (17) existed in the eastern segment of the Northern Calcareous Alps (Fig. 1). Only one site is currently known in the southern part of Austria.
- All mines were small operations involving probably less than a handful of informed people.
- This artisan-type of mining used primitive, but nonetheless effective techniques of moonmilk extraction.
- The wet moonmilk had to be dried and this was accomplished by forming hand-sized balls and letting them dry on wooden racks. Interestingly, according to an old encyclopedia, *Nihilum album* (the true zinc oxide) was also sold as balls in past centuries (Hübner, 1721, p. 874).
- No official maps, reports or photographs exist about the work in these *Nixbergwerke* and all reports indicate that these activities were intentionally kept secret (e.g., Waldner, 1942, p. 2)
- As has been suggested previously (e.g., Topitz, 1974), experienced prospectors (termed *Nixsucher* or *Nixgräber*) apparently searched for moonmilk deposits in caves in the Eastern Alps and started these operations.
- *Nixbergwerke* were most likely worked during the snow-free season only.
- The timing of the onset of moonmilk mining in the Alps is still hidden in the darkness, but certainly goes back at least half a millennium (cf. Gesner, 1555). The oldest reliable report from Austria is one hundred years younger (Scheukofen, 1650).
- *Nixbergwerke* in Austria were in operation until the first half of the 20th century. This is in contrast to Shaw (1992, p. 224) who concluded that the medical use of moonmilk ceased about the middle of the 18th century in the western world. Due to the lack of historical data it can only be speculated that the abandonment of the Austrian sites was at least in part related to the advent of antibiotics, which are much more efficient than the previously used zinc oxide (and moonmilk).
- The use of moonmilk, however, was not restricted to human medical purposes; it was widely applied also to cure animal diseases. In addition, people used it for a variety of other purposes (e.g., Mattes, 2015, p. 108).

OUTLOOK

For a long time it has been supposed that dried moonmilk was used as an essentially illegal substitute for zinc oxide – with little or no pharmaceutical effect. Already Gesner (1555, p. 66) and later Kappeler (1767; reprint 1967; see also Jans, 1983) ridiculed that superstitious people use moonmilk to cure any sort of disease. On the other hand, the Swiss pharmacist Sidler (1939/40, p. 228), who studied the use of moonmilk, concluded by quoting a local physician, Hans Portmann, that it would be interesting to examine moonmilk closely, because our ancestors were known to be sensitive observers.

Although quackery, superstition and placebo were certainly involved in the century-long business of moonmilk as a medical product, it is interesting to note that recent microbiological studies suggest that moonmilk might "effectively treat various infectious diseases thanks to the presence of a highly diverse population of prolific antimicrobial producing Streptomyces, and thus may indeed constitute a promising reservoir of potentially novel active natural compounds" (Maciejewska et al., 2016, p. 1-2).

ACKNOWLEDGEMENTS

I am grateful to the following colleagues for providing information and feedback: Georg Auer, Eckart Herrmann, Walter Klappacher, Günter Krejci, Rudolf Pavuza, Lukas Plan and Martin Trüssel. Gina Moseley kindly eliminated grammar mistakes. Two journal referees are thanked for their helpful comments.

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International Journal of Speleology	47 (2)	137-144	Tampa, FL (USA)	May 2018

Available online at scholarcommons.usf.edu/ijs

International Journal of Speleology
Official Journal of Union Internationale de Spéléologie

Replication and reinsertion of stalagmites sampled for paleoclimatic purposes

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Abstract: Sampling stalagmites for paleoclimatic study can enter into conflict with preserving the beauty and integrity of caves. To minimize this impact, a variety of sampling strategies have been used by researches aware of cave-conservation issues. Based on our experience in two caves (El Soplao and La Buenita, Cantabria, N Spain), we propose to apply molding and casting laboratory techniques to create replicas of stalagmites, placing the replicas back in the original cave locations so that the impact of sampling to the cave is severely reduced. We provide detailed descriptions of the molding and casting methods, which vary depending on stalagmite size. For relatively small specimens (less than ~35 cm tall), we use a single-piece mold and two jackets. For larger stalagmites (~40-70 cm tall), we use a two-piece mold and two jackets. In a first casting step, we obtain a master piece in dental plaster that is preserved. In a subsequent casting step, we use epoxy resin to generate the replica that will be placed in the cave. We use extra-hard plaster coated with epoxy resin to fix the replicas to their original substrates. Both the epoxy resin and plaster are carefully dyed to match the original surface texture and color of the sampled stalagmites. Once in place, the stalagmite replicas are almost indistinguishable from the natural specimens.

