International Journal of Speleology | 55 (1) | ijs2564 | Tampa, FL (USA) | January 2026

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International Journal of Speleology
Official Journal of Union Internationale de Spéléologie

Non-destructive characterization of variously colored gypsum and aragonite/calcite speleothems from the Cigalère Cave (Ariège, France)

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Abstract: The Cigalère Cave is a 21 km-long karstic cave located in the Ariège Department, in the French Pyrenees, and underlies directly the Bentaillou Pb-Zn-Fe sulfide ores. The cave hosts abundant gypsum mineralizations, some of them exhibiting various colorations including blue, yellow, purple, orange and black. Due to strict preservation policies, these colored mineralizations have not been studied much. Here we propose a non-destructive characterization of five distinct gypsum or carbonate speleothem structures from the Cigalère, exhibiting different colorations. To comply with the preservation policies, no sample was taken from the cave, and all speleothems were analyzed *in situ* using portable X-Ray fluorescence spectrometry (pXRF), with two custom-made calibrations respectively adapted to carbonate and sulfate speleothems. The "Cascade Noire" is suggested to be colored black and orange by coatings composed respectively of hematite/goethite and jarosite. The "Chapelle de Donnea" speleothems are likely colored black by different Mn oxides (likely birnessite) covered by a thin gypsum or calcite layer. The cores of gypsum speleothems are colored blue by Cu^{2+} substitution, which may be influenced by the presence of blue Zn-bearing phases. Yellow carbonate speleothems from the "Gino affluent" may be colored by the presence of humic substances, which could not be detected by pXRF. Field observations and comparison of the speleothems' composition with ores from the overlying Bentaillou mine suggest that all the metallic elements and sulfate ions originate from the weathering of sulfide ores by groundwater and subsequent transportation through joints and fractures. This work also shows the capabilities and limitations of pXRF analysis and its potential application in other preserved caves.

Keywords: Speleothem, geoheritage, Pb-Zn ores, coloration, sulfates, pXRF

Received 29 July 2025; Revised 14 November 2025; Accepted 19 November 2025

Citation: Vlieghe, M., Wouters, J., Fanuel, G., Drion du Chapois, J.-F., Gallez, A., Pire-Stevenne S., Rochez, G., Yans, J., 2026. Non-destructive characterization of variously colored gypsum and aragonite/calcite speleothems from the Cigalère Cave (Ariège, France). International Journal of Speleology, 55(1), ijs2564. https://doi.org/10.5038/1827-806X.ijs2564

INTRODUCTION

In karstic caves, most speleothems (i.e. cave mineral structures, comprising stalactites, stalagmites, flowstone, shields and helictites) are composed of calcite or aragonite, which is linked directly to the composition of the overlying rocks (Fairchild et al., 2006; White, 2019). Due to their typical mineral composition, most speleothems are white when pristine and usually take a brownish hue when some detrital material is incorporated within the speleothems' structure. However, several causes are known to induce various unusual colorations in speleothems, which can be of chemical, crystallographic or even biological origin. Chemical variations inducing coloration include substitution of divalent transition metals in the calcite or aragonite structure, such as Cu^{2+}, Cr^{2+}, Pb^{2+}, Mn^{2+}, or Ni^{2+} associated with various hues (White, 1997; Turner, 2002; Caddeo et al., 2011; Martín-García et al., 2014; Vlieghe et al., 2025). In some cases, the color can be caused by the presence of a separate mineral phase, either intertwined with the calcite or aragonite crystals or as a coating on the external parts of the structures. Examples include nepouite, $(Ni,Mg,Zn)_3Si_2O_5(OH)_4$ in green speleothems from the Aven du Marcou (Vlieghe et al., 2023), iron

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oxides and hydroxides (hematite, goethite, etc.), which create reddish colorations and manganese (Mn) oxides (most often birnessite) that induce black colorations (White, 1997; Rossi et al., 2010), as well as deep blue amorphous Zn-bearing gels in Malaval Cave (Vlieghe et al., 2025). A review of all 364 minerals found in caves was published by Onac (2025). Chromophore pigments in speleothems can also be of organic origin, as humic substances (mostly humic and fulvic acids) are easily incorporated in speleothems, commonly creating yellow to brownish-black colorations. This was described in various caves in the Kraków-Wielund Upland (Gradziński et al., 2003), in El Soplao Cave (Gázquez et al., 2012) or in samples from different caves across North and South America or elsewhere (Van Beynen et al., 2001; Smailer & White, 2013). Two occurrences (one in Georgia, USA, and one in Texas) of yellow colorations induced by textural variations within speleothems were also described (Beck, 1978). Finally, the presence of microbial biofilms on speleothems can also induce coloration, as was observed in Lascaux Cave, France (Alonso et al., 2018, 2023; Bontemps et al., 2024), although the action of microbes on speleothems are more often linked to structural changes, such as finger pools or moonmilk deposits (Melim et al., 2001; Maciejewska et al., 2015; Martinet et al., 2023).

After calcite and aragonite, gypsum is the third most common mineral found in karstic caves speleothems. The presence of gypsum in a carbonaceous environment is most often associated with the oxidation of sulfide minerals (Hill & Forti, 1997). The Cigalère is well-known to host an exceptionally high amount of gypsum speleothems, found in several areas of the cave. Several gypsum speleothems in the Cigalère exhibit stunning colorations, including blue, yellow and black, which may be due to the presence of various metallic elements associated with the gypsum. The cave also hosts calcite and aragonite speleothems, some exhibiting various hues of yellow. Due to the exceptional nature of these speleothems, the Cigalère is highly protected, making it impossible to collect samples from the cave for further analyses in the laboratory. Therefore, alternative, non-destructive techniques are used to complete this study.

Here we describe a study of the coloration causes in the gypsum and carbonate speleothems from the Cigalère. The analysis of colored concretions was performed using a handheld X-Ray Fluorescence spectrometer (pXRF), allowing a quantitative, non-destructive and non-invasive analysis of the speleothems' chemical composition. Analysis by pXRF has become a very important tool in a wide range of disciplines including earth sciences, archeology and mining, as it allows a quick a non-destructive multi-elemental analysis on any surface (Craig et al., 2007; Potts & West, 2008; Lemière, 2018). One of our objectives is to show that, despite pXRF having a lower spectral resolution than a classical micro XRF spectrometer, such a study remains reliable by using proper calibrations and concentrations ratios. This work follows some previous studies that aimed at developing various analysis techniques adapted to the study of precious or fragile materials, such as cultural or geological heritage using Raman spectroscopy or XRF analysis (White, 2006; Finné et al., 2015; Triantafyllou et al., 2021). Samples of host rocks on the surface and ores from the overlying mines were also analyzed to further investigate the metals that might be responsible of the coloration of gypsum speleothems in the cave. The non-destructive quality of the pXRF technique is critical for this study, as the Cigalère lies under strict preservation policies enforced both by the Association de Recherche Souterraine du Haut Lez (ARSHaL) and by the local subprefecture. Therefore, no sample whatsoever could be carried outside the cave, meaning that every analysis had to be performed in situ in a non-destructive way. Considering all this, pXRF was an appropriate tool to fulfill the needs of this study. It allowed a broad and quick screening of the elemental composition of the various colored speleothems found in the Cigalère, while strictly complying with the cave's preservation policies. Even though rough cave conditions (humidity, unevenness of analyzed surfaces, etrc.) limit the accuracy of this technique, the tests performed both in cave environments and in the lab show that this limitation can be overcome by different means, detailed in the Methods section and in Supplementary information file.

In addition to presenting new insights on the causes of the Cigalère speleothems coloration, this work also emphasizes the capabilities of the pXRF technique. When properly calibrated, it can provide useful insights about the chemical composition of these unusual speleothems, which would be unobtainable otherwise without damaging them. We want to show that, despite the harsh conditions having an impact on quantitative analysis, our results are suitable for the purpose of this study, which is to identify foreign metallic elements in colored gypsum speleothems and to suggest plausible causes of those colorations.

GEOLOGICAL CONTEXT

The Cigalère is located in the Pyrénées of southern France in the Ariège Department, near the village of Sentein. The cave's entrance lies at an altitude of 1,700 m. The site is about 2-3 km north of the Spanish border.

The Cigalère has been developed in in the Upper Ordovician Bentaillou Formation, which is mainly composed of white Cippolino marble with argillaceous horizons. The Bentaillou Formation is overlain by two Upper Ordovician formations mainly composed of schists containing sulfide ores. The Silurian formations are largely composed of black shale. The Devonian formations are mostly composed of limestone and calcschist (Fig. 1) (Roucheux, 1990).

The upper part of the Bentaillou Formation hosts extensive Pb-Zn deposits (SEDEX type, named Bentaillou ores) which were heavily exploited throughout the 19th and 20th century (Pouit, 1978; García-Sansegundo et al., 2014). These ores are easily accessible through a dense network of mine galleries located above the entrance of the Cigalère. The sulfide ores are mostly composed of stratabound or vein mineralizations. They are largely dominated by sphalerite with lesser amounts of galena, pyrite, pyrrhotite, chalcopyrite and arsenopyrite (Cugerone et al., 2018).

