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RESEARCH

ExTraS program: documenting the processes of fixation, recording, and preservation of combustion products in speleothems

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Abstract
In recent years, pyroarchaeology has expanded rapidly and included experimental approaches. However, analyses of the combustion products carried by smoke (mainly soot and microcharcoal) and the study of fixing, recording, and preserving processes of this material on parietal surfaces remain limited. We therefore launched the ExTraS (Experiments on Traces of Soot) program, which aims to document the processes of fixation, recording, and preservation of combustion products in speleothems. We focused on various parameters, including the influence of wall surfaces, meteorological and seasonal conditions, and the nature of the fuel. Here, we present results acquired over several years (2015–2023) that combine macroscopic, microscopic, and colorimetric observations, as well as Raman microspectroscopy characterization. Our findings improve our understanding of the formation process of sooty speleothems observed at archaeological sites in rock shelters and caves.

Keywords Archaeology · Pyroarchaeology · Experimentation · Speleothems · Parietal crust · Soot

Introduction

Since its prehistoric domestication, fire has been central to human societies. Multifunctional (Bentsen 2020) fire use informs us about multiple human behaviors: technological changes, food, exploration of the underground environment, settlement patterns, etc. For several years, fire has been studied as an artifact conveying this diverse information suite. In this context, the archaeological community has been performing more experiments to create reference data and understand the formation of fire-related remains to obtain the maximum information on past human behavior.

Related experiments have focused on hearths, pyres, lamps, torches, etc. (e.g., Aldeias 2017; Carroll and Smith 2018; Medina-Alcaide et al. 2021). These experiments have identified the remains left by these various uses of fire at archaeological sites and the effects of these fires on materials. From these fundamental studies, archaeologists can

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formulate hypotheses on fire functions and related behaviors at dig sites. Hearths are the most-studied fire-related feature, with experiments focusing on parameters such as the fuel used (e.g., Théry-Parisot 2002; Albert and Cabanes 2007; Costamagno et al. 2010; Henry and Théry-Parisot 2014; Henry et al. 2018; Vanlandeghem et al. 2020; Hoare 2020) as well as soil alteration and the thermal impact of fire on previous deposits (Bennett 1999; Sievers and Wadley 2008; Nieto-Márquez and Preysler 2015; Smolderen and Jimenez 2016; Aldeias et al. 2016). These deposits can be analyzed through various approaches, including micromorphological analyses (Wattez 1992; Miller and Sievers 2012; Mallol et al. 2013a, b; Mentzer 2014), magnetic susceptibility (Hrouda et al. 2003; Herrejón Lagunilla et al. 2019), and colorimetry (Ferro-Vázquez et al. 2022; Murray et al. 2022). The study objectives are also diverse (Stahlschmidt et al. 2020); they include documenting the reuse of hearths, identifying the direct and indirect traces of fire to identify ancient hearths, and documenting taphonomic processes. These approaches aim to better understand the formation, conservation, and alteration processes of specific archaeological remains and, as such, create experimental references to allow comparisons or the development of interpretative hypotheses. In this context, multimethod approaches are recommended (Stahlschmidt et al. 2015) and are increasingly applied to extract maximum data from a fire-related site.

Nevertheless, few experiments have focused on the impact of fires on walls. The CarMoThaP project (Ferrier et al. 2017; Ferrier and Leblanc n.d.) is an exception to this absence and focuses mainly on the thermomechanical impacts of fire on walls (thermal desquamation and rubefaction) as part of the study of the transformation of the walls of the Chauvet Cave (Mindeguia et al. 2013; Guibert et al. 2015). Moreover, whereas analyses of combustion residues on the ground (e.g., Braadbaart et al. 2012; Chrzazvez et al. 2014; Pérez et al. 2017; Medina-Alcaide et al. 2021; Karkanas 2021) and the circulation of smoke (e.g., Ferrier et al. 2017; Lacanette et al. 2017; Kedar et al. 2020; Salmon et al. 2020) are numerous, analyses of the combustion products transported by smoke (mainly soot and microcharcoal) and the processes of fixing, recording, and preserving these traces on the walls remain underdocumented.

These smoke-related traces exist and have been documented in Paleolithic (Brochier 1997, 2008; Vandevelde et al. 2017, 2018; Slimak et al. 2022; Angelucci et al. 2022) and more recent archaeological contexts (Genty et al. 1997; Gradziński et al. 2003, 2007; Verheyden et al. 2006; Martínez-Pillado et al. 2014; Gheco et al. 2019; Koç et al. 2020; Vandevelde et al. 2020; Moya-Cañoles et al. 2021; Kaal et al. 2021; Chiarini et al. 2022), in both caves and rock shelters. Understanding smoke deposition, fixation, and recording processes is fundamental, especially in open and well-ventilated environments where the recording conditions are not ideal, given the exposure and the openness of the site. Within the framework of our study on the Mandrin Cave—a rock shelter located in the Rhône Valley in southeastern France that records archaeological occupations—we launched the ExTraS (Experiments on Traces of Soot) program, which aims to document the processes of fixation, recording, and preservation of combustion products in speleothems. In the Mandrin Cave, such archaeological soot deposits have been identified on wall fragments, preserved in thin parietal speleothems (inframillimetric carbonated crusts; their average thickness is approximately 630 µm, i.e., 0.63 mm; $\sigma = 0.58$; Vandevelde 2019). Therefore, this site offers an ideal location to perform smoke-related experiments.

Fireplace structures and charcoal concentrations were identified in Mandrin Cave's archaeological layers E, D, C, B, and A. In layers E and C and at the base of layer B (level B3), the main hearth structures were identified in the same location, in the middle of the rock shelter porch. The repeated use of the same location is linked to the geometry of the rock shelter and is probably related to smoke evacuation. Besides this main hearth in layers E, C, and B, small secondary hearths were identified in layer D; as for the cremation events in layer A (Holocene), they left more extensive traces, mainly located under the rock shelter vault. It should be noted that layers F to J were only excavated in two test pits and that layer F was only partially excavated in the central area. This explains why no hearth structures have yet been formally identified for these units. Nevertheless, burnt elements (flint, bone, wood) can be found in each layer (Vandevelde et al. 2017). The soot traces, evidence of past fires, were recorded on the walls near the hearths in inframillimetric speleothems. Due to the gradual disintegration of the wall over time, speleothems trapping soot deposits can now be found in the sedimentary fill of the rock shelter, in all archaeological layers.

Research questions

Relying on these fuliginous (sooty) speleothems in the Mandrin Cave site, we developed a method to analyze soot deposits trapped in parietal crusts. Documentation of multiple soot films using fuliginochronology indicates that humans came into the cave and lit fires. These sequences of fire result in soot becoming trapped in speleothems found in the cave. These humans then left the cave, and carbonates continued to form on the speleothems. Humans again used the cave and again lit fires, and a new soot layer became trapped in the carbonated parietal deposits; this process continued repeatedly. The end result is a "barcode" of soot-stained carbonates alternating with "clean" carbonates that documents human presence at the site (Vandevelde et al. 2017, 2018). This soot-deposition model must be confirmed and many related questions answered. In this study, we address the following questions:

- Does every fire leave a trace that can or will be recorded?
- How long must a fire burn to leave a trace?
- Does the specific fuel affect soot fixation and conservation processes?
- Can soot deposits form at any time of the year, or do seasonal conditions (e.g., dry vs. wet season) determine preservation? Do these meteorological conditions influence the fixation of soot on the walls?
- Why do we observe on some archaeological samples soot only on parts of a sample? Is this differential preservation linked to fixation, or does it reflect post-depositional taphonomic processes altering soot conservation?

Methods and experimental setting

To answer these questions, we designed the Experiments on Traces of Soot (ExTraS) program. Our experiments were conducted at the Mandrin Cave site in southeastern France. We chose to undertake our experimentation at an actual site to understand the deposition, fixation, recording, and preservation of soot in speleothems in a non-artificial (Mandrin Cave) context. Other studies have used an "experimental cave" or laboratory setting; for example, the CarMoThaP program took place in a quarry and laboratory (Ferrier and Leblanc n.d.; Lacanette et al. 2017). The Mandrin Cave site is a rock shelter where parietal crusts have been documented on walls' fragments throughout the stratigraphy of the site, from the Pleistocene (J to B) to Holocene (A, A′) levels (Vandevelde 2019; Slimak et al. 2021; Vandevelde et al. 2021a). These speleothems continue to grow at the site today. Although the climatic conditions have changed during the periods of human occupation of the cave, the site's altitude and relative proximity to the Mediterranean Sea have remained stable (Fig. 1). These geographical factors can influence the formation of parietal speleothems in rock shelters (Brochier 2008).