Keywords: speleothem sampling, stalagmite reinsertion, molding and casting, paleoclimatology, geoethics

Received 24 January 2018; Revised 2 April 2018; Accepted 2 April 2018

Citation: Baeza E., Lozano R.P. and Rossi C., 2018. Replication and reinsertion of stalagmites sampled for paleoclimatic purposes. International Journal of Speleology, 47 (2), 137-144. Tampa, FL (USA) ISSN 0392-6672 https://doi.org/10.5038/1827-806X.47.2.2183

INTRODUCTION

Stalagmites can preserve valuable paleoclimate information with high temporal resolution compared to other proxy records (e.g., marine or lacustrine sediment cores), and provide important paleoclimate information for most continental regions (Fleitmann & Spötl, 2008; Fairchild & Baker, 2012). Also, stalagmites can be precisely dated using U-series methods. Therefore, stalagmites are increasingly being used for paleoclimate research, as there is a need to understand the climatic past in order to evaluate the magnitude, causes and consequences of the present day climate change.

The paleoclimatic study of a stalagmite normally requires its removal from the cave for petrographic and geochemical analysis, hence disturbing to some extent the integrity of the cave and potentially creating a conflict between scientific sampling and cave conservation (Springer, 2012; Truebe, 2013).

The paleoclimatic interpretation of stalagmite records is not straightforward, partly because they may be influenced by local factors that overlap with climatic controls. Therefore, some stalagmites may not be ideal for paleoclimatic study. Even in the case of stalagmites showing textures consistent with the preservation of paleoclimatic signals, it is advisable to obtain at least two coeval stalagmite records from the same cave or region to test their sensitivity to local versus climatic factors (i.e., a replication test; Dorale et al., 2002; Dorale & Liu, 2009). In addition, the number of sampled stalamites may increase if they contain abundant detrital material, which complicates U-Th dating (Hellstrom, 2006), or specimens are affected by diagenetic alteration.

Therefore it is clear that most paleoclimatic studies based on stalagmites normally require sampling several specimens. Because the number of stalagmites in a cave is finite, sampling conflicts with cave conservation, especially for caves containing few speleothems. Therefore, the sampling strategy must be selective and trying to reach a compromise between the scientific goal and cave conservation issues. For instance, the shape and diameter of stalagmites may provide clues about their usefulness for paleoclimatice studies. This allows a screening,

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and commonly narrows the search down to those with constant diameters of about 11 cm or more (Dreybrodt & Romanov, 2008; Dreybrodt & Scholz, 2011).

To minimize the impact of stalagmite sampling, researchers have developed a variety of strategies. Frappier (2008) designed a screening strategy aimed to select paleoclimate-sensitive stalagmites. For instance, this author recommends the preferential sampling of already broken specimens due to natural causes (collapses), accidents, or modern or historical vandalism. This approach was followed by Domínguez-Villar et al. (2009) and Baldini et al. (2015), among others. Another strategy is coring the central part of stalagmites, either in the cave (Brook et al., 2006; Verheyden et al., 2006; Yang et al., 2007) or in the laboratory, in the latter case placing the drilled specimens back in their original location in the cave (Dorale et al., 1992). In any case, patching the drill holes is simple. Details of these methods are rarely published, with the notable exception of Spötl & Mattey (2012).

Drilling stalagmites minimizes the visual impact of sampling. However it has some disadvantages. The best paleoclimatic records are those obtained from the axis of maximum extension (Dreybrodt & Scholz, 2011). The growth axis of a stalagmite can change in time due to drip displacement. Therefore is almost impossible to anticipate if a given drill core will follow the growth axis in deeper parts of the stalagmite. Also, the small diameter of the cores only permits a limited view of the general structure of the stalagmite, especially when compared to longitudinal sections of the entire specimen. However, actually most coring is normally not done vertically (in order to obtain a complete profile) but horizontally near the base, simply to get a basal age of the specimen (Spötl & Mattey, 2012).

In this paper we propose applying molding and casting laboratory techniques to create replicas of stalagmites sampled for paleoclimatic purposes, placing the replicas in the original cave locations so that the impact of sampling is severely reduced. For stalagmites that were actively growing when sampled, the deposition of new $CaCO_3$ layers will likely make the replicas virtually undistinguishable from the natural specimens within a few years. The main objective of this article is to provide a detailed description of the methods. We report our experience in two caves (El Soplao and La Buenita, Cantabria, N Spain). Both caves are profusely decorated with speleothems and they were discovered during mining activities, which have resulted in considerable damage.