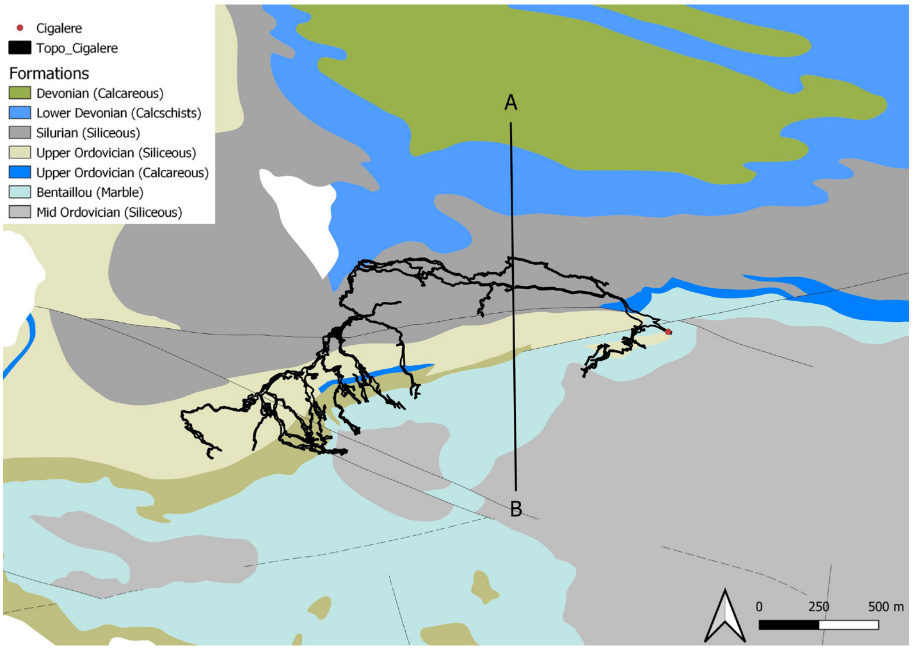

Fig. 1. Geological map of the vicinity of the Cigalère. See Figure 11 for A-B cross-section.

MATERIALS AND METHODS

Sampling and in situ analysis

As mentioned before, due to its unique and quite fragile gypsum mineralization, the Cigalère is extremely well-protected. No samples were taken from inside the cave, and all the results presented here were obtained non-destructively in situ (Fig. 2). See the Analytical methods section for more details.

A total of 51 samples were taken from the outcropping host rocks on the surface and from the Bentaillou mines. The samples were crushed to a powder or made into a thin or polished section for further analysis. Samples from the mines were selected to represent the widest range of ore mineralization, including galena, sphalerite, ankerite and other oxide or sulfide minerals. Samples from the surface comprise fragments of the host rock from every geological formation in the cave's vicinity (ranging from Middle Ordovician to Devonian), primary sulfide deposits in the Ordovician formations and secondary deposits linked to the mining activity.

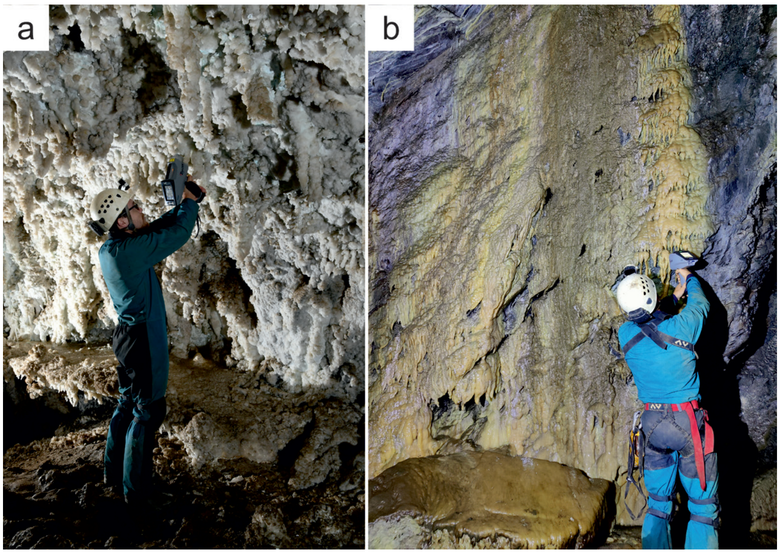

Fig. 2. Speleothems in the Cigalère. a) pXRF measurement on white gypsum speleothems in the main network. b) pXRF measurement on yellow-colored speleothems in the "Affluent Gino".

Analytical methods

Portable X-Ray Fluorescence spectrometry (pXRF)

pXRF measurements were performed using a Bruker Tracer 5G portable X-Ray Fluorescence Spectrometer from the University of Namur. Two separate calibrations were created using Bruker EasyCal software, to analyze carbonate and sulfate samples respectively. The X-Ray beam was generated by 25 kV and 13 µA, for a counting time of 30 s and using an 8 mm spot size. The illumination parameters for the sulfate calibration were 25 kV and 31 µA, for a measurement time of 30 s. These parameters were determined empirically to achieve the highest possible signal while maintaining a dead time of maximum 30%. Wet surfaces were thoroughly dried using a towel to limit signal absorption. Several tests performed beforehand in other caves showed that drying the analyzed surfaces allowed recovery of most of the signal, based on the theoretical Ca amount of pure calcite speleothems (39 wt% measured versus 40 wt% theoretically). Despite this, some sample locations showed strong signal absorption despite being dried. Such locations are readily recognized and, therefore, were omitted from consideration. See Supplementary information file for a detailed report of the pXRF calibrations, the various limitations of the techniques and how they were addressed.

Our pXRF measurements were performed in several zones of interest within the cave. Each of the five zones selected for analysis (Fig. 3) were chosen based upon (i) the presence of colored gypsum or aragonite and (ii) the possibility of straightforward and safe XRF analysis. Two of the selected zones (labeled “Gino Z1” and “Gino Z2”) contain yellow-colored carbonate speleothems, and both are located in the “Affluent Gino”, the cave passage that branches to the left directly after the entrance, close to the surface. The “Blue Zone” is located further in the cave, in the main network just before the “Trou Souffleur”. Several light blue-colored gypsum and aragonite speleothems were analyzed in this area. The “Cascade Noire” hosts a 10 m-wide mineral structure, mostly composed of black and purple-colored gypsum speleothems. Finally, the “Chapelle de Donnea” contains several velvet black stalactites and stalagmites as well as a black flowstone. These zones represent the wide variety of speleothem colors present within the Cigalère.

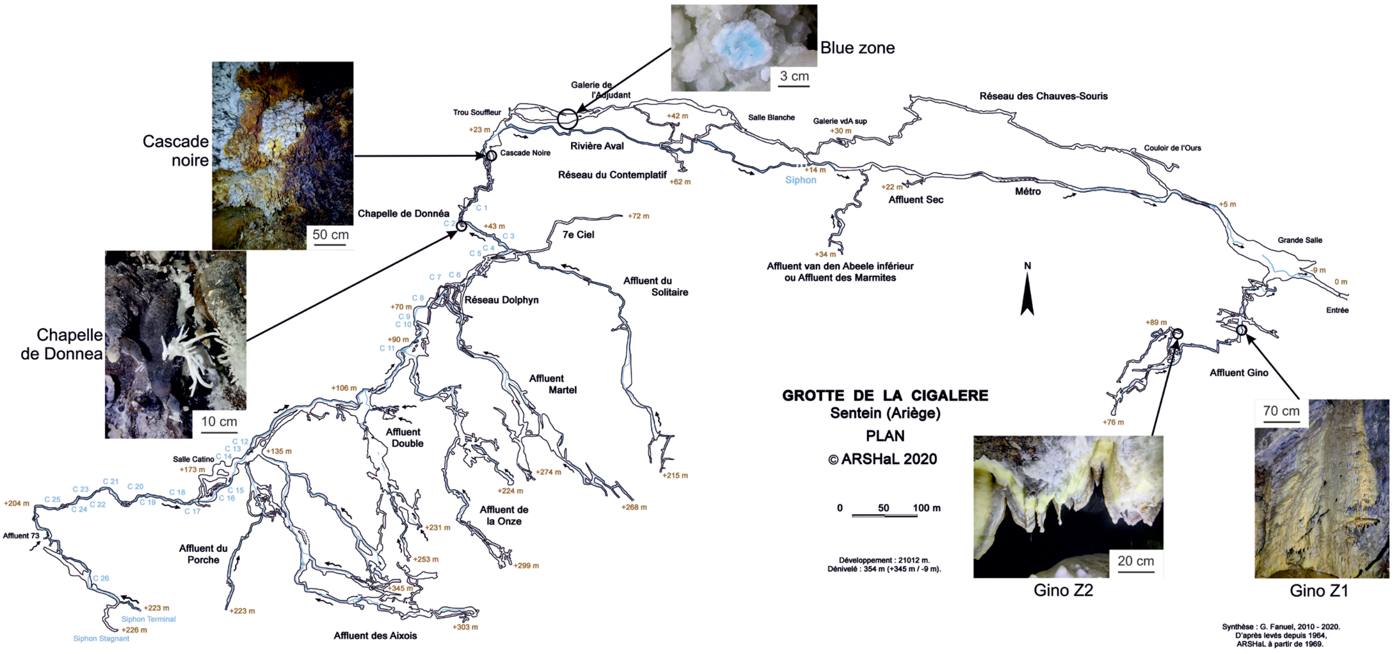

Fig. 3. ARSHaL 2020 topography of the Cigalère with the location of all five zones (arrows and circles) where pXRF measurements were performed.

pXRF calibrations

To obtain accurate and repeatable measurements, it is essential to use a calibration that reflects the general composition of the sample matrix, as XRF analysis can be drastically influenced by matrix effects and other interferences (Gallhofer and Lottermoser, 2018). To this end, it is often useful to use a dedicated calibration whenever undertaking pXRF measurements, as pre-built calibrations obtained from the manufacturers have been shown to create uncertainty in many cases (Da Silva et al., 2023). As this cave hosts both calcite/aragonite and gypsum speleothems, two distinct calibrations were created: one using carbonate-based standards, the other using sulfate-based standards. The methodology we used is largely based on the workflow proposed by Da Silva et al. (2023), although with some key changes described below.

Both calibrations were created prior to the fieldwork and were refined afterwards to make them as close as possible to the analyzed material. The calibrated elements, chosen based on the preliminary results taken in different caves, are Mg, Ca, Mn, Fe, Ni, Cu, Zn and Pb. These elements were chosen to represent a wide array of potential chromophore elements, as it is meant to be applicable in many different caves rather than just the Cigalère. Artificial standards were created by mixing pure carbonate or sulfate compounds, with a concentration range matching the expected concentrations (Table 1). This represents the complete concentration ranges for both calibrations, which may vary from the real limits of quantification determined by the validation process. The methodology used to create the calibrations is described in Supplementary information file.