The experimental device comprises a furnace in which the fuel can be introduced, a chimney (flexible and able to direct the smoke to a specific spot on the wall) for evacuating the smoke, and a collecting basin for the charcoal. We set up the device to deposit soot on a very limited area of the rock shelter walls by constraining the smoke through the chimney to produce blackened spots. The charcoal recuperation system was included to avoid any anthracological contamination at the site and to avoid the furnace contacting the shelter floor and causing a possible rubefaction of the shelter floor (Fig. 2). Carrying out experiments at an archaeological site raises ethical concerns. We took all the necessary precautions to ensure that our study had no deleterious impact on the site and future research. In addition to our precautions for avoiding soil rubefaction and anthracological contamination of the site and limiting the surface

Fig. 1 Left: Location of the Mandrin Cave site, southeastern France (44° 28′ 10″ N, 4° 46′ 17″ E). Right: Photograph of the interior of the shelter. Shelter dimensions are 12 m wide, 8 m deep, maximum 2 m high (before excavation). Note that the walls exhibit no "classic" speleothems but rather very thin carbonated wall crusts. The shelter's walls and ceiling have crumbled over time, producing clasts that constitute most of the sedimentary filling. These wall fragments covered with thin speleothems have been found at all archaeological levels of the shelter. Today, parietal-crust speleothems continue to form on the walls; these crusts continue to crumble gradually

Fig. 2 Experimental device comprising a furnace to introduce the fuel (72 × 32 cm), a flexible and modifiable chimney, and a basin to avoid anthracological pollution and the rubefaction of the shelter floor. The device blackens a limited area of the wall (formation of black spots)

area of the walls stained by soot, we paid particular attention to the site's appearance. Observation of the walls prior to experiments also enabled us to assess that recent traces of soot would disappear fairly quickly, either covered by veils of calcite or through the gradual crumbling of the walls. Our experiments would therefore have no medium-term impacts on the overall appearance of the site.

We tested differences in fuel burned, the role of the parietal surfaces (orientation and the prior presence or absence of speleothems), and the influence of meteorological and seasonal conditions on soot deposits. We selected fuels that were similar to those used by prehistoric groups; these humans left traces of soot that can still be seen, several tens of thousands of years after the site occupation, in the form of black micrometric films trapped in the parietal carbonated crusts (Vandevelde et al. 2017).

- Spot 1: resinous wood (mixture of dry and fresh *Pinus pinaster*). We chose a resinous wood (*Pinus* sp.) because the wood used throughout the Pleistocene sequence of Mandrin Cave was *Pinus sylvestris* (de Beaulieu et al. 2021). *Quercus* and *Buxus* were only burned in the most recent level (layer A).
- Spot 2: *Pinus pinaster* and dry ox bones.
- Spots 3 and 4: *Pinus pinaster*, dry ox bones, charred dry bone remains, and animal fat.

We selected the blackening areas (spots) to vary the targeted parietal surfaces. The first spot was located on a slightly oblique overhanging section of the wall. Spots 2 and 3 were on more vertical sections; therefore, they will experience different runoff conditions than the first spot (Fig. 3). The second spot encompassed both encrusted wall and fresh fractures resulting from recent wall desquamation and contained both wet and dry areas. The third spot was situated on an encrusted area characterized by a large clast in the process of detaching from the wall. We selected this spot to observe how (if) soot entered cracks. Spot 4, which was only blackened in the second phase of experiments, was located on the shelter ceiling, almost horizontal, and its surface was very encrusted.

We conducted our experimental phases in winter and summer to determine whether seasonal conditions and weather influenced the fixation, recording, and preservation of soot in speleothems. Within the framework of this experimental program, we conducted several field missions (2015–2023). Our last experimental fire was in 2018; we are currently documenting the evolution of the blackened spots

Fig. 3 Location of the four experimental black spots (here the 4th spot is not yet blackened) and orientation of the wall. 1: subhorizontal; 2–3: subvertical; 4: horizontal. Scale bar, 1 m

over an extended period (as of June 2023, it had been 90 months since the first fire). Tables 1 and 2 present, respectively, the program's experimental schedule and the experimental conditions and site parameters.

We made macroscopic observations in the field during the experiments, followed by microscopic observations on thin sections made from sampled wall fragments after the experimental blackenings (from sampling S1 at t_3, one and a half years after the first fire and 1 year after the second blackening).

In caves, black deposits are common and have numerous causes. They can be formed by organic compounds such as bacteria and guano (Kaal et al. 2021), by inorganic compounds such as ferro-manganic oxides (Jones and Northup 2021), or by deposited soot (Vandevelde et al. 2018). The characterization of the black deposit is therefore an essential step. We characterized the archaeological black deposits and the experimentally produced soot deposits using Raman microspectroscopy. This method has been proven successful for characterizing combustion residues (Deldicque et al. 2016, 2023; Lambrecht et al. 2021). This analysis was conducted at the geology laboratory of the ENS (École Normale Supérieure, Paris, France), running a Renishaw® inVia Raman microspectrometer with a 514-nm cobalt laser. Laser intensity was set at low (between 1 and 5% of the maximum power depending on the samples, i.e., 0.5–2.5 mW) to not alter the material during the analysis. The acquisition time was 60 s, and three accumulations were performed for each sample.

To study the color differences between the four experimental soot spots objectively, we measured colors using a colorimeter (SpectroDens) directly on the soot spots in the field (t_3: 2017 field season, Fire 3) and also from photographs (of the blackening episodes of Fires 1 and 2); in the second case, all spots were present on the same photograph, to avoid differences between the spots induced by the camera settings (white balance, brightness, contrast). The colors were documented according to the CIE $L^*a^*b^*$ (Lab) system, which can be represented as a cylinder: L^*, which represents lightness, constitutes the vertical axis; the two parameters a^* and b^* express the deviation of the color from an achromatic (gray) point at the center of the color circle. The values range from 0 (black) to 100 (white) for lightness L, from −300 (green) to +299 (red) on a green–red axis for the a component, and from −300 (blue) to +299 (yellow) on a blue–yellow axis for the b component (Crettez and Hardeberg 1999; International Commission on Illumination 2004).

Results and discussion

Sooty speleothem formation model

Characterization of black deposits

Soot is composed of nanoparticles constituting a turbostratic stacking of polyaromatic sheets with a concentric organization (onion-like structure; Rouzaud et al. 2015). A Raman spectrum of the experimental soot comprised two main bands in the first-order Raman region labeled D and G and located around 1360 cm^{-1} and 1600 cm^{-1},

Table 1 Blackening and sampling schedule

Blackening of the walls	Sampling of blackened wall fragments	Date	Duration
Blackening 1—Spots 1 to 3		15/12/2015	$t_1 = 0$
Blackening 2—Spots 1 to 4		26/07/2016	$t_2 = t_1 + 1/2$ year
	S1	08/08/2017	$t_3 = t_2 + 1$ year
Blackening 3—Spots 1 to 4		09/08/2017	$t_3 = t_2 + 1$ year
	S2	09/08/2017	$t_3 = t_2 + 1$ year + fire
	S3	10/09/2018	$t_4 = t_3 + 1$ year
Blackening 4—Spots 1 to 4		10/09/2018	$t_4 = t_3 + 1$ year
Long-term observations of the evolution of the blackened areas		Between 2018 and 2023; ongoing	From t_4 to t_N

Table 2 Summary of the experimental conditions and macroscopic observations made during the three first blackening tests

		Experimental observations										
		Spot 1			Spot 2			Spot 3			Spot 4	
Characteristics of black spots	Location on the wall	Front-western part of the shelter; horizontal oblique position (approx. 150°)			Front-western part of the shelter; oblique vertical position (approx. 110°)			Front-western part of the shelter; oblique vertical position (approx. 110°)			Front-western part of the shelter; horizontal position (approx. 180°)	
	Description of the area before the fire	In the center: area without crusts; adjacent areas: grayish budding crusts (small buds) and some areas of flat crusts dotted with occasional small buds			Zone generally with budding and white crusts at the base of the spot; zone without concretion in the center; zone with rather flat and slightly ferruginous crusts (pinkish) above; presence of microorganisms (rock covered with small green zones)			Slightly ferruginous (pinkish) crust and rather flat for the upper part of the spot; crustless area in the center, immediately above a clast that is starting to fall off (possibility to examine soot deposit on the inner and outer side); crusting rather budding at the base (grayish) and left side (light gray) of the spot			Entirely encrusted area; whitish and rather flat crusts, with a few isolated buds for the northwestern half of the spot; grayish budding crusts for the other half of the spot; small areas of rather flat (punctuated with small holes), whitish or light brown crusts	
	Fuel	*Pinus pinaster* (dry and green parts)			*Pinus pinaster* (dry and green parts) + dry (ox)			*Pinus pinaster* (dry and green parts) + dry bones (ox) + fat (pork for Fires 1 and 3; pork and beef for Fire 2; approx. 250 mL)			*Pinus pinaster* (dry and green parts) + dry bones (ox) + fat (pork—250 mL)	
Experimental settings	Fire	1	2	3	1	2	3	1	2	3	2	3
	Date	15 December 2015	26 July 2016	09 August 2017	15 December 2015	26 July 2016	09 August 2017	15 December 2015	26 July 2016	09 August 2017	26 July 2016	09 August 2017
	Season	Winter	Summer	Summer	Winter	Summer	Summer	Winter	Summer	Summer	Summer	Summer
	Wall aspect before fire	Cold, dry	Dry	Dry	Cold, wet	Dry	Dry	Cold, dry	Dry	Dry	Dry	Dry
	Fire start ($t=0'$)	9:55	16:30	8:00	10:40	17:30	8:40	11:35	18:00	9:15	18:30	9:50
	Fire end ($t=$end)	10:25	17:15	8:30	11:25	17:52	9:10	12:15	18:22	9:45	18:52	10:10
	Fire duration	30 min	45 min	30 min	45 min	22 min	30 min	40 min	22 min	30 min	22 min	20 min
Meteor. station data, Montélimar (infoClimat)	Outdoor $T°$ at $t=0$ (°C)	9.1	32.2	17.1	9.3	32.3	17.9	10.4	32.3	19.7	31.8	20.3
	Outdoor $T°$ at $t=$end (°C)	9.3	32.4	17.9	10.4	32.3	18.8	11.2	31.8	23.0	31.2	20.8
	Precipitation (mm/h)	0	0	0	0	0	0	0	0	0	0	0
	Average wind (km/h)	0	12	3	0	9	4	1.4	11	7	10	7
	Relative humidity (%)	96	38	79	96	37	75	93	37	67	39	65