PREVIOUS WORK

To date, most replicas of stalagmites have been produced in prehistoric cave-art settings, where certain parts of caves with paintings have been reproduced entirely to preserve the fragile cave environments while allowing public display of the reproductions (Altamira Cave, Cantabria, Spain: Laheras et al., 2002 and Chauvet Cave, Ardèche, France: Pigeaud, 2014). Also, speleothem replicas have been produced to restore vandalized caves, such in Vatnshellir (Snæfellsnes, Iceland), where 37 replicas were generated to replace broken specimens (Stefánsson, 2010).

In the case of stalagmites sampled for scientific purposes, replicas are rarely considered and, when employed, technical details are typically not provided (Spötl & Boch, 2012). Muñoz-García (2007) elaborated polyurethane-resin replicas of several stalagmites sampled for paleoclimatic purposes in Cobre Cave (N Spain). Vaks et al. (2013) replaced an active stalagmite by a ceramic replica in Okhotnichya Cave (Siberia, Russia), but no technical details about the replication process were provided. Truebe et al. (2011) elaborated a replica of a stalagmite sampled for a paleoclimatic study using a mixture of cement and crushed marble and temporarily placed a replica back in the cave (Kartchner Caverns, Arizona, USA) to determine whether the materials were suitable for the cave environment. Baeza & Durán (2015) describe the replication of a peculiar speleothem from Las Maravillas Cave (Huelva, Spain). The original speleothem remained in the cave, and the replica was made for preserving its shape from possible future alteration. Finally, D. Tremaine and C. Scott-Smith created reproductions of stalagmites used for paleolimate research from Hollow Ridge Cave (Florida, USA), using polyurethane-resin molds and a cement-glass mixture for casting (Florida State University, 2011).

EL SOPLAO AND LA BUENITA CAVES

El Soplao Cave is located in the Arnero Sierra (Cantabria, N Spain; Fig. 1). It contains ~23 km of surveyed passages, developed in Aptian dolostone hosting Mississippi-Valley-type Pb-Zn deposits. With no known natural entrances, El Soplao Cave was discovered during mining operations in 1908. El Soplao contains abundant calcite and aragonite speleothems (Gázquez et al., 2012; Rossi & Lozano, 2016), including outstanding helictites and anthodites, which prompted the development of the westernmost section of El Soplao as a show-cave in 2005. U-series dating (Rossi et al., 2016) indicates that aragonite and calcite stalagmites and flowstones have grown intermittently in the caves at least for the last 1.5 Ma. El Soplao is particularly noteworthy for its unique ferromanganese stromatolites (Rossi et al., 2010), formed in water-

Fig. 1. Location of El Soplao and La Buenita caves.

table canyons during the early Pleistocene as revealed by ^{234}U-^{238}U and paleomagnetic dating (Rossi et al., 2016). The stromatolites contain zaccagnaite-*3R*, a new polytype of the hydrotalcite group (Lozano et al., 2012) and unusually well preserved Mn-oxidizing microbes (Lozano & Rossi, 2012). La Buenita Cave is located in the same region (Fig. 1), develop in the same Aptian dolostone formation as El Soplao was also discovered during mining operations.

SAMPLED STALAGMITES

Four stalagmites were sampled for paleoclimatic purposes in El Soplao (La Sirena passage) and one stalagmite in La Buenita (Table 1). La Buenita is not open to tourism, and la Sirena passage in El Soplao is located relatively far from the show-cave section. Three of the sampled stalagmites were located under active drips. The stalagmites consist of calcite passing laterally into flowstone. In the case of El Soplao, the speleothems grew on sand, gravel and clay with intercalated manganese speleo-stromatolites (Rossi et al., 2010). In both caves, the stalagmites were extracted using a portable diamond saw equipped with a 2-mm-thick diamond blade). After performing typically one of two low-angle basal cuts, the stalagmite was removed with the aid of a hammer and a broad and flat chisel. This procedure minimizes the loss of material from the stalagmite base, so that placing back the replica is facilitated.

Tab. 1. Main relevant features of the replicated stalagmites.

Stalagmite ID	Drip activity	Height (cm)	Basal diameter (cm)	Mold type	Emplacement date
Soplao-1	Inactive	71	23	2-piece	June 2017
Soplao-2	Inactive	34	11	1-piece	March 2012
Soplao-3	Active	21	18	1-piece	March 2012
Soplao-4	Active	17	11	1-piece	June 2017
Buenita-1	Active	40	12	2-piece	June 2017

MOLDING AND CASTING

Molding and casting procedures are slightly different depending on the stalagmite size, as detailed below. Also, resin pouring becomes more difficult with increasing mold size. For relatively small specimens (less than ~40 cm tall), we use a single-piece silicone mold and two jackets, the resin being poured directly into the mold. For larger stalagmites (~40-70 cm tall), we use a two-piece mold and two jackets, the resin being introduced into the mold using a spatula and a brush. The precise molding and casting procedure for each case is described below.