The choice of which calibration to use at each sampling location was based on a visual determination of the speleothem mineral composition, as both calibrations are optimized for a carbonate or sulfate matrix composition. In some limited cases, the carbonate calibration was used on sulfate matrixes, to avoid detector saturation and unwanted pile-up effects. Usage of the carbonate calibration on sulfate materials introduces a relative error of about 1 to 2 wt% based on the calcium concentration only, but results obtained like this were treated as semi-quantitative as the error for other elements is unknown.

Table 1. Concentration range (wt%) of each calibrated element for both calibrations.

Calibration	Mg	Ca	Mn	Fe	Ni	Cu	Zn	Pb
Carbonate	0.12–26.4	6.82–40.0	0.007–14.8	0.004–34.8	0.001–1.76	0.001–1.47	0.001–1.69	0.001–1.84
Sulfate	0.003–14.7	7.23–29.7	0.005–29.9	0.006–22.2	0.001–0.98	0.001–1.18	0.001–1.18	0.001–0.77

Optical microscopy

Microscopic observations were performed on the samples collected in the mines and on the surface at the University of Namur on standard polished thin sections (thickness 30 µm, for transmitted light observations) and on samples mounted in epoxy resin and polished (for reflected light observations), using an Olympus Evident BX53M polarizing microscope coupled with an Olympus DP23 camera.

Scanning electron microscopy

Electron microscope observations were performed on the polished sections using a JEOL 6010 LV scanning electron microscope coupled with an Ultra Nine 30 JED-2300F Energy Dispersive X-ray Spectrometer (EDS). The samples were coated with ~20 nm of carbon using a Quorum Q150 T/ES to ensure good conductivity and avoid charge buildup. Acceleration voltage was set to 20 kV. Observations were made using a backscattered electrons detector. Semi-quantitative EDS analyses were obtained using a standardless method and ZAF correction.

Powder X-ray diffraction (XRD)

XRD measurements were performed on the mine and surface samples after pulverization with a RETSCH PM 100 planetary ball mill, using opal bowls and marbles to avoid metal contamination. The powdered sample were sieved using a 125 µm mesh. The analyses were performed using an X-Ray Panalytical X'Pert Pro diffractometer and a PHILLIPS PW3710 (CuKα radiation) at the PC2 platform (UNamur), operating at 40 kV and 30 mA in the 5-70° 2θ range. CuKβ radiation was filtered out using a Ni filter placed along the diffracted beam path.

Inductively coupled plasma mass and optical emission spectrometry (ICP-MS/OES)

ICP-MS and ICP-OES measurements were performed on the powdered samples at Activation Laboratories (Ancaster, Canada) to obtain their bulk geochemical composition. Samples were fused with sodium peroxide and underwent an acid dissolution. Samples are then analyzed by ICP-MS and ICP-OES. Calibration is achieved by using calibration based on five synthetic standards. Quality control was performed through analysis of ten to twenty fused certified reference material in every batch of samples. The samples exceeding the upper limit of detection for Zn and Pb were assessed by titration.

Photogrammetry

Photogrammetry was used to create a 3D model of the Cascade Noire zone. A total of 51 pictures were taken at various angles to create the model. Lighting was provided by a set of four Yongnuo yn560 iv flashes, placed at fixed locations to ensure a homogeneous light distribution. The pictures were then loaded in the Agisoft Metashape software, which created a textured mesh of the whole structure. Finally, the mesh was flattened by setting all *Z* coordinates to 0 using the CloudCompare software, which allowed us to get a complete view of the Cascade Noire in a single picture. This was necessary, because the cave's configuration makes it impossible to take such a picture in the field.

RESULTS

pXRF measurements

Cascade Noire zone

The Cascade Noire consists of a 10 m-wide area within the main network of the cave, where the cave wall, 19 m in height, is almost entirely covered by colored gypsum mineralizations. The structure extends further down in two separated flows. Numerous speleothem colorations are observed in this place, including black (hence the name "Cascade Noire"), but also brown, orange, yellow and purple.

Forty-six points have been analyzed on the Cascade Noire by pXRF. The points were selected to represent well the color diversity of the structure (Fig. 4a-e).

Based on field observations, the Cascade Noire is separated into two distinct zones, here termed the "light zone" and "dark zone". The light zone is located on the left-hand side of the structure and is dominated by white to orange colorations (Fig. 4a-b). The dark zone, located on the right-hand side of the Cascade Noire, is largely dominated by dark brown to black colorations, with occasional iridescent purple areas (Fig. 4d-e). The limit between both zones is very abrupt, with a sharp change from light to dark colorations clearly visible in the field (Fig. 4c).

Observed crystal structures and pXRF results (about 15-20 ± 5 wt% Ca and a clear S signal in most analyzed points) suggest that the light zone is mostly composed of white to lightly colored gypsum. The coloration is due to powder-like minerals deposited as thin layers on top of the gypsum crystals. Those powders are sometimes easily washed off, indicating that they are not included in the internal crystal structure of the gypsum and thus deposited after the end of the gypsum mineralization. The texture and color of the powdery minerals suggest that they are likely sulfate phases. As the colored points contain significant S, up to 22-23 wt% Fe and no other significant metallic element, the phases are most likely Fe-bearing sulfates. These results and observations, along with the small but significant K peak observed in the spectra, allows us to suggest that these phases may be composed of jarosite, $KFe^{3+}_3(SO_4)_2(OH)_6$. This is a very common weathering product of Fe sulfides and is often found as microcrystalline brownish coatings (Santoro et al., 2014; Feige Gault et al., 2015)

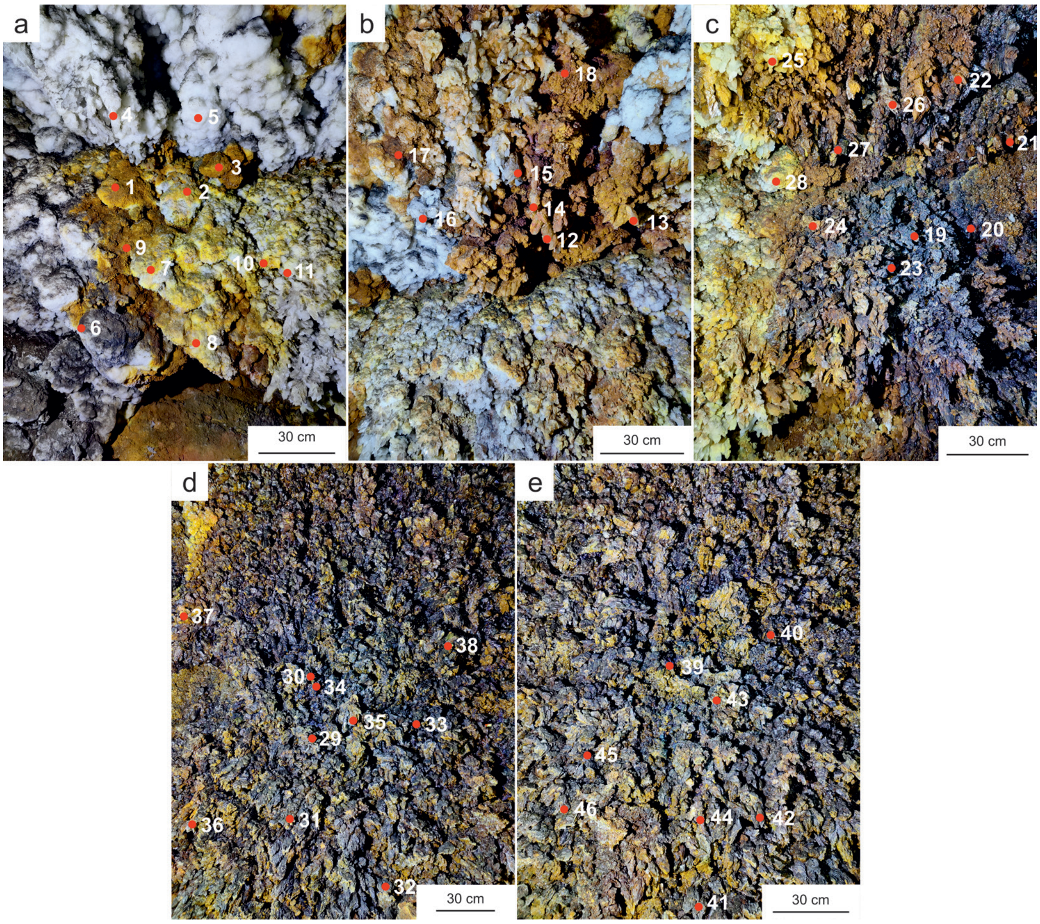

Fig. 4. Points measured by pXRF on the Cascade Noire. a-b) Light zone. c) Limit between light and dark zones. d-e) Dark zone. The size of the red points corresponds to the actual analysis spot size (8 mm).

Observation of mineral structures in the dark zone suggests that it is also mainly composed of gypsum crystals. Still, the measured Ca concentrations vary strongly across those points, being either smaller than 5 wt% or higher than 15 wt%. Each of the Ca-depleted points is associated with an elevated Fe concentration, and vice-versa (Fig. 5). Figure 5 shows that black, orange and white-yellow areas are clearly distinguished by the Ca/Fe ratio. Ca and Fe content show a general negative correlation, suggesting that the Fe-rich minerals do not contain Ca and vice-versa. The Fe content of most of those points largely exceeds the upper limit of quantification given by the calibrations, making reliable quantification impossible, but the calibration still allows a rough estimate. Fe content in the most enriched points yields approximately 50 to 70 wt%, which strongly suggests a matrix mostly composed of Fe-oxide compounds. The rare iridescent purple zones and the brown zones are also associated with high abundances of Fe. Further observations on broken pieces of the structure indicate that, as in the light zone, the gypsum itself is uncolored. The colored minerals in this zone are much more massive than in the light zone, sometimes being several centimeters thick. They exhibit a dark brown to black coloration and a dull, earthy luster. Based on all these elements, the dark colored spots are likely composed of iron oxide compounds, probably of a mixture of hematite (possibly "rainbow" hematite in the iridescent purple points; Lin et al., 2018) and goethite, two very common weathering products of Pb-Zn-Fe sulfide ores (Reichert & Borg, 2008; Skarpelis & Argyraki, 2009).