Table 2 (continued)

		Experimental observations										
		Spot 1			Spot 2			Spot 3			Spot 4	
Observations	Smoke	White smoke	Little smoke, white	Light gray smoke then black smoke	Gray smoke and black smoke	Lots of smoke, black, thick	Gray smoke and black smoke	Black smoke	Black smoke	Black smoke	Black smoke	Black smoke
	Soot color	Black–brown	Black–brown	Anthracite	Anthracite	Anthracite	Anthracite	Very black	Very black	Very black	Very black	Very black
	Notes and remarks	Wood particles and ashes were deposited on the wall with the soot; hot fire on a cold wall: created condensation even if the wall was initially dry; this condensation fixed the soot well	No condensation phenomenon on the walls as in December 2015; weather in July 2016: sun + mistral	Resin odor; at $t=5'$, a soot deposit was already visible on the fresh areas (experimental sooty encrusted clasts sampled the day before); at $t=10'$, wood was added; there was already a significant deposit; flames came out of the chimney with the dry wood, very hot fire; at $t=15'$–$20'$, black smoke observed; the periphery of the spot started to blacken; at $t=30'$: big layer of bister + lots of ash and wood particles stuck to the wall on the spot	Spot 2 much darker than Spot 1; hot fire on a cold wall: created condensation; accentuated the wet look of the wall; this condensation fixed the soot well	Acrid smell; fire was hotter than for Spot 1; a lot of diffusion above the spot; the wall darkened much faster than at Spot 1 (shorter burning time than for Spot 1 to obtain a similar staining)	Strong smell of burnt bones (acrid, a bit like chlorine); very little smoke and deposits at the beginning; then at $t=5'$: black smoke flicking at the wall + some gray smoke in the cavity but nothing settled; at $t=10'$, addition of wood and bones (the first bones put in at $t=0$ were already black); at $t=20'$, spot was covered with soot, even on the fresh areas where clasts were sampled the day before. Deposition of a little ash	Soot settled evenly on non-crusted or flat crusted areas; soot settled mainly on the buds for the budding crusts; hot fire on cold wall: created condensation; increased the dampness of the wall and even caused a slight dripping; this condensation fixed the soot well	Pork + beef fat, very noisy fire, very hot; at $t=30'$, the soot settled preferentially on the buds when moving away from the spot; in the center of the spot, it settled everywhere; the soot spread over a large area, wider than that observed in December, because the wall was dry	Smell of grease; black smoke from the beginning and crackling fire; at $t=5'$, the spot was already blackened; a lot of black smoke, no gray smoke; at $t=10'$: addition of grease and very black smoke; spot already completely covered with soot; at $t=20'$, the deposit was more extensive than for Spots 1 and 2; there was more black smoke, which appeared stickier. Some ash was also deposited	Blackened wall after t = 5′; the fire was hot and roaring, flames came out of the chimney	At the initial addition of grease, the smoke spat fire; big extension of the spot; the fire was so hot that air deformation was observed; no other fuel was added until extinction at t = 20′; soot deposited in larger spots when the wall was dry, but also when the grease was burned (Spots 3 and 4): hotter fire made particles fly more

respectively (Sadezky et al. 2005). The G band is associated with the vibrational modes of the sp^2 hybridized carbons of the aromatic rings, and the D band is associated with the vibrational modes of the aromatic ring edges (Ferrari and Robertson 2000; Deldicque et al. 2023). Comparisons of the experimental and archaeological Raman spectral bands (Fig. 4) confirm that the black deposits observed in the speleothems of Mandrin Cave and the experimental samples are both soot films (ruling out other black-like materials). Moreover, the D and G band positions and the intensities of experimental and archaeological Raman spectra of soot deposits were very comparable. All spectra were acquired on black layers, and we avoided sampling wood charcoal microparticles. Microcharcoal particles can be identified (and distinguished from soot) by microscopy on thin sections and then be characterized by Raman microspectroscopy (Fig. 4c; bottom spectrum). Experimental soot gives a signal that is comparable to archaeological black deposits, confirming the latter as soot deposits.

Microscopic observation of experimental samples

The experimental samples were prepared as thin sections having a thickness of 30 µm. We analyzed two thin soot deposits recorded in the inframillimetric parietal crust (Fig. 5). Microscopic observations of thin sections show that the speleothems recorded two distinct soot films, representing two experimental fires separated by 6 months. Soot is therefore fixed, recorded, and preserved by the carbonate record. Moreover, these observations confirm a lack of secondary deposition of soot particles, which could have migrated during carbonate growth to form a "phantom" film unrelated to a new fire event. Thus, the crust records a minimum number of fires, as a series of temporally close fires would likely be recorded as a single visible film because the carbonates would not have grown sufficiently to separate the fire-related deposits. And these experiments confirm that a minimum number of fires is recorded and that no "phantom soot films" are added. Furthermore, these experimental

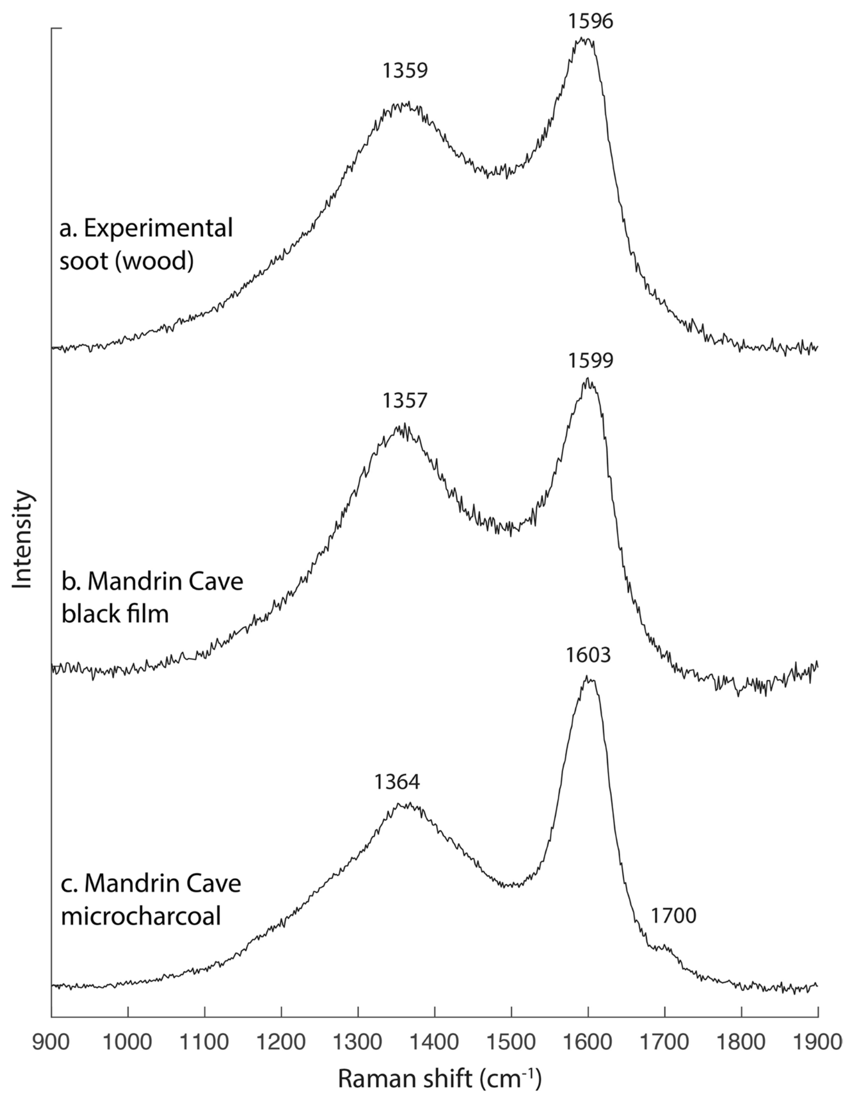

Fig. 4 From top to bottom: Raman spectra recorded on (a) experimental soot (Spot 1—MAN-Exp-2018-s1-wood), (b) archaeological soot (MAN-EF-1081), and (c) archaeological microcharcoal (MAN-EF-1081). Microspectrometer settings were a 514 nm laser, 1 to 5% laser intensity—0.5 to 2.5 mW, 60-s time exposure, and 3 accumulations. The fluorescence signal was removed using a linear baseline or quadratic function when it was particularly large. D and G carbon bands, typical of carbon materials, can be recognized respectively around 1360 and 1600 cm^{-1}. The shape (relative intensity and width) of the two first spectra is typical for strongly defective carbonaceous materials and confirms the identification of soot. The third band at 1700 cm^{-1} is characteristic of oxidized wood charcoal. The similarity between the experimental and archaeological soot demonstrates the good preservation of soot in speleothems