Case 1: Small stalagmites

First, the stalagmite is placed vertically on a block of non-sulphure plasticine (Fig. 2A; Fig. 3A). Then, a layer of room-temperature-vulcanizing silicone (Down Corning 3481) is applied on the specimen with the aid of a brush (Fig. 2A; Fig. 3B). During this step, silicone viscosity exerts a major control on the quality of the replica. If the silicone is too fluid, it could penetrate into pores of the specimen, complicating demoulding. If the silicone is too viscous, bubbles may form, decreasing the quality of the replica. Optimal viscosity levels are achieved by adding 7% wt. of curing Agent 3481-F.

After applying a second layer of thixotropic silicone (Fig. 3C) and immediately before curing, a nylon network is fixed to the silicone to increase its stability (Fig. 2B; Fig. 3D). Then, a third, 1-cm thick, blue-dyed thixotropic silicone layer is applied. When all silicone layers are cured, the plasticine basal stand is removed (Fig. 3E).

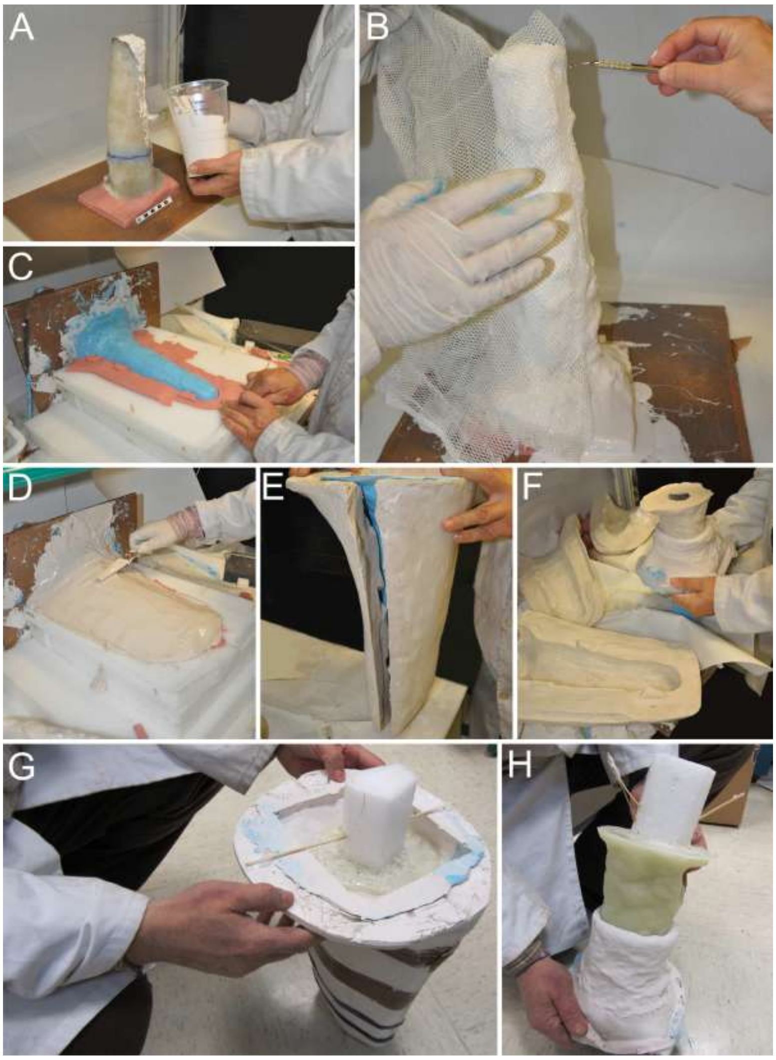

Fig. 2. Molding and casting procedures for the Soplao-2 stalagmite (34 cm tall). A) Silicone is applied on the specimen using a brush; B) Nylon network fixing; C) Adaptation of the assembly to the polyethylene sheet; D) Manufacture of the plaster jacket; E) Opening of the jackets for the extraction of the silicone mold; F) Extraction of the dental-plaster master replica; G) Inserting a thick polyethylene rod into the axis of the mold with the aid of a thin wooden stick; H) Extraction of the resin replica with the polyethylene core.