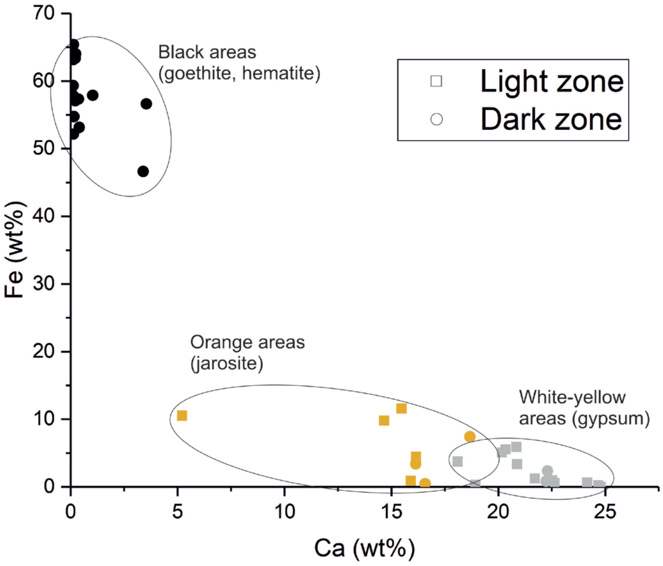

Fig. 5. Plot of Fe (wt%) vs Ca (wt%) at the Cascade Noire. The relation between Fe and Ca concentration across the light and dark zones is emphasized. Point color represents the coloration of the analyzed areas (black, orange or white/uncolored).

To confirm the role of Fe compounds in the colorations, the analyzed points are plotted on the flattened 3D model that was realized by photogrammetric techniques (Fig. 6). Every analyzed point is located on the image, and the approximate limit between the light and dark zones is represented. Note that the model extends from the ground level, but not all the way to the top as any higher point would be difficult to reach. The whole structure is at least 10 meters higher.

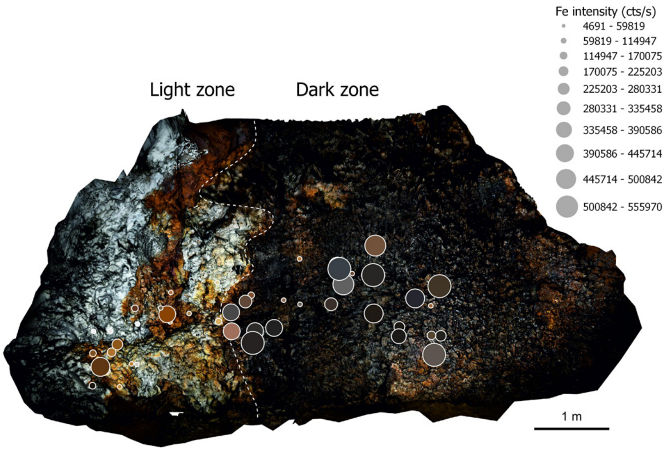

Fig. 6. Flattened 3D model of the Cascade Noire. All the 46 points measured by pXRF are highlighted. The dashed line separates the structure into the “light zone” of the flowstone, dominated by white to orange colorations, and the “dark zone” dominated by brown to black colorations. Each points exhibits the coloration of the analyzed zone and their size reflects the measured Fe concentration.

Each point exhibits its real color extracted directly from the image, and their size represents the intensity of the FeKα peak, showing the relative Fe enrichment across the whole structure. This shows that Fe is generally more concentrated in the dark zone, in which it is associated to dark brown to black colorations as well as iridescent purple. The few Fe-depleted points in this zone are associated with lighter hues such as orange. In the light zone, Fe is much scarcer and is generally only observed in the orange part that crosses the zone in the middle. Yellow to white points yield little to no Fe.

Chapelle de Donnea zone

The “Chapelle de Donnea” is a remote place within the cave. It can only be accessed by climbing a narrow vertical passage covered with gypsum crystals, which leads to a very small room (about 3 m wide for 5 m long with a low ceiling). In this well protected area, numerous velvet black speleothems are observed (Fig. 7a-b), with a distinctively different hue than the black gypsum at the Cascade Noire. Most of these structures are stalactites, stalagmites and columns, either jet black or bright white in color. Some brownish-black dendritic crystals are also observed at some spots in this room (Fig. 7c). The black concretions exhibit a matte and earthy luster, despite being completely coherent and “clean” to the touch. Field observations suggest that the black material is completely covered by a translucent mineral layer of millimeter thickness. Just outside the room, a black-colored flowstone is present, exhibiting the same luster as the velvety speleothems inside the Chapelle (Fig. 7d). Numerous gypsum crystals are observed in the Chapelle itself.

A total of 16 points were analyzed by pXRF in this zone (Fig. 7a, b-d). The goal was to compare the chemical composition of black and white speleothems and identify the difference between them, and thus the element(s) responsible for the black coloration. Some dendrites and a black flowstone were also analyzed to confirm whether they can be linked to the other black speleothems. The main hypothesis as to the cause of this coloration was the presence of Mn oxides within the speleothems.

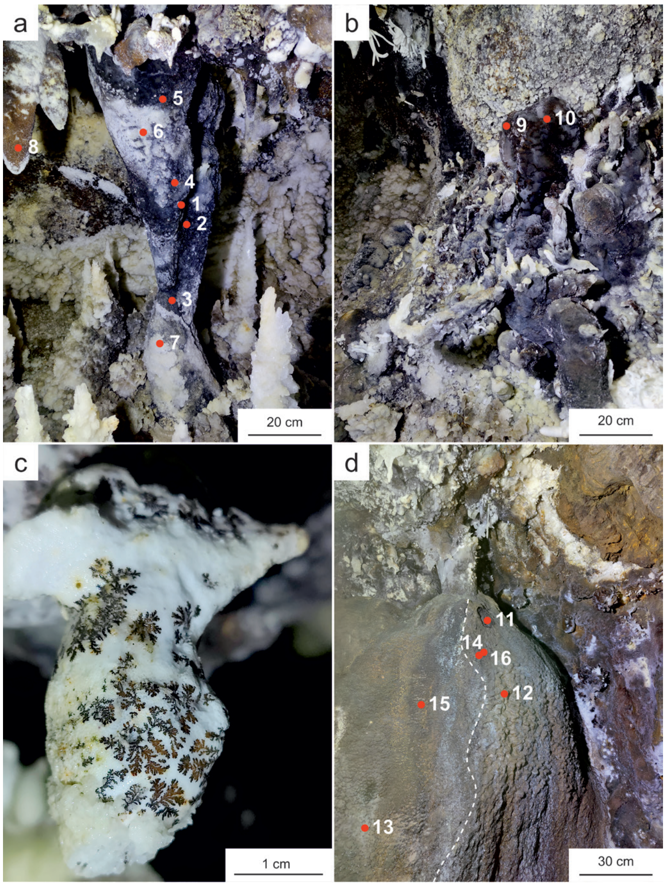

Fig. 7. pXRF measurements on black speleothems in the Chapelle de Donnea zone. a, b) Points analyzed by pXRF inside the Chapelle de Donnea. c) Dendritic brownish-black minerals from the Chapelle de Donnea. Point 8 (a) also exhibits such dendrites. d) Points analyzed on the black flowstone just outside the Chapelle de Donnea. The size of the red points corresponds to the actual analysis spot size (8 mm).

Ten points were analyzed by pXRF in the Chapelle despite the black phases being covered by another mineral. All analyses yielded calcite or gypsum compositions regardless of their color. The thickness of the mineral cover made it impossible to get any signal of the black parts or the dendrites without damaging the speleothems. Traces of Mn are detected in some black points but cannot be quantified due to peak interferences (see calibration details in Supplementary information file for details).

The black flowstone outside the Chapelle was also analyzed. Although the mineral cover is also present on this speleothem, it is naturally damaged, making it possible to analyze the black phases directly. These measurements yielded much higher Mn concentrations. As they are largely above the upper quantification limit, they could not be quantified but are likely higher than 50 wt% Mn (points 11, 12, 14, and 16 in Figure 7d). Mn was undetected on points 13 and 15, corresponding to the undamaged zone of the flowstone. Results show that the black phase is composed of a centimetric layer of soft, earthy material yielding very high Mn concentrations, which suggests the presence of members of the birnessite group, which has the general chemical formula of $(Na,Ca)_{0.5}(Mn^{4+},Mn^{3+})_2O_4 \cdot 1.5H_2O$. The flowstone also exhibits a clear textural variation (Fig. 7d), which separates the Mn-rich and the Mn-depleted points.

Blue zone

Numerous gypsum stalactites are present near the location called “Trou Souffleur”. Those stalactites have a white external part, but their core exhibits a different mineral structure and a distinct blue coloration. The number of points analyzed was limited, because as only the stalactites’ cores are colored, only the broken ones could be analyzed. In total, eight points could be analyzed. Five analyses were performed on the blue cores and three on the white external parts, using two different calibrations: GeoExploration, a proprietary calibration produced by Bruker, which was chosen for its wide variety of quantified elements, and the sulfate calibration, as both the external parts and the cores seem to be mostly composed of gypsum. Note that as the Zn upper quantification limit is 1.18 wt% for the sulfate calibration (see Supplementary information file), those measurements should be treated as semi-quantitative as shown by the high estimated relative error.

The white parts of the stalactites (Fig. 8a) yield a significant S and 22.88 ± 0.03 wt% Ca concentration, confirming that they are likely composed of gypsum as initially hypothesized.

The pXRF results (Fig. 8b) do not indicate high base metal abundances, although two analyses record significant Zn and Pb contents (respectively ~1.78 ± 0.50 wt% and ~1.12 ± 0.02 wt% Zn and 0.201 ± 0.003 wt% and 0.261 ± 0.011 wt%) Pb), with Cu contents very low (110 ppm maximum) for all three analyses.