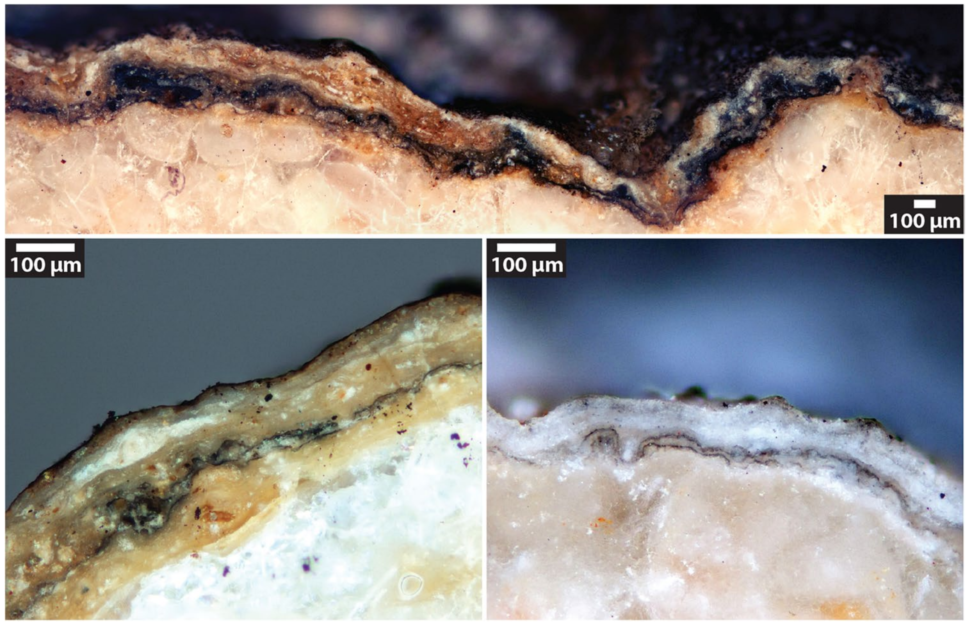

Fig. 5 Polished sections of experimental sooty speleothems (Sampling 1, August 2017). Microscopic observation in reflected light (×50 and×100 magnification). Two soot films were recorded after a pair of experimental fires set 6 months apart. Sampling occurred 1 year after the second fire

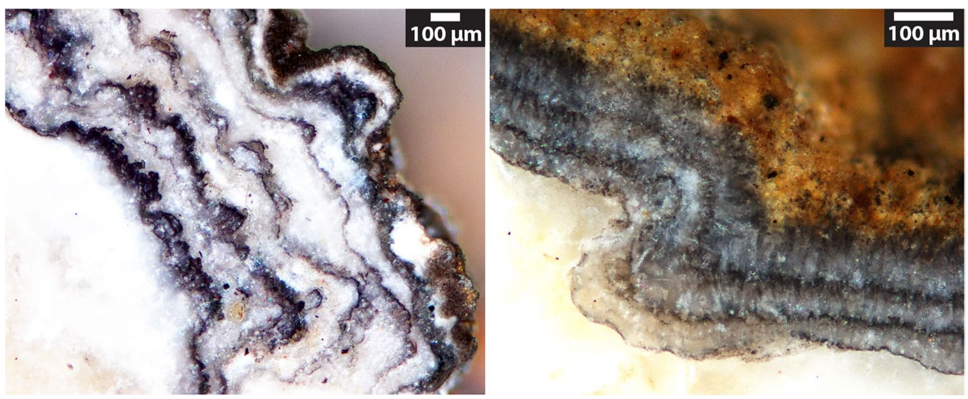

Fig. 6 Polished sections of archaeological sooty speleothems; microscopic observations in reflected light (×50 and×100 magnification for the left and right microphotographs, respectively). Multiple soot films are recorded. Left: budding coralloid-like carbonated crust from layer E. Right: plane thin carbonated crust with calcite laminae growing parallel to the rock surface, from layer B (level B3)

deposits appear very similar to the soot deposits observed in archaeological samples (Fig. 6).

Identifying distinct types of speleothems

We identified two types of speleothems from the microscopic and macroscopic observations of the experimental samples: (i) flat or plane thin carbonated crusts and (ii) thin budding coralloid-like carbonated crusts (Figs. 5 and 7). Coralloids (coral-like in shape) are characterized by spheroidal growth and growth laminae of varying thickness (Bassel 2017). Both speleothem types were found in the archaeological forms documented in the archaeological sedimentary filling of Mandrin Cave (Fig. 6). We can therefore deduce that past speleothem formation processes were quite similar.

Fig. 7 Spot 4 in July 2016, before blackening. Note the areas of budding/coralloid (white arrows) and flat (black arrows) carbonated crusts. Scale bar, 5 cm

Identification of different modes of soot covering by speleothems

Macroscopic observations during the experiments improved our understanding of the processes of coating formation and soot recording in speleothems. We identified two primary mechanisms: (i) the formation of a colonizing speleothem, covering the blackened area from an encrusted zone located beyond the blackened spot, and (ii) the formation of lenticular speleothem, forming a new encrusted area within the blackened spot (Fig. 8). These experimental observations provide a better understanding of the formation process of sooty speleothems in the past.

Soot recording on several sides of a clast

The location of the fire in relation to the cracks in the walls can explain the presence of soot on both sides of the clasts (external and fissural sides), a pattern observed on some of the archaeological samples. From these observations, we developed a model to explain the formation of sooty crusts (Fig. 9). Our experimental observations and the patterns found on the archaeological remains are highly similar, thereby confirming our soot-forming model for speleothems.

Understanding influence of the parietal surface

We then investigated how the state of the parietal surfaces influences the fixation and recording of soot in the parietal crust. First, we noted that the carbonated crust grows relatively fast and therefore favors the separation of individual soot films in cases where the parietal surface is more horizontal than vertical (Fig. 10). Spot 1 is subhorizontal, Spot 4 is horizontal, and both were re-covered by fresh, clean carbonated deposits much faster than Spots 2 and 3 that are subvertical.

We also observed that crust grows faster in cases where there is already a growing carbonated coating on the walls before soot deposition. Secondary carbonate formation requires more time to cover a fresh surface. At Mandrin Cave, carbonate deposition is partly biologically induced, leading to this characteristic coralloid structure of these microcrystalline carbonated deposits (Frisia 2015; Bassel 2017; Vandevelde et al. 2021b). Therefore, epilithic microorganisms must re-settle before accelerating carbonate precipitation on the wall. This biologically induced process is also supported by our observations that when the underlying fire was very hot and burned the parietal surface, we saw the forming of a flat carbonated crust rather than a biologically induced budding (coralloid) crust, suggesting reduced microbial activity.

We also observed that, although the soot was deposited uniformly on the wall at the exit of the chimney, away from the spot, the soot settled preferentially on the buds. We observed a preferential fixation at the top of the coralloids, as observed on the archaeological samples (Fig. 11). This depositional pattern is therefore not a feature of differential conservation; and thus, the absence of soot between the small stalactitic pendants is therefore unrelated to post-depositional processes.

Understanding the influence of meteorological and seasonal conditions

We then evaluated the influence of the meteorological conditions and seasons on soot fixation, recording, and preservation. In winter, the shelter walls are cold; we noted that

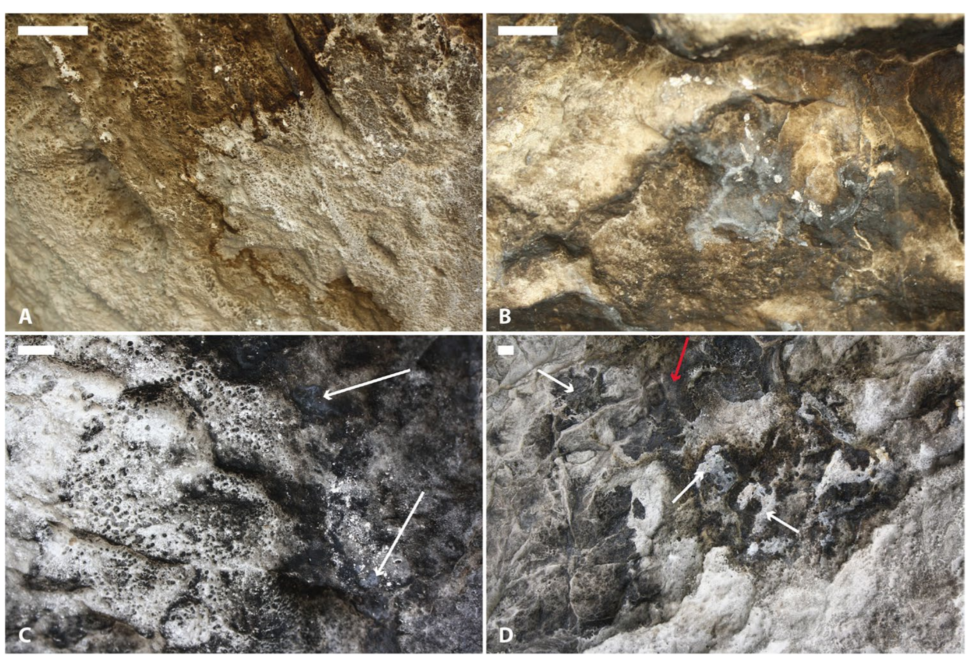

Fig. 8 **A** Spot 1 (July 2016) after being covered by the colonizing speleothem. **B** Spot 2 (July 2016) covered by the formation of a lenticular speleothem. **C** Center of Spot 2 in August 2017, 1 year after the last fire event. The center is the area where the most soot remains visible. Arrows identify the lenticular-flat speleothems, and colonizing-budding speleothems are on the left of the image. **D** Spot 4 in August 2017. Note the budding lenticular speleothems (white arrows) and the flat colonizing speleothems (red arrow indicating the direction of "colonization"). Scale bars, 1 cm