Once cured, the silicone mold can be easily deformed. Therefore, pouring resin or plaster into the mold will likely result in deformed replicas. To avoid this, two rigid jackets plaster (low hardness, type II; Alamo 70) are prepared to be fixed to the mold. To prepare the first jacket, the silicone-covered stalagmite is placed horizontally over a thick section of polyethylene foam, which is previously prepared to fit the specimen by removing material from its central part (Fig. 3F). Plasticine is used to improve the fit between the silicone and the polyethylene foam (Fig. 2C). The jacket is fixed to the silicone mold by using swallowtail keys made of plasticine. To improve stability, an additional piece of polyethylene foam is adjusted to the base of the stalagmite (Fig. 3F). Finally, to prevent plaster from penetrating the surface of the silicone mold, the latter is wrapped in polyethylene film. Following hardening of the first plaster jacket, both the sillicone-covered specimen and the jacket are flipped together (Fig. 3H), so that a second plaster jacket can be prepared, similar to the first one (Fig. 3I).

A first casting is performed using high-hardness type-IV dental plaster (a 50% mixture of Hebodur and Arquero). The resulting master replica is preserved, so that a new mold can be prepared in case the first mold is damaged. A second casting provides the replica to be placed in the cave. For this casting, we used epoxy resin (Fetadit 55/63), charged with silica powder. To reduce replica weight and cost prior to pouring the resin we fixed a thick polyethylene rod into the axis of the mold with the aid of a thin wooden stick (Fig. 2G; Fig. 3K-L). This procedure also prevents unwanted increases in temperature during resin curing.

To obtain a color as close as possible to that in the surface of the original specimen, we first perform several tests by combining dyes, obtaining several