The blue stalactites’ cores (Fig. 8a) are significantly different, both mineralogically and chemically. First, the observed mineral structure of the cores is distinctly different from the external parts, with much smaller crystals and texture heterogeneities. Second, chemical variations are observed both between the cores and external parts and within each zone (Fig. 8b). Significant amounts of Zn (up to ~10 ± 1.1 wt%) and Cu (0.028 to 0.110 ± 0.001 wt%) are detected in every blue core analyzed, except for one (point B2), which is devoid of Cu and particularly Zn-rich (8.6861 ± 0.027 wt%). Pb is measured in most analyzed points, regardless of color, and varies from 0.036 ± 0.005 wt% to 0.261 ± 0.011 wt% when present. Pb concentration do not show clear differences between the white parts and the blue cores. Some other metals are detected in trace amounts (Ti, Cr, and Fe), but none of these are consistently observed in the blue cores.

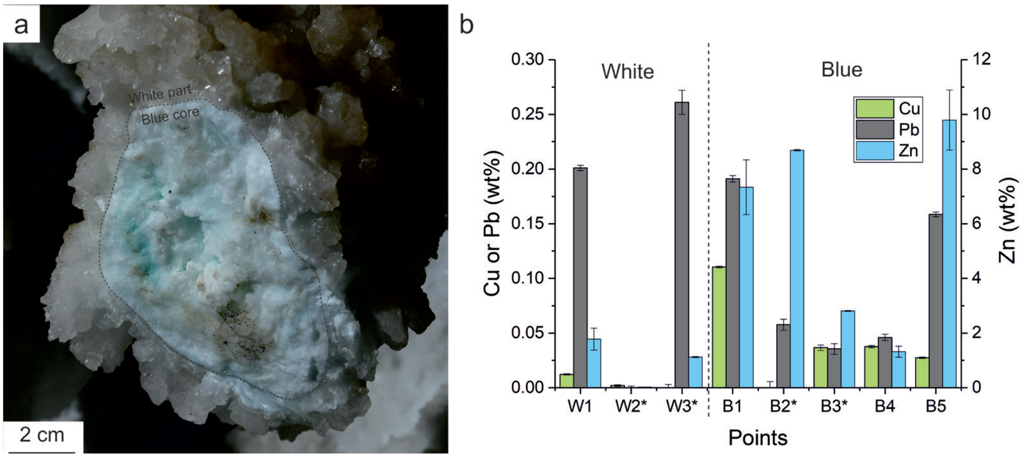

Fig. 8. pXRF measurements on blue speleothems from the Blue zone. a) Area of pXRF measurements on a stalactite from the Blue zone and b) Concentrations for Cu, Zn, and Pb in the blue core and white portion of the speleothem.Measurements with a * sign were performed using the GeoExploration calibration, and the others with the sulfate calibration.

Affluent Gino zones 1 and 2

The Affluent Gino is the network branching to the left, just after the cave’s entrance (Fig. 3). Unlike most other networks and galleries in the cave system, it is not known to contain any gypsum mineralization. This network does contain numerous, yellow-colored aragonite and calcite speleothems. Two of the largest ones are analyzed here: 1) a several meters-high yellow and white flowstone which sits near the entrance of the Affluent Gino (Fig. 9a, labeled Gino Z1 in Figure 3), and 2) a smaller structure hidden inside a niche further into the network and exhibiting a lemon yellow coloration (Fig. 9b, labeled Gino Z2 in Figure 3). Ten points were analyzed in the first zone and 5 were analyzed in the second one. All points yielded 37-40 wt% Ca and no detected S signal regardless of the zone, confirming the absence of gypsum in this part of the cave.

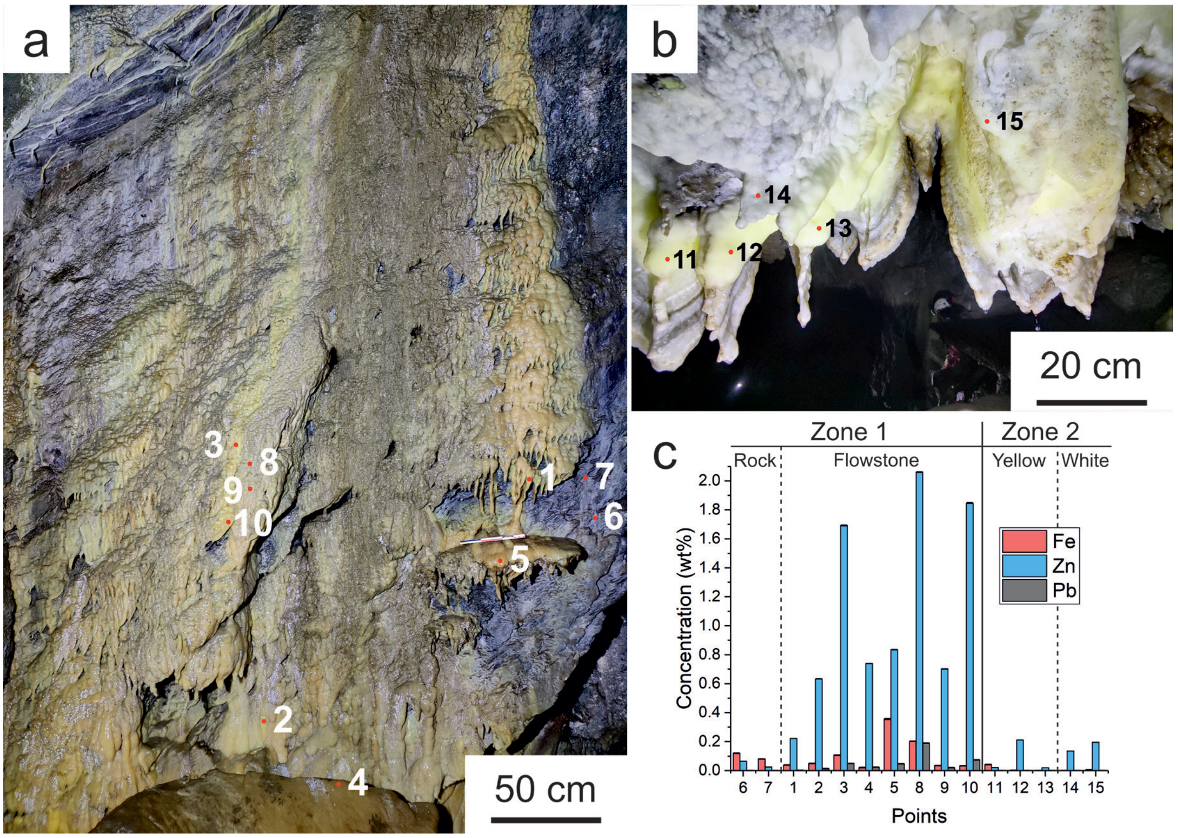

Fig. 9. pXRF measurements on yellow speleothems from both Gino zones. a) Points analyzed by pXRF on the yellow flowstone in the Gino Zone 1. b) Yellow and white stalactites analyzed by pXRF in the Gino Zone 2. c) Measured concentrations of Fe, Zn, and Cu in yellow-colored speleothems in both Gino zones. The size of the red points corresponds to the actual analysis spot size (8 mm).

The points analyzed on the Gino zones speleothems were chosen to compare different hues and the elemental content between them. These flowstones (Fig. 9a) exhibit clear variations in the yellow coloration. The limits between the different hues run parallel to the seepage water flow, suggesting a direct link between the speleothem color and seepage water trace element composition.

Observations of small broken pieces found on the ground show that the yellowish coloration is very evenly distributed at a small scale, with no visible hue or saturation variation whatsoever. Overall, Zn and Pb are the only elements that yield significantly different concentrations between the yellow flowstone and the host rock (Fig. 9c). In zone 1, the only significant detected metals are Fe, Zn, and Pb. Fe is quite evenly distributed across all points regardless of their color and lithology, except point 5 and 8 where it is significantly more concentrated (Fig. 9c). Traces of Ti and K are also detected in point 5 but are not quantified. Zn is especially abundant in the Zone 1 flowstone, at concentrations >1 wt% around points 3, 8, and 10, but also elevated above 0.3 wt% at points 2, 4, 5, and 9. Zn abundances are lower in the Zone 2 flowstone, only reaching maximum concentrations of ~0.2 wt% in both white and yellow colorations. Both points analyzed on the cave wall rock are depleted in Zn compared to the flowstones, displaying Zn contents below 0.07 wt%. Pb is generally less concentrated than Fe and Zn in the speleothem (0.002 ± 0.003 to 0.190 ± 0.004 wt%) but is undetected in the host rock.

The yellow speleothems in Gino zone 2 (Fig. 9b) are much smaller and the yellow coloration is less widespread. Observed crystal structure suggests an aragonitic composition. The yellow areas are located inside a small niche, and only some layers of the stalactites are colored. However, the hue observed in this zone is distinctively different from the flowstone in Gino zone 1. All points analyzed yield very similar results regardless of their color. All contain minor amounts of Fe and Zn (respectively 0.0 ± 0.003 to 0.043 ± 0.004 wt% and 0.020 ± 0.001 to 0.212 ± 0.002 wt%), and no other metal was detected by our XRF analysis. No clear link is observed between the yellow coloration and the metal concentration.

Mineralogical analyses on samples from the mine

The XRD measurements performed on the samples from the Bentaillou mine give an overview of the general ore composition. Most of the samples contain significant amounts of sphalerite, which is the most abundant primary mineral in the mine and sometimes found on its own. Galena is also very widespread and is always associated with sphalerite. Pyrite, chalcopyrite and pyrrhotite are also observed in minor amounts, but only in a few areas. Oxide and sulfate phases were detected in some samples. These include minor amounts of goethite, hematite, cerussite and hydrozincite. These observations confirm several previous studies performed on the Bentaillou ores (Pouit, 1978; García-Sansegundo et al., 2014; Cugerone et al., 2018).