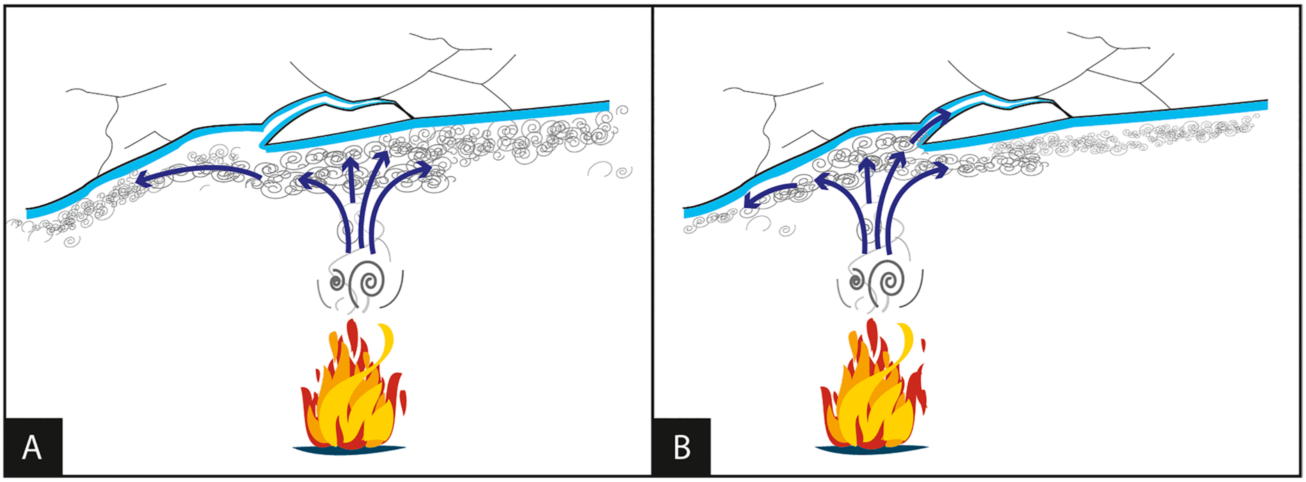

Fig. 9 Schematic representation of soot dispersion from the fire to the walls and along the walls, derived from observations made during the experimental fire events (2015–2018). Depending on the position of the clast on the wall and its opening angle in relation to the position of the fire, soot may or may not penetrate between the clast and the wall

the walls became damp in winter because of condensation created by the temperature differences related to the heat of the fire. The shelter walls are warmer and drier in summer. We observed two different behaviors of soot in relation to the seasons. In winter, the soot settles very quickly within a restricted area when it encounters a wet surface; soot therefore spreads less in winter. In summer, however, the soot spreads more widely and blackens a larger area when the shelter walls are dry. We also noted that walls can be wet in the summer during rainy periods; percolation and circulation of water in the microcracks during rainfall events wet the rock shelter walls regardless of the season.

Speleothems also record seasonal cycles. Calcite can precipitate in annual doublets, similar to tree rings. One type of lamina (sparitic calcite) forms during periods of hydric excess, whereas micritic calcite laminae form during drier periods. In the Mandrin Cave, µLIBS analyses of strontium (Sr) variations (Sr is a trace element showing annual fluctuations) confirmed the annual nature of these calcite doublets (Vandevelde et al. 2021b). On the archaeological samples, we observed soot films within both the micrite and sparite deposits, confirming that soot is recorded regardless of the season.

On-site temperature and hygrometry measurements and regional soil hygrometry (data from the Berzème, Ardèche, meteorological station) demonstrate that the present-day wet season occurs from autumn to spring and that summers are the dry season (Fig. 12). Experimental fires in the winter (December) and summer (in July and August) confirmed that soot was recorded in both seasons and that rains did not remove the soot deposits. Because soot is recorded in both wet and dry seasons, we can access the prehistoric occupation dynamics of the site by analyzing the position of soot films within the calcite doublets. We can, for example, access the (hydric) seasonality of each occupation and occupation frequency over time. Fire residues, such as soot deposits in speleothems, can thus serve as a proxy record of past human behavior by providing information on human mobility and settlement patterns (Vandevelde 2021).

It should be noted, however, that although the present-day dry season for this site is in summer, this pattern was not necessarily true during the different climatic phases recorded at the Mandrin Cave. During temperate or warm periods recorded in the shelter (e.g., layers D and I), we could expect a climatic situation similar to the present. For levels representing colder periods (e.g., layers C and F), the dry season could correspond to winter, as water would be unavailable, trapped as snow or ice. The melt period would then correspond to a period of hydric excess. To determine, for each archaeological level of the site, the correspondence between solar (spring, summer, autumn, or winter) and hydric (dry or wet) seasons, fuliginochronological data (the hydric seasonality of occupation documented from the study of soot films trapped in speleothems), and zooarchaeological data (solar season of occupation documented from the study of faunal remains to determine the time of death of hunted animals) should be compared.

Understanding fuel influence

Our final experimental observations focused on the role of fuel type on soot formation and fixation. We observed that soot color differed depending on the fuel burned. We performed a colorimetric analysis to document the color differences.

Fig. 10 Right column (top to bottom): evolution of black spot coverage by speleothems at 6 months, 1 year, 2 years, and 4 years after the last experimental fire episode. Left column: the initial appearance of the spots post-fire. See Table 1 for the experimental schedule. Numbers indicate the location of Spots 1 to 4

In the first two blackenings, a noticeable difference in soot color was noted between Spot 1 (wood), Spot 2 (wood + dry bone), and Spot 3 (wood + dry bone + fat). We observed no difference in color between Spot 3 and Spot 4; both spots have the same fuel, although the fires were in different areas of the cave. Color differences relate therefore to the nature of the fuel (with different components) and possibly differences in fire temperature produced by the fuel.

At a more detailed level, the soot was black for all four spots, but shades of black were visible in these black spots (Table 3). To better discern these shades, we multiplied the colors' *L*, *a*, and *b* values by four. This coefficient was chosen arbitrarily, as the shades do not contrast as well when multiplied by a coefficient of less than 4; conversely, when the coefficient is too high, the colors become too pale for the shades to be well-observed.

Thus, Spot 1 is a warm black, tending toward reddish brown. Spot 2 is much greener, and Spots 3 and 4 have the particular characteristic of remaining very dark, even with the $L^*a^*b^*$ value multiplied by four. The result was a neutral dark gray (neither warm nor cold) or a cold dark gray that tended toward blue. These results confirm the first field observations: browner soot for Spot 1, anthracite for Spot 2 (in fact, grayer – greener than at Spot 1), and darker (and with a lower chromaticity) for Spots 3 and 4.

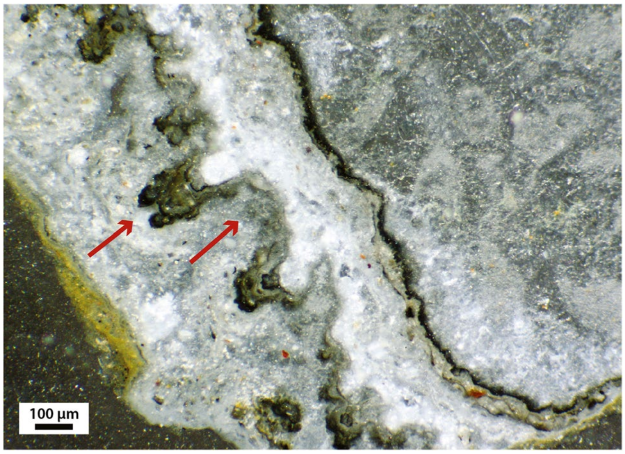

Fig. 11 The buds are the preferred recording area for soot films. Photograph of the thin section of archaeological sample MAN49a in reflected light at × 50 magnification

At the time of the first fire episode (Blackening 1), the furnace had never been used and therefore, there were no traces of bone and/or fat inside for Spot 1. The color differences between Spots 1, 2, and 3 were quite conspicuous. During the subsequent experiments, a slight contamination was possible from the previously burned bones and fat (and certainly re-carbonized). This may explain the less striking differences of black shading between the spots in 2016 and 2017, which were nevertheless noted (Table 3). Spots 1, 2, and 3 demonstrate that the different fuels produced soot deposits of a distinct color (shades of black).

We also observed that soot deposits formed after introducing grease into the fire were blacker but also greasier and thickened faster. It should also be noted that there is a difference in color between the soot deposited during Blackening 1 and that resulting from Blackening 3 for the same Spot 1. In both cases, the fuel was *Pinus pinaster*. However, during Blackening 1, the wood was less dry and the fire much cooler than for the summer Blackening 3 experiment, where the flames went along the chimney as far as flickering against the wall. This temperature difference likely also explains the difference in color among the spots, with blacker soot produced by a hotter fire. The possible remains of charred fat and bones in the furnace must also be considered for this