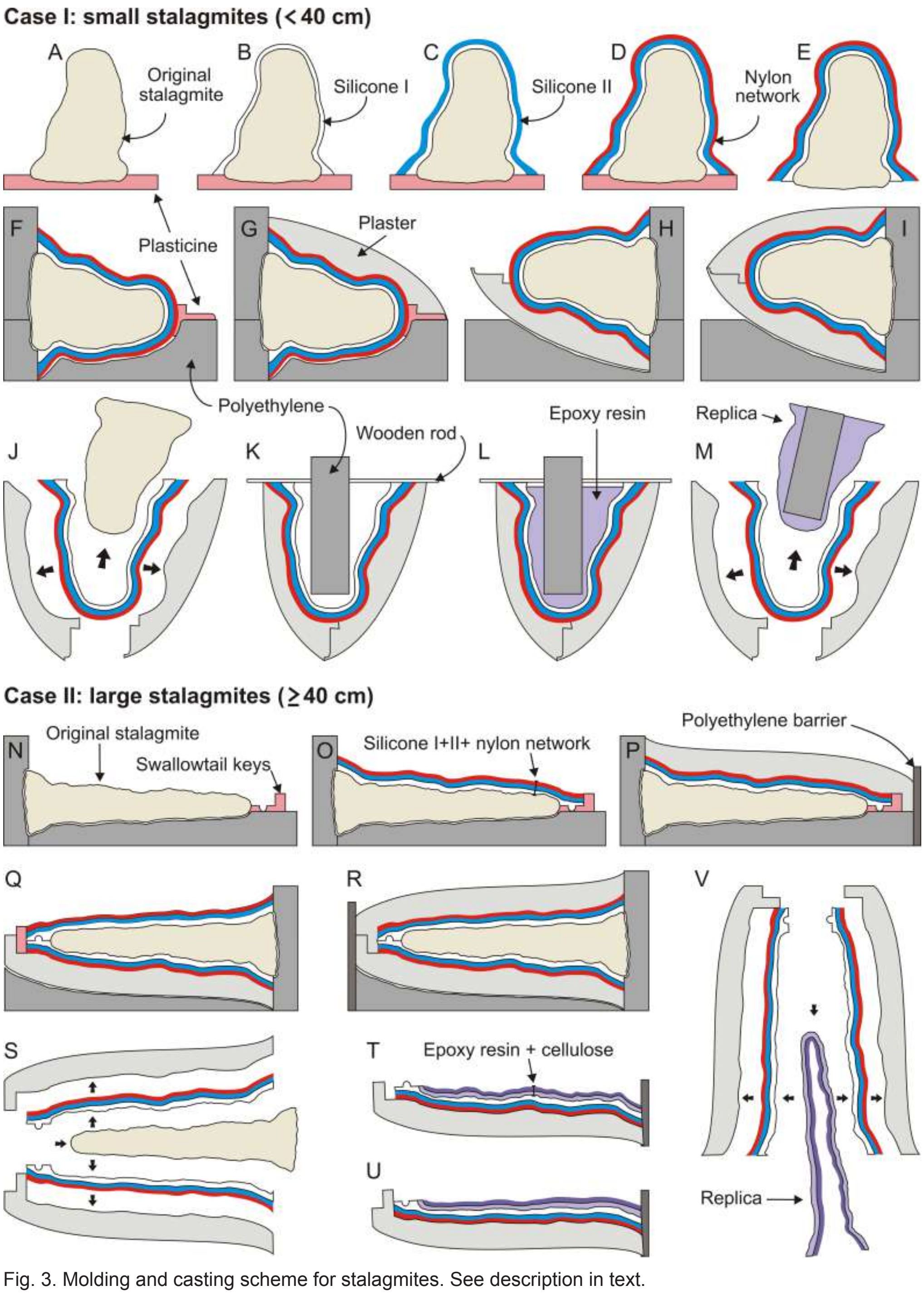

Fig. 3. Molding and casting scheme for stalagmites. See description in text.

fragments of colored resin. To achieve best results, we do not apply the chosen dyes on the finished replica, but on the internal part of the silicone mold, before introducing the epoxy resin of the casting. Thus the dye penetrates the resin, permanently coloring the selected sectors. To make sure that the resulting color is right, we previously did a series of color tests using a silicone mold divided into several hollow spaces (5 x 5 cm section and 1 cm deep). We impregnate the bottom of each space with the selected mixture of dyes and introduce the epoxy resin. After curing, we check the surface color obtained. The application of the pigment to the silicone can be done in dry or wet conditions. However, we recommend the wet application because it produces a glossy aspect in the finished replica very similar to most of the original specimens.

Case 2: Large stalagmites

For larger stalagmites (~40-70 cm tall) inserting polyethylene rods in the mold axis before resin pouring is more delicate, as it becomes more difficult to prevent the rods from touching the mold walls. Therefore, in these cases it is advisable to elaborate a two-piece instead of a single-piece mold so that it is easier to safely insert polyethylene rods in the mold and the volume of resin used is minimized. Also, as the silicone molds become larger they are more prone to break during casting.

First, a cavity is carved into a thick piece of polyethylene foam to fit one longitudinal half of the stalagmite. A layer of plasticine is then applied on the surface of the polyethylene foam, and a groove is carved in the plasticine near the edges of the stalagmite. This groove is the link between the two silicone molds and prevents possible spills during casting. Plasticine swallowtail keys are prepared to obtain a good fit between the future jacket and the specimen (Fig. 4A; Fig. 3N) and to improve stability when both are placed in a vertical position. The exposed half of the specimen is covered by three layers of silicone-bearing nylon network, similar to case 1 (Fig. 4B; Fig. 3O). A barrier of paper-covered polyethylene foam sheets is then glued to the base of the polyethylene foam. Finally, the first jacket is obtained by covering the silicone-covered stalagmite with low-hardness plaster (Fig. 4C; Fig. 3P).

Following hardening of the first plaster jacket, both the sillicone-covered specimen and the jacket are flipped together, removing the basal piece of polyethylene foam in order to expose the other half of the stalagmite. Again, plasticine swallowtail keys are prepared (Fig. 4D). Before covering the corresponding half of the stalagmite with silicone, a release agent (black soap) must be applied to the first mold to prevent the molds from sticking together. After applying the silicone layers (Fig. 3Q) and wrapping with polyethylene film, a barrier of polyethylene foam is spread around the set. This prevents plaster spills during the elaboration of the second jacket (Fig. 4E-F; Fig. 3R). Once the plaster of the second jacket is hard, the polyethylene foam barriers are removed (Fig. 4G) and the set is opened (Fig. 4H) to release the stalagmite (Fig. 4I; Fig. 3S).

Similar to case 1, a first casting is performed using type-IV dental plaster to obtain a master replica, and the replica is obtained by means of a second casting using dyed epoxy resin (Fetadit 55/63). This is done by applying a ~0.5 mm thick resin layer to the inner parts of each mold, with the aid of a brush (Fig. 3T-U). Then, ~6% cellulose is added to the epoxy resin, which is applied over the epoxy layer using a spatula (layer thickness: 1-2 cm). The purpose of adding cellulose is to regulate the transparency of the epoxy resin. Then, both molds and their respective jackets are assembled together. After resin curing, a light-weight and hollow replica is obtained, ready to be placed into the cave (Fig. 3V). The procedure to obtain the final color of the replicas is similar to that described for case 1.