The samples taken from the surface in the Upper Ordovician formations are mostly composed of Cippolino marble or schists containing various amounts of ore minerals. Those minerals include mostly sphalerite with lesser amounts of galena and occasionally pyrite. Pure Cippolino marble is mostly composed of calcite with variable amounts of quartz and muscovite. Schists contain quartz, illite and minor chlorite, and are often intersected by quartz veins. Some of the Silurian ampelites contain minor amounts of pyrite, but most are devoid of any ore minerals. Finally, Devonian calcschists contain various amounts of calcite, quartz, illite and vermiculite, but no ore mineral was observed in these rocks.

pXRF measurements on gossan oxides from the surface

Field observations revealed the presence of secondary gossan oxide deposits near the Pb-Zn orebodies that are commonly observed in fractures and orthogonal joints in Ordovician outcrops. XRD analysis indicates that this secondary mineralization is mostly comprised of goethite that contains minor amounts of Zn, Pb, and S (Fig. 10). They are typically observed in fractures and orthogonal joints in Ordovician outcrops.

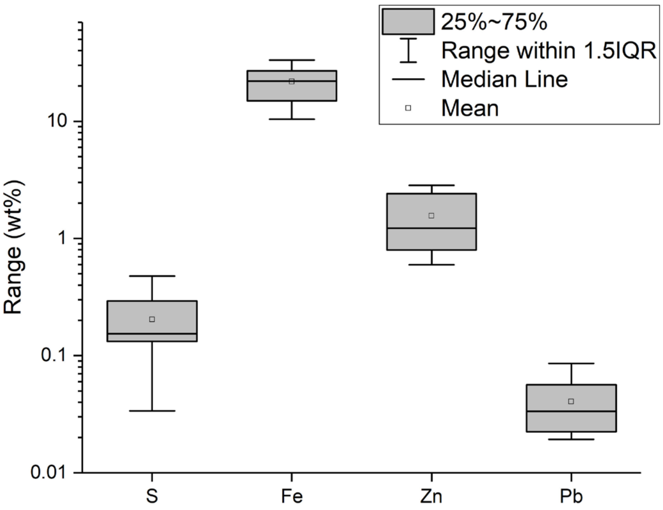

Fig. 10. pXRF measurements of gossan oxide deposits.

DISCUSSION

Causes of the coloration in the Cascade Noire zone

The pXRF results suggest that the various colorations observed at the Cascade Noire may be attributed to several distinct causes. As can be inferred by the structure and color of the mineralizations, a clear compositional difference exists between the left-hand side of the Cascade, dominated by yellow to orange colorations, and the right-hand side which is mostly brown to black.

The left side of the Cascade Noire (light zone, see Fig. 6), dominated by yellow and orange colorations, is likely colored by the presence of Fe-bearing sulfates. As mentioned before, in this part of the flowstone, color is due to powder-like mineral phases which seem to have been deposited on top of the gypsum as a thin layer by the seepage water, either dissolved or particulate. This layer washes off easily, indicating that it is not included in the gypsum's mineral structure and was likely deposited after it. Considering the pXRF results, this layer may be composed of Fe-bearing sulfate minerals. This concurs with the measured concentrations of Fe and S in the orange-colored zones. Furthermore, several Fe-bearing sulfate minerals, including jarosite and copiapite, typically exhibit orange to brownish hues, which correspond to field observations. These minerals commonly form through weathering of Pb-Zn deposits (Skarpelis & Argyraki, 2009) and have been observed in other caves as well (Onac, 2025), further supporting this hypothesis. A more thorough quantification of K would be needed to clearly differentiate between jarosite, $KFe^{3+}_3(SO_4)_2(OH)_6$ and copiapite, $Fe^{2+}Fe^{3+}_4(SO_4)_6(OH)_2\cdot 2H_2O$, but the observation of a variation in the pXRF K signal might indicate that a mixture of both is present in the Cigalère. Although the theoretical Fe content of these minerals is generally ~20-30 wt% Fe, which is higher than the measured Fe concentrations in the light zone, this can be explained by the very small thickness of the sulfate phases covering the gypsum (see Supplementary information file, section pXRF limitations). The detection of several wt% Ca in every measurement point confirms that the underlying gypsum partially interferes with the results, explaining the smaller Fe concentrations.

Similarly, the black, brown and dark purple colorations on the right-hand side (dark zone, see Figure 6) are due to the presence of iron oxides deposited on top of uncolored gypsum. This is largely supported by the pXRF results, as darker zones are always associated with elevated Fe concentrations and clear Ca and S depletion. This also concurs with field observations: pieces of the flowstone picked up from under the Cascade show that gypsum grains are uncolored and transparent but partly covered by dark brown to black phases with a visibly different texture. These phases exhibit the typical earthy and dull luster of Fe oxides such as goethite or hematite. Hematite and goethite are also commonly associated with a brownish-black coloration (Schwertmann, 1993). The rare iridescent purple phases may be associated with so-called "Rainbow hematite", or "turgite". This refers to a mixture of hematite with either goethite or amorphous Fe oxide, creating a structure variation which gives rise to iridescent colors (Lin et al., 2018). This could be due to structural coloration, where a natural material contains a periodic structure in dimensions close to visible light wavelengths. Those structures, called photonic crystals, interfere with visible light and can generate colorations (Mouchet et al., 2013). Electron microscope observations on samples from the Cascade Noire zone would be necessary to confirm this hypothesis.

Based on further observations performed in the field, we suggest that speleothem differences in coloration at the Cascade Noire are caused by two distinct mineralizing fluids with varying compositions. Further investigation would be needed to clearly determine those differences, but it could be explained by spatial or temporal variation in the Bentaillou deposits which could lead to variation in chemical content of the seeping water. This would explain the major mineralogical differences between the light and dark zones, and it is supported by several observations. First, the limit between both zones is roughly vertical, parallel to the water flow's direction, and extends further down in two distinct flows. Furthermore, water flow is still active on the whole structure, suggesting that both orange Fe-sulfates and black Fe-oxides are contemporary to one another as mineralization is still ongoing. No Fe oxide compound was observed in the light zone. Again, isotopic analyses would be needed to determine more precisely the differences between the mineralizing fluids, which will be done in future works.

Causes of the coloration in the Chapelle de Donnea zone

Field observations suggest that the black-colored phases in the Chapelle de Donnea speleothems are covered by a translucent layer of calcite or gypsum. Therefore, non-destructive analysis of these black phases is impossible. Despite that, field observations and pXRF analyses performed on the black flowstone just outside the Chapelle strongly suggest that the unknown black phases may comprise various Mn oxides, which most likely cause the coloration in this area.

The observed mineralogical characteristics and the measured concentrations concur with Mn oxides of the birnessite group. The phases are brown to jet black with an earthy luster, and they sometimes form dendrites which is typically observed for all Mn oxides (Hou et al., 2025). These characteristics are also observed on the blackish flowstone, on which the pXRF analyses revealed the presence of high amounts of Mn and almost no other metallic elements. Birnessite is a very common product of Mn oxidation processes, and is very often observed in carbonaceous environments, further supporting this determination (Post, 1999). Our results suggest that the brown to jet black coloration of the speleothems in the Chapelle de Donnea are caused by the presence of birnessite or other members of the birnessite group (rancieite, takanelite) underneath a thin layer of calcite or gypsum. Further mineralogical and chemical analyses on samples from this area would be useful to obtain a definitive answer on that matter and to further characterize the nature of those oxides.

Causes of the coloration in the Blue zone

Despite the limited number of analyses performed in this zone, the results strongly suggest Cu^{2+} substitution for Ca^{2+} in $CaCO_3$ as one of the causes of the blue coloration. Cu^{2+} in aragonite is known to cause a desaturated blue coloration, which has been observed in numerous other caves (White, 1997; Turner, 2002). First, Cu is absent in every white gypsum part of the speleothems and significant in almost every blue core analyzed. Second, the macroscopic observations and pXRF results suggest that the blue cores are mostly composed of aragonite with minor amounts of gypsum. As mentioned before, aragonite is reportedly known for obtaining a blue coloration when it contains Cu. However, Zn and Pb might also partly be linked to the observed coloration, as was shown in a previous study about Malaval Cave in Lozère, France (Vlieghe et al., 2025). In Malaval Cave, we showed that the presence of Zn-rich phases within the speleothems' lattice and Pb2+ in substitution can greatly impact the coloration caused by Cu2+ substitution. Based on the important variations observed in the blue parts and on the highly variable Zn content locally approaching 10 wt%, we suggest that Zn-bearing phases might be present in the blue speleothems of the Cigalère as well. However, further research including microscopic observations and Raman spectroscopy would be needed to determine if these phases are identical to the ones described in Malaval Cave, and to assess their impact on the observed coloration. Further analysis is planned to address this matter.

Causes of the coloration in the Gino zones 1 and 2

Despite Zn, Fe and Pb being detected in zone 1, no clear correlation is shown between the concentration of these elements and the yellow coloration. Indeed, Fe concentration is quite evenly spread across the flowstone regardless of the coloration, and Fe is not typically linked with a yellow coloration (White, 1997). Zn^{2+} in substitution within aragonite or calcite could not be linked to any coloration (White, 1997), and we have not found any mention of Pb^{2+} being responsible for yellow coloration either. This rules out metal substitution as the coloration cause in Gino zone 1. Nevertheless, the particularly high amounts of Zn (and Pb to a lesser extent) in the whole flowstone and their absence in the host rock suggest that both elements were transported by ground water. The potential presence of undetermined Zn- or Pb-bearing phases that deposited alongside calcite in the flowstone, potentially giving rise to the observed coloration, can also be ruled out. Indeed, the yellow coloration is very homogeneous at a small scale, with no variation whatsoever that could indicate the presence of a foreign, yellow-colored mineral. In addition, no mineral of our knowledge containing either Zn or Pb could create such a coloration. Our preferred hypothesis is thus the presence of humic or fulvic acids as impurities in the calcite lattice, which is known to produce yellow colorations in speleothems (Van Beynen et al., 2001). However, it is not possible to confirm the presence of organic substances based solely on the non-destructive elemental analysis provided by the pXRF. This matter would require further, destructive analyses.