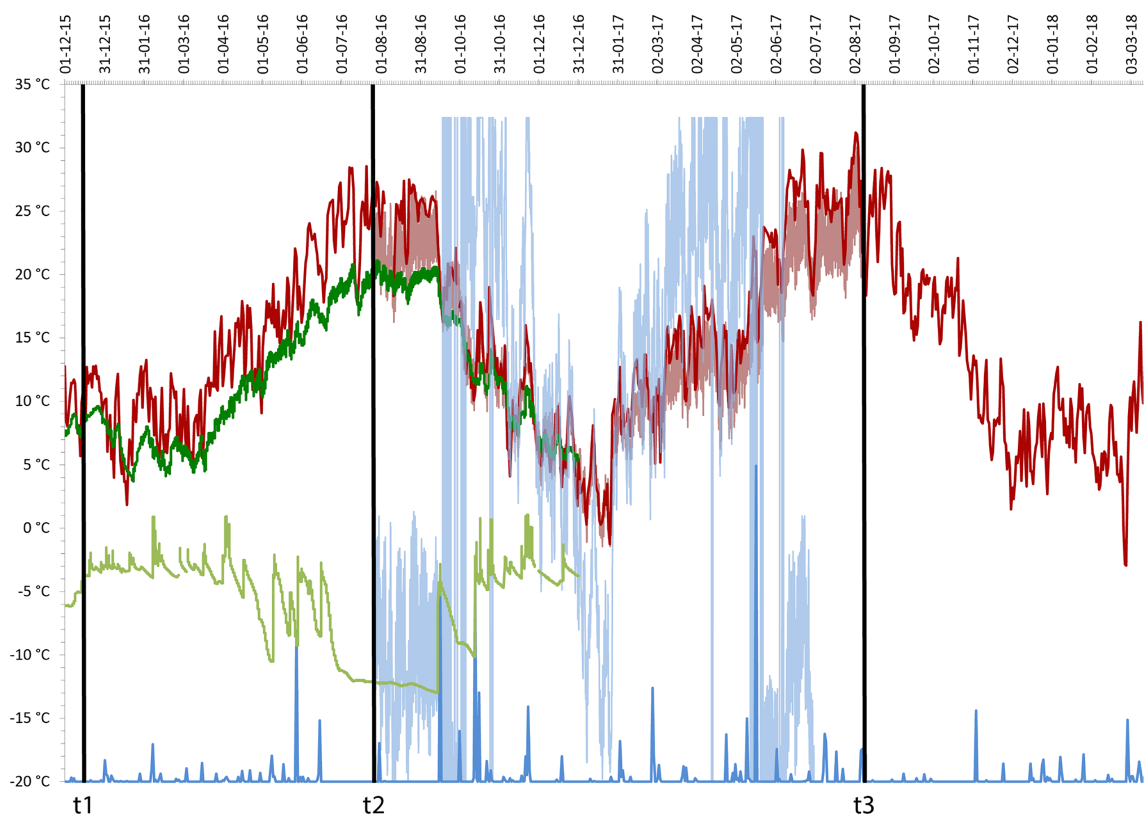

Fig. 12 Thermohygrometry at Mandrin Cave, southeastern France, and microregional meteorological data (from the Montélimar, Drôme, and the Berzeme, Ardèche, stations). Recording of temperature (°C, light red line) and humidity (%RH, light blue line) by a Hobo captor (controlled by TinyTag captor, data not presented) from July 2016 to August 2017. Temperature (°C, green line) and hygrometry (% volumetric water content, light green line) of soils at 30 cm depth, Berzème: data from December 2015 to December 2016. Average temperature (°C, red line) and pluviometry (mm, blue line) at the Montélimar station. Experimental fire events are represented by black vertical lines

Table 3 List of the true colors of each spot ($L^*a^*b^*$) at t_1, t_2, and t_3 after each fire experiment and modified colors by multiplying the $L^*a^*b^*$ components of the true colors by 4 to better visualize the shades ($L^*a^*b^* \times 4$ and average $L^*a^*b^*$ color $\times 4$ for each spot)

Spot	Blackening event	Date of fire	colour (L*a*b*) 1			colour (L*a*b*) 2			colour (L*a*b*) 3			colour (L*a*b*) 4			average colour			average colour		
			L	a	b	L	a	b	L	a	b	L	a	b	L	a	b	Lab	x4	x4 average
1	1	15/12/15	19	2	3	17	-3	3	11	5	5	12	5	1	15	2	3			
1	2	26/07/16	9	2	-2	11	0	-1	8	2	0	12	-1	0	10	1	-1			
1	3	09/08/17	6	0	0	2	0	0	13	1	1	12	0	0	8	0	0			
2	1	15/12/15	11	-3	3	11	0	-1	12	-1	0	9	1	0	11	-1	1			
2	2	26/07/16	9	-1	0	10	0	-1	9	-2	2	11	-5	4	10	-2	1			
2	3	09/08/17	17	0	1	15	2	3	16	1	3	18	1	3	16	1	3			
3	1	15/12/15	7	-3	3	11	4	-7	7	-1	0	5	0	-5	8	0	-2			
3	2	26/07/16	5	0	-1	9	0	0	6	0	-1	5	-1	0	6	0	-1			
3	3	09/08/17	4	0	0	14	0	0	14	0	0	11	0	0	11	0	0			
4	2	26/07/16	6	1	-3	12	0	0	6	1	-3	7	0	0	8	1	-2			
4	3	09/08/17	1	0	0	1	0	0	2	0	1	10	1	2	4	0	1			

observation for Blackening 3 (possible fat and bone residues were not present in the device during Blackening 1). On the other hand, Blackenings 1 and 3 produced similarly textured soot: much lighter, less thick, and less greasy in appearance than soot produced by burning fat.

In summary, the different fuels therefore induce soot deposits of different colors (black–brown for wood alone; black–green or gray for wood + bone; black–blue for wood + bone + fat) and textures (thicker, greasier, and stickier deposits in the case of fat burning). The temperature difference between the fires also appears to influence soot color but not soot texture.

We also observed differences between fuels at the microscopic level. Soot from burned wood or bones was not always recorded as a clearly discernable soot film in the carbonate; a deposit could also be a simple deposition of microcharcoals and some isolated soot particles. Thus, both soot and microcharcoals are recorded and preserved in the speleothems. Raman spectroscopy can be applied to these microcharcoal deposits to obtain more information about the fuel and combustion conditions (Deldicque et al. 2023). Soot from fat burning is stickier, forms quicker, and is preserved in speleothems as an obvious and well-defined soot film. Note that if a fire burns sufficiently long, then the soot from wood burning will also be recorded.

Thus, both the nature of the fuel and burning times (Table 2) influence the recording of soot in speleothems. In a relatively open rock shelter environment such as Mandrin Cave, only long-burning fires or fires over which animal products were burned (or rather cooked) will leave traces in the speleothems. Thus, *at this site*, only occupations that we can qualify as installations or settling events are recorded. Our experiments therefore show that in such an open context with relatively dry wall surfaces, when we study soot films, it is therefore not the study of every visit but rather a study of occupation/settlement events (with cooking or overnight stays on the site) whose dynamics can be accessed. This signal can therefore be used as a proxy to study the rhythms of occupations of the site by different human cultural groups. These observations are valid in an environment such as the Mandrin Cave, an open and relatively dry rock shelter. From our observations of the importance of a wet vs. dry surface, we can expect that soot is fixed and recorded better in enclosed karstic systems. This pattern explains why visits (and not only long occupations) are so well-recorded in stalagmites (e.g., as in Han-sur-Lesse, where touristic visits with lit torches are recorded by a succession of soot films; Genty et al. 1997; Verheyden et al. 2006; Vandevelde et al. 2020).

If we can see differences in colors and microscopic recording and preservation of soot films, these differences may also be seen in the soot structure and revealed by Raman microspectroscopic analysis. We can expect that if different combustion precursors can be identified from charcoal and animal char analyses (Lambrecht et al. 2021; Deldicque et al. 2023), we should expect to observe similar patterns with soot. And indeed, we observed variations in the positions of the D and G bands among experimental samples and even within the same sample. Between-sample differences relate to the fuel type or the fire temperature, as fires were hotter in our experimental setting when fat was burned (Table 2). Within the same sample, variations in soot polymerization relate to different heating temperatures and conditions. Our experimental design prevents separating the roles of fuel and temperature influence. Future research must be designed to isolate these specific factors. In addition, similar to our recent work on the oxidative weathering of charcoal and animal chars (Deldicque et al. 2023), we need to further investigate how soot can change over time as a result of diagenesis (changes in color, composition, structure, etc.).

Conclusion

In recent years, there has been much research on fires but not much on the traces left on the walls. We created the Experimentation on Traces of Soot (ExTraS) program to help fill this knowledge gap. Our observations focus on the fixation, recording, and preservation of soot in speleothems and, more specifically, in the thin parietal carbonated deposits of the open, exposed rock shelter of the Mandrin Cave, southeastern France.

Through the ExTraS program, we show that the formation of thin parietal speleothems (a few micrometers thick) is sufficient to record and preserve films of soot and other residues (i.e., microcharcoal) that escape with the hot smoke and attach to the walls by thermophoresis. We also show that burned remains are sufficiently well-preserved in the carbonate to permit the study of soot structure (via Raman microspectroscopy) even for archaeological samples. Our work involving numerous macroscopic and microscopic observations, as well as the characterization of material, demonstrates that the state of the walls' surfaces, the meteorological and seasonal conditions, and the nature of the fuel all influence the fixation and recording of the soot. Nevertheless, a more precise answer to our question, "How long must a fire burn to leave a trace?", requires conducting experiments using a campfire closer to actual prehistoric conditions. This scenario is, of course, not possible at the Mandrin Cave archaeological site; however, another rock shelter could be used for this purpose because only soot fixation on the walls would be studied (not its recording and preservation in the speleothems).

Future research should establish a complete experimental reference data set; early human practices (e.g., the addition and cooking of grease, use of bones) could be identified by studying archaeological combustion residues, including those trapped in speleothems, which can provide further information on human behavior, particularly through fuliginochronological analyses, to reconstruct the occupation dynamics at archaeological sites.

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Author contribution S.V. wrote the main manuscript text and prepared the figures and tables, except for Fig. 3 prepared by D.D. The ExTraS program was designed and lead by S.V. Experimentation was performed by S.V. and T.B., who also built the experimental device. L.M. prepared the thin sections, and S.V., A.B. and D.D. performed the characterization analyses. L.S. directed the excavations at the Mandrin Cave. C.P. supervised the PhD of S.V., who set up this experimental program during her PhD thesis.