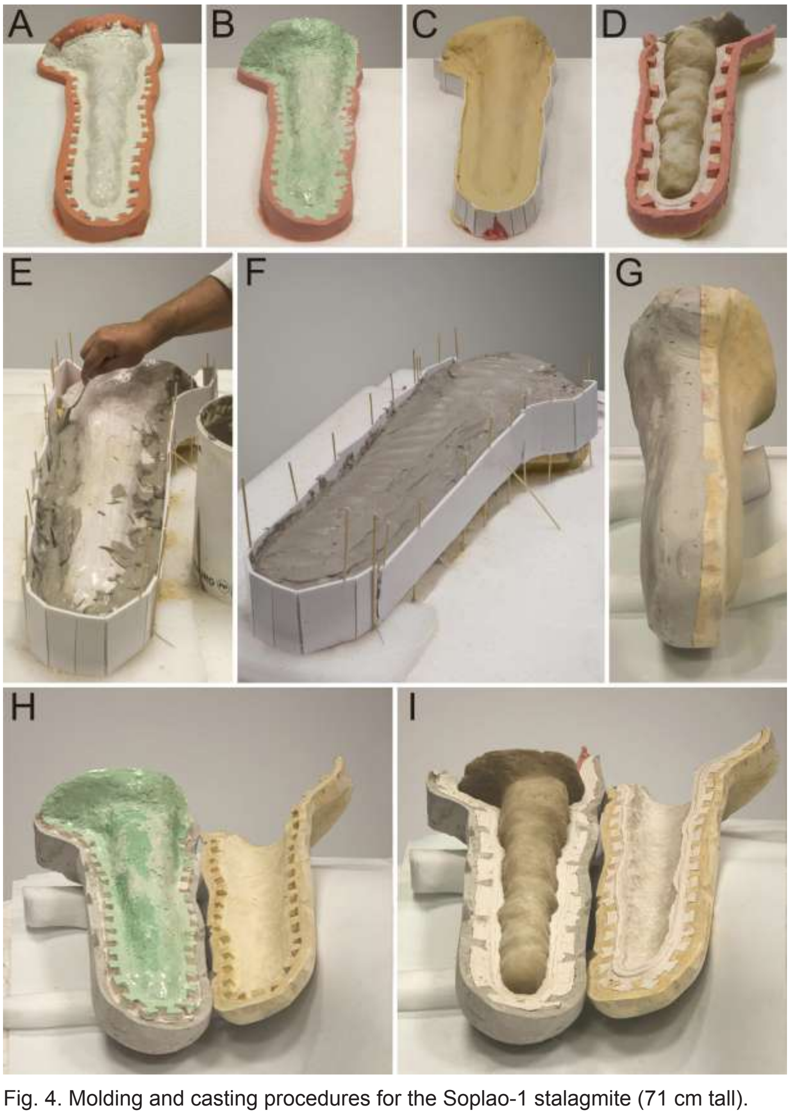

Fig. 4. Molding and casting procedures for the Soplao-1 stalagmite (71 cm tall). A) Original stalagmite covered with the first brush of silicone and placed on a thick polyethylene plate; B) Application of the second layer of silicone and polyethylene film; C) Installation of polyethylene barriers and application of plaster to manufacture the first jacket; D) Manufacture of new plasticine swallowtail keys for the second mold production; E-F) Installation of new polyethylene barriers for the application of the plaster of the second jacket; G) Set of molds and carcasses with the original stalagmite inside; H-I) Extraction of the original stalagmite.

ANCHORING OF STALAGMITE REPLICAS TO THE ORIGINAL SUBSTRATES IN THE CAVES

After cleaning and drying the substrate of the stalagmite, the replica is placed to match the original orientation using images taken before extracting the specimens and the impact location of the drops falling from the corresponding stalactite. To fix the replica to the cave floor, we used high hardness plaster (Arquero; type IV) coated with epoxy resin. We use an umbrella to avoid the impact of drops during plaster and resin hardening. In the case of relatively flat substrates, the insertion of the replicas is relatively easy (Fig. 5A-D) and simply involves dying the plaster to match the appropriate color.

However, the insertion on inclined substrates, such as for stalagmite Soplao-1, is more difficult. This stalagmite passed laterally into a thin flowstone overlying unconsolidated detrital sediments (Fig. 5E), which was partially broken during stalagmite extraction. Therefore, a layer of dyed plaster, resembling the original flowstone, was applied during the insertion of the replica (Fig. 5F).

LONG-TERM STABILITY OF THE REPLICAS

The long-term stability of the materials used in the replicas is of great importance because they can deteriorate easily under cave conditions (Werker, 2006ab; Werker & Hildreth-Werker, 2006). The epoxy resin we have used for both casting and covering the insertion plaster is manufactured locally, so it does not appear in the lists published by Werker (2006a) or Werker & Hildreth-Werker (2006). This resin is of relatively good quality and we have used it for more than two decades in diverse restoration projects with excellent results and durability. However, its long-term stability inside the caves has not been described so far. After almost six years in the cave, replicas Soplao-2 and Soplao-3 (emplaced in March, 2012) have not experienced any obvious signs of alteration, suggesting that the used epoxy is rather stable in the cave environment.