Based on the observed hue, Gino zone 2 speleothems might be colored by different causes than in zone 1. In zone 2, although some metals are detected (mostly Fe and Zn again), their concentration exhibits little variation regardless of the color analyzed, effectively ruling them out as the coloration cause. This particular hue in aragonite has been linked to Ni^{2+} substitution in the literature (White, 1997). However, due to limitations of the pXRF technique (specifically pile-up effects, see Supplementary information file), the LOQ for Ni is higher than 1 wt%, making it impossible to detect Ni traces that might be associated with the coloration in this case. Therefore, no definitive cause can be determined for the Gino zone 2 speleothems. Once again, this would require further analysis that could be carried out with samples from the cave.

Suggested origin of the metallic elements

Several observations lead us to suggest that the metallic elements giving rise to colorations in the cave originate from the Zn-Pb-Fe sulfide deposits overlying the cave.

First, the ores and the now abandoned mines are of the same Upper Ordovician age as the cave's formation. Ores are only found in the same formation as the cave (Bentaillou limestone) and in the one on top of it. The mine is also spatially very close to the cave, partially overlapping it directly. The most prominent place where this is observed is the Cascade Noire zone, where the cave and mine are exceptionally close to one another. This proximity in both time and space constitute favorable conditions for the transportation of metals from weathered ores of the mines and their subsequent deposition in the cave, through groundwater. Second, except for the colorations in the Gino Affluent, all other colored speleothems are associated to gypsum, which illustrates the abundance of sulfate ions in the cave's environment. Sulfate compounds are commonly observed in sulfide ores weathering areas (Dutrizac & Chen, 1987; Poot et al., 2024). The various host rocks analyzed are largely S-depleted, and the only samples that yielded significant amounts of S are sulfide ores and their weathering products, retrieved both from the mine and the surface. This supports that the S detected in the cave originates from the overlying sulfide ores. We suggest that the abundance of gypsum in the cave is linked to the association of Ca2+ ions from the Bentaillou Formation (Cippolino) and the sulfate ions created by weathering and oxidation of the sulfide ores. Considering that significant concentrations of numerous chalcophile elements (Zn, Pb, Fe, Mn, Cu, etc.) are also measured in the mine samples, we suggest that all the metals coloring the gypsum speleothems in the Cigalère originate from the sulfide ores. This might also be true for the calcite speleothems in the Gino affluent, despite the absence of sulfate. Indeed, the abundance of Zn and Pb within the speleothems and their clear depletion in the host rock are a clear indicator that both metals were transported from elsewhere, most likely from the overlying Zn-Pb ores.

Several observations support that metallic elements and S are transported to the cave by groundwater, after weathering of the ores. First, secondary sulfate and oxide minerals are observed in the mines, in close vicinity to the primary sulfides, suggesting strong weathering processes and oxidizing Eh conditions. Second, secondary minerals (mostly iron oxides) are also observed on the surface, in the formations underlying Bentaillou limestone. These mineralizations are exclusively localized in fractures and orthogonal joints, which concurs with their transportation by groundwater, as water preferably flows through fractures. pXRF measurements performed on these deposits show an important Fe enrichment and minor amounts of S, Zn, and Pb. This can be explained by the acidic conditions created by the oxidation of sulfide ores to sulfuric acid, as typically observed in such environments. Such acidic conditions enhance the mobility of Zn and Pb, while Fe mobility is mostly determined by Eh conditions (Verhaert et al., 2017; Poot et al., 2024). Finally, gypsum mineralizations on the ceiling of the cave are also commonly observed alongside orthogonal joints, supporting the previous affirmations. The complete weathering and transportation model we suggest is represented in Figure 11.

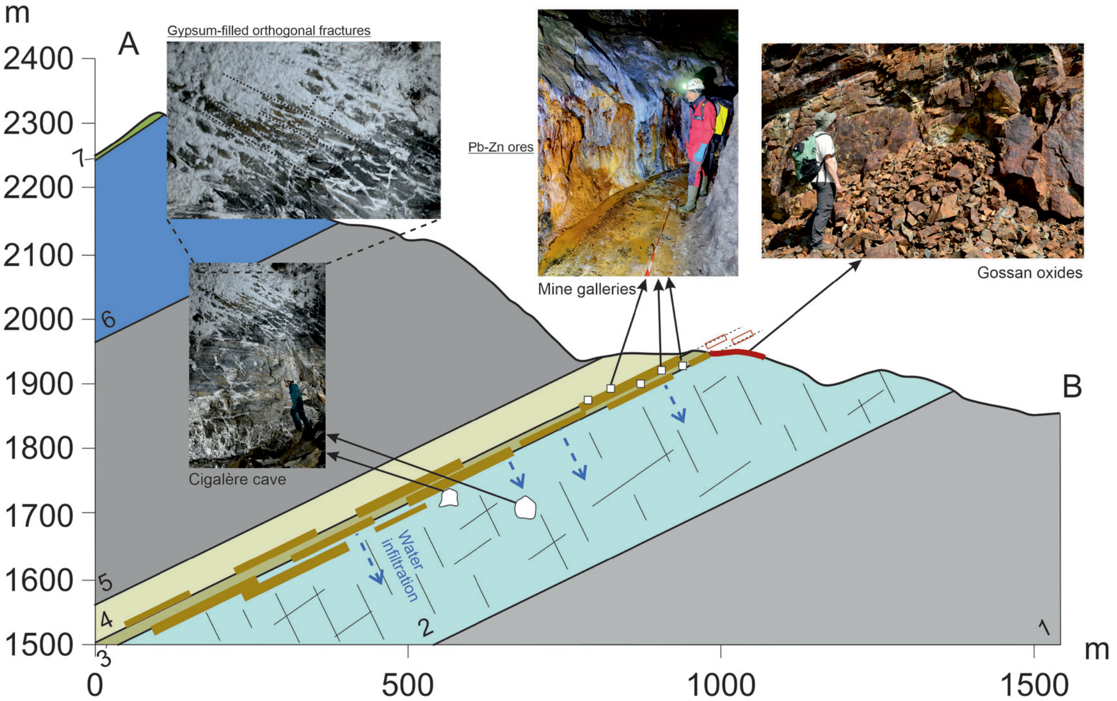

Fig. 11. Schematic cross-section of the Cigalère and its surroundings (see Figure 1 for location of A–B transect). The dashed blue lines illustrate the groundwater flow transporting elements to the cave through fractures of the rocks, due to weathering of the overlying ores. 1: Mid Ordovician siliceous formation, 2: Upper Ordovician Bentaillou limestone, 3: Upper Ordovician siliceous formation, 4: Upper Ordovician limestone formation, 5: Silurian black shale formation, 6: Lower Devonian calcschist formation, 7: Mid Devonian siliceous formation.

Isotopic analyses performed both on rock samples from the cave and the mine, and on water collected from the cave, would be required to get a definitive answer on that matter. However, this is outside the scope of this paper and will be addressed in future works.

CONCLUSION AND PERSPECTIVES

The Cigalère contains abundant gypsum and carbonate speleothems of diverse color. The main objective of this study is to analyze speleothems of different color by using pXRF spectrometry, a non-destructive and non-invasive elemental analysis technique. We also wanted to assess the feasibility of such a study using only this non-destructive method, despite the known limitations, to determine its potential in studying any fragile or preserved karstic environment.

The five colored zones investigated all gave different results, showing again the great variability that exists in this cave. We suggest that the Cascade Noire is colored by jarosite (light zone, orange hue) and goethite/hematite (dark zone, black hue), which are likely deposited from distinct mineralizing fluids with different concentrations of dissolved sulfate. Black speleothems from the Chapelle de Donnea are covered by thin layers of calcite or gypsum, but results and field observations suggest that the brown-black phases are mostly composed of Mn oxides, most likely birnessite. Gypsum speleothems with blue aragonitic cores are likely mainly colored by Cu^{2+} in substitution for Ca^{2+} in the $CaCO_3$ lattice. Comparison with a previous study (Vlieghe et al., 2025) leads us to suggest that this color might be influenced by the presence of some unidentified Zn-bearing phases, but this needs to be investigated further. The causes of the yellow coloration in Gino zone 1 might be the presence of undetermined Zn- or Pb-bearing mineral phases or by the presence of organic acids, but this requires further investigation. In Gino zone 2, no metal could be detected by pXRF, so this coloration remains unexplained. All the metallic elements as well as the sulfate compounds most likely originate from the sulfide ores in the overlying Bentaillou mines.

This work constitutes the first part of the Cigalère's study, which was necessary due to sampling restrictions in the cave. Although we were able to determine probable causes for several colorations, the analysis is impacted by some limitations inherent to the pXRF, including pile-up peaks (inherent to the Ca- and S-rich matrixes), as well as surface roughness and humidity (inherent to the cave environment). As mentioned in section 5, small amounts of samples from the cave would be necessary to carry on further analyses and shed light on the zones where pXRF measurements are insufficient. More specifically, mineralogical techniques (XRD, Raman) would be useful to unequivocally identify the Fe-bearing phases in the Cascade Noire zone and the Mn-bearing phases in the Chapelle de Donnea zone. Microscopical observations and Raman measurements could be performed on the blue and yellow samples to determine whether the coloration is caused by metal substitution in the calcite/aragonite or by the presence of distinct mineral phases. Finally, the suggested link between the cave and the overlying mines could be investigated by comparing S, Cu, Zn, and radiogenic Pb isotopes of samples from the cave, the mine and the host rocks as well as groundwater.

ACKNOWLEDGEMENTS

Martin Vlieghe acknowledges a Research Fellow grant awarded by the Belgian F.R.S.-FNRS (grant #FC50205). We thank Bernard Lafage and all members of the Association de Recherche Souterraine du Haut-Lez (ARSHaL) for allowing us to access and study the Cigalère as well as the Bentaillou mines. We thank the anonymous reviewers for their constructive comments and helpful suggestions.