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Data availability All relevant data supporting this study are presented in the paper. Other observations and data generated during the current study but not used for the present paper can be made available from the corresponding author upon reasonable request.

Code availability Not applicable.

Declarations

Competing interests The authors declare no competing interests.

Ethics approval/declarations The experiments were carried out with the agreement of the town (owner of the site) and the person in charge of the archaeological operation, who holds authorization to carry out research on the site from the public authorities (SRA—Service Régional d'Archéologie Auvergne-Rhône-Alpes, DRAC—Direction Régionale des Affaires Culturelles, Ministère de la Culture). The results of the experiments are included in the annual excavation reports submitted to the SRA.

Consent to participate Not applicable.

Consent for publication Not applicable.

References

Albert RM, Cabanes D (2007) Fire in prehistory: an experimental approach to combustion processes and phytolith remains. Isr J Earth Sci 56:175–189

Aldeias V (2017) Experimental approaches to archaeological fire features and their behavioral relevance. Curr Anthropol 58:S191–S205. https://doi.org/10.1086/691210

Aldeias V, Dibble HL, Sandgathe D et al (2016) How heat alters underlying deposits and implications for fire features: a controlled experiment. J Archaeol Sci 67:64–79. https://doi.org/10.1016/j.jas.2016.01.016

Angelucci DE, Patauner E, Duches R (2022) Geoarchaeological characterisation of a younger dryas site in the Alpine uplands: cornafessa rock shelter (italy). Geoarchaeology 38:35–56. https://doi.org/10.1002/gea.21935

Bassel L (2017) Genèse de faciès calcitiques : mondmilch et coralloïdes : étude multiphysique des concrétions de la grotte laboratoire de Leye (Dordogne). Phd Thesis, Université Michel de Montaigne - Bordeaux III

de Beaulieu J-L, Chrzavzez J, Djamali M, Slimak L (2021) Pollens et charbons de bois de la Grotte Mandrin. Quelques données sur la végétation de la moyenne vallée du Rhône au cours de l'OIS 3. In: Slimak L, Giraud Y, Metz L, Yvorra P (eds) Des derniers néandertaliens aux premiers hommes modernes en France méditerranéenne. Les données de la Grotte Mandrin à Malataverne, MMSH. Aix-en-Provence

Bennett JL (1999) Thermal alteration of buried bone. J Archaeol Sci 26:1–8. https://doi.org/10.1006/jasc.1998.0283

Bentsen S (2020) Fire use. In: Oxford research encyclopedia of anthropology. Oxford University Press, Oxford, England. https://doi.org/10.1093/acrefore/9780190854584.013.52

Braadbaart F, Poole I, Huisman HDJ, van Os B (2012) Fuel, fire and heat: an experimental approach to highlight the potential of studying ash and char remains from archaeological contexts. J Archaeol Sci 39:836–847. https://doi.org/10.1016/j.jas.2011.10.009

Brochier JÉ (1997) Couches archéologiques ou “sols d'habitat” ? Quelques observations micro-chronologiques dans un abri-sous-roche pyrénéen. Presented at the International Workshop on Archaeological Soil Micromorphology, Basel

Brochier JÉ (2008) Estudi geoarqueològic dels dipòsits tardiglacials de la Balma de la Margineda (Capes de la 6 a la 11). In: Guilaine J, Martzluff M (eds) Les excavacions a la Balma de la Margineda (1979–1991). Minister d'Afers socials i Cultura, Andorra, pp 52–60

Carroll EL, Smith M (2018) Burning questions: investigations using field experimentation of different patterns of change to bone in accidental vs deliberate burning scenarios. J Archaeol Sci Rep 20:952–963. https://doi.org/10.1016/j.jasrep.2018.02.001

Chiarini V, Couchoud I, Chalmin É et al (2022) An early Middle-Age dark layer in Bosnian stalagmites: possible link to an historical event? In: 18th International Congress of Speleology - Savoie Mont Blanc 2022. Vol. V - Karstologia Mémoires n°25 - SYMPOSIUM 08 - Archaeology and Palaeontology in caves. pp 203–206

Chrzavzez J, Théry-Parisot I, Fiorucci G et al (2014) Impact of post-depositional processes on charcoal fragmentation and archaeobotanical implications: experimental approach combining charcoal analysis and biomechanics. J Archaeol Sci 44:30–42. https://doi.org/10.1016/j.jas.2014.01.006

Costamagno S, Théry-Parisot I, Kuntz D et al (2010) Taphonomic impact of prolonged combustion on bones used as fuel. P@lethnologie 2:169–183. https://doi.org/10.4000/palethnologie.8995

Crettez J-P, Hardeberg JY (1999) Analyse colorimétrique des peintures : étude comparative de 3 tableaux de. J b Corot TECHNE 9–10:52–60

Deldicque D, Rouzaud J-N, Velde B (2016) A raman – HRTEM study of the carbonization of wood: a new raman-based paleothermometer dedicated to archaeometry. Carbon 102:319–329. https://doi.org/10.1016/j.carbon.2016.02.042

Deldicque D, Rouzaud J-N, Vandevelde S et al (2023) Effects of oxidative weathering on raman spectra of charcoal and bone chars: consequences in archaeology and paleothermometry. Comptes Rendus Géoscience 355:1–22. https://doi.org/10.5802/crgeos.186

Ferrari AC, Robertson J (2000) Interpretation of raman spectra of disordered and amorphous carbon. Phys Rev B 61:14095–14107. https://doi.org/10.1103/PhysRevB.61.14095

Ferrier C, Auguin G, Aujoux A et al (2017) Les feux de la grotte chauvet-pont d'arc : approches expérimentales. Ardèche Archéologie 34:3–12

Ferrier C, Leblanc JC (n.d.) CarMoThaP : Caractérisation et Modélisation des Thermo-altérations et des résidus de combustion sur les Parois. https://carmothap.wixsite.com/feux. Accessed 10 Feb 2023

Ferro-Vázquez C, Mallol C, Aldeias V (2022) Simply red? a systematic colour-based method for identifying archaeological fires. Geoarchaeology 37:284–303. https://doi.org/10.1002/gea.21886

Frisia S (2015) Microstratigraphic logging of calcite fabrics in speleothems as tool for palaeoclimate studies. Int J Speleol 44:1–16. https://doi.org/10.5038/1827-806X.44.1.1

Genty D, Dauphin Y, Deflandre G, Quinif Y (1997) Exemples de particules d'origine anthropique piégées dans les lamines de croissance de stalagmites - intérêt pour la reconstitution des environnements humains anciens [examples of anthropogenic particles trapped into stalagmite growth laminae - interest for the study of prehistoric human activity.]. Quaternaire 8:149–157. https://doi.org/10.3406/quate.1997.1569

Gheco L, Tascon M, Gastaldi M et al (2019) Hidden paintings, forgotten histories: a micro-stratigraphic approach to study coated rock art. Archaeol Anthropol Sci 11:5037–5052. https://doi.org/10.1007/s12520-019-00854-z

Gradziński M, Górny A, Pazdur A, Pazdur MF (2003) Origin of black coloured laminae in speleothems from the Kraków- Wieluń upland, Poland. Boreas 32:532–542. https://doi.org/10.1080/03009480310003414

Gradziński M, Hercman H, Nowak M, Bella P (2007) Age of black coloured laminae within speleothems from domica cave and its significance for dating of prehistoric human settlement. Geochronometria 28:39–45. https://doi.org/10.2478/v10003-007-0029-7

Guibert P, Brodard A, Quiles A et al (2015) When were the walls of the chauvet-pont d'arc cave heated? a chronological approach by thermoluminescence. Quat Geochronol 29:36–47. https://doi.org/10.1016/j.quageo.2015.04.007

Henry A, Théry-Parisot I (2014) From Evenk campfires to prehistoric hearths: charcoal analysis as a tool for identifying the use of rotten wood as fuel. J Archaeol Sci 52:321–336. https://doi.org/10.1016/j.jas.2014.09.005

Henry A, Zavadskaya E, Alix C et al (2018) Ethnoarchaeology of fuel use in northern forests: towards a better characterization of prehistoric fire-related activities. Ethnoarchaeology 10:99–120. https://doi.org/10.1080/19442890.2018.1510601

Herrejón Lagunilla Á, Carrancho Á, Villalaín JJ et al (2019) An experimental approach to the preservation potential of magnetic signatures in anthropogenic fires. PLoS ONE 14:e0221592. https://doi.org/10.1371/journal.pone.0221592

Hoare S (2020) Assessing the function of Palaeolithic hearths: experiments on intensity of luminosity and radiative heat outputs from different fuel sources. J Paleolit Archaeol 3:537–565. https://doi.org/10.1007/s41982-019-00047-z

Hrouda F, Müller P, Hanák J (2003) Repeated progressive heating in susceptibility vs. temperature investigation: a new palaeotemperature indicator? Phys Chem Earth Parts a/b/c 28:653–657. https://doi.org/10.1016/S1474-7065(03)00119-0

International Commission on Illumination (ed) (2004) Colorimetry, 3. ed. CIE, Central Bureau, Vienna

Jones DS, Northup DE (2021) Cave decorating with microbes: geomicrobiology of caves. Elements 17:107–112. https://doi.org/10.2138/gselements.17.2.107

Kaal J, Martínez-Pillado V, Martínez Cortizas A et al (2021) Bacteria, guano and soot: source assessment of organic matter preserved in black laminae in stalagmites from caves of the sierra de Atapuerca (N Spain). Int J Speleol 50:121–135. https://doi.org/10.5038/1827-806X.50.2.2382