Regarding the plaster used for anchoring the replicas to the substrate, we initially tested its stability in the laboratory by submerging a ~125-cm^3 piece in deionized water for one year in an isolated environment. After this time the conductivity of the water barely increased, implying no significant dissolution of the plaster. Therefore this material seemed adequate to fix the replicas to the substrate. However, tests at the El Soplao Cave showed that the plaster partially disintegrated rapidly (in a few months) when dripwater hit it directly, but much slower when it was at the base of the stalagmite. We solved the problem by coating the base of the stalagmite with a layer of epoxy resin, which effectively waterproofed the plaster. This epoxy resin is the same used in the casting of the replicas.

In the replicas, we have only used inorganic dyes that should be relatively inert in the cave environment: iron oxi-hydroxides (light yellow to dark brown), titanium oxide (white) and graphite (black). Furthermore, these dyes are not exotic in the caves we are dealing with: in El Soplao Cave, titanium and iron oxides are abundant in detrital sediments, speleo-stromatolites, and cave walls (Rossi et al., 2010; Lozano et al., 2012), and coal fragments are locally present in the host rock (García et al., 2007).

Fig. 5. Replicas installed in La Buenita Cave (A) and in La Sirena Passage (El Soplao Cave) (B, C, D, E, F). A) Replica of the Buenita-1 stalagmite; B-C-D) Replicas of Soplao-4, Soplao-3 and Soplao-2 stalagmite, respectively; E) Soplao-1 stalagmite before sampling; F) Replica of Soplao-1 stalagmite placed in its original location.

Given the significant anthropogenic influence in the caves associated with mining during the 20th century (García et al., 2007), we did not sterilized the replicas before placing them in the caves. Even though, so far we have not observed any perceptible microbial disturbances on the surfaces of the replicas that have remained in the cave for ~6 years.

For the replicas of stalagmites that were actively growing when sampled (3), it is reasonable to assume that the deposition of new $CaCO_3$ layers will further stabilize the replicas in the cave environment. Two of these replicas (Soplao-4 and Buenita-1) were placed in the caves in June 2017, so significant layers of recent calcite are probably not developed yet on their surfaces. The remaining "active" replica was placed in 2012, but recent calcite precipitation is prevented by the presence of a drip-counting device on its surface. Therefore, we have no information yet on how modern calcite is adhering to and growing over the replicas. However, in drip sites of El Soplao Cave characterized by relatively high $CaCO_3$ supersaturations (saturation index for calcite around 0.8-1.2: Rossi & Lozano, 2016), obvious crusts of recent calcite are covering stalagmite surfaces that were restored with epoxy putty after localized sampling (Rossi & Lozano, 2016). Such crusts have developed in less than two years, suggesting that the epoxy replicas located under active drips will be eventually covered by calcite too.

CONCLUSIONS

Elaborating replicas of stalagmites sampled for paleoclimatic studies is an effective means to reconcile scientific research and cave conservation. Once in place, the stalagmite replicas are almost indistinguishable from the natural specimens. In the case of originally active stalagmites, the impact of sampling will be likely erased in a few years, depending on the rate of calcite deposition.

The molding and casting methods vary depending on stalagmite size. For relatively small specimens (less than ~35 cm tall), we use a single-piece mold and two jackets. For larger stalagmites (~40-70 cm tall), we use a two-piece mold and two jackets.

To reduce replica weight and costs, and to prevent unwanted temperature increases, for relatively small specimens we introduce polyethylene rods into mold axes during casting. For larger specimens, we use techniques to produce hollow casts.

We use extra-hard plaster coated with epoxy resin to fix the replicas to their original substrates. Both the epoxy resin and plaster are carefully dyed to match the original surface texture and color of the sampled stalagmites.

The epoxy used to elaborate and emplace the replicas, as well as the dyes used, are apparently stable in the cave environment, at least for periods of at least six years.

ACKNOWLEDGEMENTS

Financial support was provided by grant ICT-Soplao- 53.5.00.12.00 (IGME - Provincial Government of Cantabria – Turismo del Nansa). We specially thank A. Argumosa, manager of El Soplao S.L., for greatly supporting and facilitating our research in the cave. The highly constructive comments by reviewers C. Spötl, S. Truebe, and by editor B.P. Onac, greatly improved the manuscript.

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