Karkanas P (2021) All about wood ash: long term fire experiments reveal unknown aspects of the formation and preservation of ash with critical implications on the emergence and use of fire in the past. J Archaeol Sci 135:105476. https://doi.org/10.1016/j.jas.2021.105476

Kedar Y, Kedar G, Barkai R (2020) Setting fire in a Paleolithic cave: the influence of cave dimensions on smoke dispersal. J Archaeol Sci Rep 29:102112. https://doi.org/10.1016/j.jasrep.2019.102112

Koç K, Koşun E, Cheng H et al (2020) Black carbon traces of human activities in stalagmites from Turkey. J Archaeol Sci 123:105255. https://doi.org/10.1016/j.jas.2020.105255

Lacanette D, Mindeguia J-C, Brodard A et al (2017) Simulation of an experimental fire in an underground limestone quarry for the study of Paleolithic fires. Int J Therm Sci 120:1–18. https://doi.org/10.1016/j.ijthermalsci.2017.05.021

Lambrecht G, Rodríguez de Vera C, Jambrina-Enríquez M et al (2021) Characterisation of charred organic matter in micromorphological thin sections by means of raman spectroscopy. Archaeol Anthropol Sci 13:13. https://doi.org/10.1007/s12520-020-01263-3

Mallol C, Hernández CM, Cabanes D et al (2013a) The black layer of middle Palaeolithic combustion structures. interpretation and archaeostratigraphic implications. J Archaeol Sci 40:2515–2537. https://doi.org/10.1016/j.jas.2012.09.017

Mallol C, Hernández CM, Cabanes D et al (2013b) Human actions performed on simple combustion structures: an experimental approach to the study of middle Palaeolithic fire. Quat Int 315:3–15. https://doi.org/10.1016/j.quaint.2013.04.009

Martínez-Pillado V, Aranburu A, Arsuaga J et al (2014) Upper Pleistocene and holocene palaeoenvironmental records in cueva mayor karst (atapuerca, Spain) from different proxies: speleothem crystal fabrics, palynology, and archaeology. Int J Speleol 43:1–14. https://doi.org/10.5038/1827-806x.43.1.1

Medina-Alcaide MÁ, Garate D, Intxaurbe I et al (2021) The conquest of the dark spaces: an experimental approach to lighting systems in Paleolithic caves. PLoS ONE 16:e0250497. https://doi.org/10.1371/journal.pone.0250497

Mentzer SM (2014) Microarchaeological approaches to the identification and interpretation of combustion features in prehistoric archaeological sites. J Archaeol Method Theory 21:616–668. https://doi.org/10.1007/s10816-012-9163-2

Miller CE, Sievers C (2012) An experimental micromorphological investigation of bedding construction in the middle stone age of sibudu, South Africa. J Archaeol Sci 39:3039–3051. https://doi.org/10.1016/j.jas.2012.02.007

Mindeguia J-C, Sirieix C, Brodard A et al (2013) Simulation de l'impact thermomécanique d'un feu expérimental en carrière calcaire. Implications pour l'étude des feux paléolithiques de la grotte Chauvet-Pont-d'Arc (Ardèche). 21ème Congrès Fr Mécanique 26 Au 30 Août 2013 Bordx Fr FR

Moya-Cañoles F, Troncoso A, Armstrong F et al (2021) Rock paintings, soot, and the practice of marking places a case study in north-Central Chile. J Archaeol Sci Rep 36:102853. https://doi.org/10.1016/j.jasrep.2021.102853

Murray JK, Oestmo S, Zipkin AM (2022) Portable, non-destructive colorimetry and visible reflectance spectroscopy paired with machine learning can classify experimentally heat-treated silcrete from three south african sources. PLoS ONE 17:e0266389. https://doi.org/10.1371/journal.pone.0266389

Nieto-Márquez IO, Preysler JB (2015) Experiments around the fire. discovering human and natural processes in middle Paleolithic hearths. Anthropol 53:501–518

Pérez L, Sanchis A, Hernández CM et al (2017) Hearths and bones: an experimental study to explore temporality in archaeological contexts based on taphonomical changes in burnt bones. J Archaeol Sci Rep 11:287–309. https://doi.org/10.1016/j.jasrep.2016.11.036

Rouzaud J-N, Deldicque D, Charon É, Pageot J (2015) Carbons at the heart of questions on energy and environment: a nanostructural approach. Comptes Rendus Geosci 347:124–133. https://doi.org/10.1016/j.crte.2015.04.004

Sadezky A, Muckenhuber H, Grothe H et al (2005) Raman microspectroscopy of soot and related carbonaceous materials: spectral analysis and structural information. Carbon 43:1731–1742. https://doi.org/10.1016/j.carbon.2005.02.018

Salmon F, Ferrier C, Lacanette D et al (2020) Numerical reconstruction of Paleolithic fires in the chauvet-pont d'arc cave (ardèche, France). J Archaeol Method Theory 28:604–616. https://doi.org/10.1007/s10816-020-09484-5

Sievers C, Wadley L (2008) Going underground: experimental carbonization of fruiting structures under hearths. J Archaeol Sci 35:2909–2917. https://doi.org/10.1016/j.jas.2008.06.008

Slimak L, Zanolli C, Higham T et al (2022) Modern human incursion into Neanderthal territories 54,000 years ago at mandrin. France. Sci Adv 8:eabj9496. https://doi.org/10.1126/sciadv.abj9496

Slimak L, Giraud Y, Metz L, Yvorra P (eds) (2021) Des derniers néandertaliens aux premiers hommes modernes en France méditerranéenne. Les données de la Grotte Mandrin, MMSH. Aix-en-Provence

Smolderen A, Jimenez E-L (2016) Dans le foyer ou sous le foyer? vers Une caractérisation macroscopique des ossements indirectement thermo-altérés. Notae Praehistoricae 36:59–72

Stahlschmidt MC, Miller CE, Ligouis B et al (2015) On the evidence for human use and control of fire at Schöningen. J Hum Evol 89:181–201. https://doi.org/10.1016/j.jhevol.2015.04.004

Stahlschmidt MC, Mallol C, Miller CE (2020) Fire as an artifact—advances in Paleolithic combustion structure studies: introduction to the special issue. J Paleolit Archaeol 3:503–508. https://doi.org/10.1007/s41982-020-00074-1

Théry-Parisot I (2002) Fuel management (bone and wood) during the lower aurignacian in the pataud rock shelter (lower Palaeolithic, les eyzies de tayac, Dordogne, France). Contribution of Experimentation J Archaeol Sci 29:1415–1421. https://doi.org/10.1006/jasc.2001.0781

Vandevelde S, Brochier JÉ, Petit C, Slimak L (2017) Establishment of occupation chronicles in grotte mandrin using sooted concretions: rethinking the middle to upper Paleolithic transition. J Hum Evol 112:70–78. https://doi.org/10.1016/j.jhevol.2017.07.016

Vandevelde S, Brochier JÉ, Desachy B et al (2018) Sooted concretions: a new micro-chronological tool for high temporal resolution archaeology. Quat Int 474:103–118. https://doi.org/10.1016/j.quaint.2017.10.031

Vandevelde S, Genty D, Brochier JÉ et al (2020) Des concrétions fuligineuses en contextes archéologiques : Quel potentiel informatif ? Géomorphologie Relief Process Environ 26:241–254. https://doi.org/10.4000/geomorphologie.14981

Vandevelde S, Lacour J-L, Quéré C et al (2021b) Identification du rythme annuel de précipitation des carbonates pariétaux pour un calage micro-chronologique des occupations archéologiques pyrogéniques : le cas de la grotte mandrin (malataverne, drome, France). BSGF - Eath Sci Bull 192:9. https://doi.org/10.1051/bsgf/2021002

Vandevelde S, Brochier JÉ, Slimak L (2021a) Micro-chronologie des installations humaines. Étude fuliginochronologique des dépôts pariétaux de suie. In: L S, Y G, L M, P Y (eds) Mandrin. Des derniers néandertaliens aux premiers hommes modernes en France méditerranéenne. MMSH, pp 76–101

Vandevelde S (2019) Y'a pas de suie sans feu ! Étude micro-chronologique des concrétions fuligineuses. Étude de cas : le site paléolithique de la Grotte Mandrin (France). Thèse de Doctorat, UFR d'Histoire de l'art et d'archéologie (UFR03), École doctorale d'archéologie (ED112), Université Paris 1 Panthéon-Sorbonne

Vandevelde S (2021) Les rythmicités d'occupation d'un site au sein d'un territoire. Approche diachronique. In: L S, Y G, L M, P Y (eds) Mandrin. Des derniers néandertaliens aux premiers hommes modernes en France méditerranéenne. a&t 4. MMSH, pp 694–709

Vanlandeghem M, Desachy B, Buonasera T et al (2020) Ancient arctic pyro-technologies: experimental fires to document the impact of animal origin fuels on wood combustion. J Archaeol Sci Rep 33:102414. https://doi.org/10.1016/j.jasrep.2020.102414

Verheyden S, Baele J-M, Keppens E et al (2006) The proserpine stalagmite (han-Sur-lesse cave, Belgium): preliminary environmental interpretation of the last 1000 years as recorded in a layered speleothem. Geol Belg 9:245–256

Wattez J (1992) Dynamique de formation des structures de combustion de la fin du paléolithique au néolithique moyen : approche méthodologique et implications culturelles. Thesis, Paris, p 1

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