Authorship statement: JY and GR designed and directed the study. JY, MV, GF, JFDdC, AG, GR, and SPS performed the measurements. JW, JY, and MV designed the calibrations. MV analyzed the data. MV wrote the paper with input from all authors.

Additional online resources: The following repository contains the full dataset of pXRF measurements collected in the Cigalère Cave, along with a document detailing the pXRF calibration procedure and its limitations: https://www.doi.org/10.6084/m9.figshare.30345046.

REFERENCES

Alonso, L., Creuzé-Des-Châtelliers, C., Trabac, T., Dubost, A., Moënne-Loccoz, Y., Pommier, T., 2018. Rock substrate rather than black stain alterations drives microbial community structure in the passage of Lascaux Cave. Microbiome, 6, 1–15. https://doi.org/10.1186/s40168-018-0599-9

Alonso, L., Pommier, T., Simon, L., Maucourt, F., Doré, J., Dubost, A., Trân Van, V., Minard, G., Valiente Moro, C., Douady, C.J., Moënne-Loccoz, Y., 2023. Microbiome analysis in Lascaux Cave in relation to black stain alterations of rock surfaces and collembola. Environmental Microbiology Reports, 15, 80–91. https://doi.org/10.1111/1758-2229.13133

Beck, B.F., 1978. Color differentiation in "fried egg" stalagmites. Journal of Sedimentary Research, 48, 821–824. https://doi.org/10.1306/212f7577-2b24-11d7-8648000102c1865d

Bontemps, Z., Abrouk, D., Venier, S., Vergne, P., Michalet, S., Comte, G., Moënne-Loccoz, Y., Hugoni, M., 2024. Microbial diversity and secondary metabolism potential in relation to dark alterations in Paleolithic Lascaux Cave. Npj Biofilms and Microbiomes, 10, 121. https://doi.org/10.1038/s41522-024-00589-3

Caddeo, G.A., De Waele, J., Frau, F., Railsback, B.L., 2011. Trace element and stable isotope data from a flowstone in a natural cave of the mining district of SW Sardinia (Italy): Evidence for Zn^{2+}-induced aragonite precipitation in comparatively wet climatic conditions. International Journal of Speleology, 40(2), 181–190. https://doi.org/10.5038/1827-806X.40.2.10

Craig, N., Speakman, R.J., Popelka-Filcoff, R.S., Glascock, M.D., Robertson, J.D., Shackley, M.S., Aldenderfer, M.S., 2007. Comparison of XRF and PXRF for analysis of archaeological obsidian from southern Perú. Journal of Archaeological Science, 34, 2012–2024. https://doi.org/10.1016/j.jas.2007.01.015

Cugerone, A., Oliot, E., Chauvet, A., Bordes, J.G., Laurent, A., Le Goff, E., Cenki-Tok, B., 2018. Structural control on the formation of Pb-Zn deposits: An example from the pyrenean axial zone. Minerals, 8, 1–20. https://doi.org/10.3390/min8110489

Da Silva, A.C., Triantafyllou, A., Delmelle, N., 2023. Portable x-ray fluorescence calibrations: Workflow and guidelines for optimizing the analysis of geological samples. Chemical Geology, 623, 121395. https://doi.org/10.1016/j.chemgeo.2023.121395

Dutrizac, J.E., Chen, T.T., 1987. Mineralogical characterization of leach residues of a pyritic Zn-Pb-Cu-Ag concentrate. Canadian Metallurgical Quarterly, 26, 189–205. https://doi.org/10.1179/cmq.1987.26.3.189

Fairchild, I.J., Frisia, S., Borsato, A., Tooth, A.F., 2007. Chapter 7: Speleothems. In: Nash, D.J., McLaren, S.J. (Eds.), Geochemical sediments and landscapes. Blackwell Publishing, Oxford, p. 200-245. https://doi.org/10.1002/9780470712917.ch7

Gault (Feige), K.B., Gammon, P., Fortin, D., 2015. A geochemical characterization of cold-water natural acid rock drainage at the Zn–Pb XY deposit, Yukon, Canada. Applied Geochemistry, 62, 35–47. https://doi.org/10.1016/j.apgeochem.2015.06.003

Finné, M., Kylander, M., Boyd, M., Sundqvist, H.S., Löwemark, L., 2015. Can XRF scanning of speleothems be used as a non-destructive method to identify paleoflood events in caves? International Journal of Speleology, 44(1), 17–23. https://doi.org/10.5038/1827-806X.44.1.2

Gallhofer, D., Lottermoser, B.G., 2018. The influence of spectral interferences on critical element determination with portable X-ray fluorescence (pXRF). Minerals, 8, 320. https://doi.org/10.3390/min8080320

García-Sansegundo, J., Martin-Izard, A., Gavaldà, J., 2014. Structural control and geological significance of the Zn-Pb ores formed in the Benasque Pass area (Central Pyrenees) during the post-late Ordovician extensional event of the Gondwana margin. Ore Geology Review, 56, 516–527. https://doi.org/10.1016/j.oregeorev.2013.06.001

Gázquez, F., Calaforra, J.M., Rull, F., Forti, P., García-Casco, A., 2012. Organic matter of fossil origin in the amberine speleothems from El Soplao Cave (Cantabria, Northern Spain). International Journal of Speleology, 41(1), 113–123. https://doi.org/10.5038/1827-806X.41.1.12

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

Hill, C.A., Forti, P., 1997. Cave minerals of the world (2nd Ed.). National Speleological Society, Huntsville, 463 p.

Hou, Z., Woś, D., Qiu, K., Rogowitz, A., Tschegg, C., Rice, A.H.N., Grasemann, B., Yu, H., Szymczak, P., 2025. Mineral dendrites: Indicators for geological aqueous environments. Earth-Science Reviews, 270, 105231. https://doi.org/10.1016/j.earscirev.2025.105231

Lemière, B., 2018. A review of pXRF (field portable X-ray fluorescence) applications for applied geochemistry. Journal of Geochemical Exploration, 188, 350–363. https://doi.org/10.1016/j.gexplo.2018.02.006

Lin, X., Heaney, P.J., Post, J.E., 2018. Iridescence in metamorphic "rainbow" hematite. Gems and Gemology, 54, 28–39. https://doi.org/10.5741/GEMS.54.1.28

Maciejewska, M., Pessi, I.S., Arguelles-Arias, A., Noirfalise, P., Luis, G., Ongena, M., Barton, H., Carnol, M., Rigali, S., 2015. Streptomyces lunaelactis sp. nov., a novel ferroverdin A-producing Streptomyces species isolated from a moonmilk speleothem. Antonie van Leeuwenhoek, International Journal of General and Molecular Microbiology, 107, 519–531. https://doi.org/10.1007/s10482-014-0348-4

Martín-García, R., Alonso-Zarza, A.M., Martín-Pérez, A., Schröder-Ritzrau, A., Ludwig, T., 2014. Relationships between colour and diagenesis in the aragonite-calcite speleothems in Basajaún Etxea cave, Spain. Sedimentary Geology, 312, 63–75. https://doi.org/10.1016/j.sedgeo.2014.08.001

Martinet, L., Naômé, A., Rezende, L.C.D., Tellatin, D., Pignon, B., Docquier, J.-D., Sannio, F., Baiwir, D., Mazzucchelli, G., Frédérich, M., Rigali, S., 2023. Lunaemycins, new cyclic hexapeptide antibiotics from the cave moonmilk-dweller *Streptomyces lunaelactis* MM109T. International Journal of Molecular Sciences, 24, 1114. https://doi.org/10.3390/ijms24021114

Melim, L.A., Shinglman, K.M., Boston, P.J., Northup, D.E., Spilde, M.N., Queen, J.M., 2001. Evidence of microbial involvement in pool finger precipitation, Hidden Cave, New Mexico. Geomicrobiology Journal, 18, 311–329. https://doi.org/10.1080/01490450152467813

Mouchet, S., Colomer, J.-F., Vandenbem, C., Deparis, O., Vigneron, J.-P., 2013. Method for modeling additive color effect in photonic polycrystals with form anisotropic elements: the case of *Entimus imperialis* weevil. Optics Express, 21, 13228. https://doi.org/10.1364/oe.21.013228

Onac, B.P., 2025. Cave minerals of the 21st century: A 2025 review and update. International Journal of Speleology, 54(1), 1–19. https://doi.org/10.5038/1827-806X.ijs2552

Poot, J., Buelens, P., Dekoninck, A., Rochez, G., Yans, J., 2024. Tracing the Eh–pH evolution of Cu–Pb–As–Zn supergene mineralization using detailed petrography in the Cap Garonne mineral deposit (Provence, France). Mineralium Deposita, 59, 1249-1271. https://doi.org/10.1007/s00126-024-01258-3

Post, J.E., 1999. Manganese oxide minerals: Crystal structures and economic and environmental significance. Proceedings of the National Academy of Sciences of the United States of America, 96, 3447–3454. https://doi.org/10.1073/pnas.96.7.3447

Potts, P.J., West, M., 2008. Portable X-ray fluorescence spectrometry: Capabilities for in situ analysis. RSC Publishing, Cambridge, 291 p. https://doi.org/10.1039/9781847558640

Pouit, G., 1978. Différents modèles de minéralisations «hydrothermale sédimentaire» à Zn (Pb) du Paléozoïque des Pyrénées Centrales. Mineralium Deposita, 13, 411–421. https://doi.org/10.1007/BF00206574

Reichert, J., Borg, G., 2008. Numerical simulation and a geochemical model of supergene carbonate-hosted non-sulphide zinc deposits. Ore Geology Reviews, 33, 134–151. https://doi.org/10.1016/j.oregeorev.2007.02.006

Rossi, C., Lozano, R.P., Isanta, N., Hellstrom, J., 2010. Manganese stromatolites in caves: El Soplao (Cantabria, Spain). Geology, 38, 1119–1122. https://doi.org/10.1130/G31283.1

Roucheux, D., 1990. Etude hydrologique et hydrodynamique d'un karst d'altitude : Le karst de

Bentaillou - Apports de l'analyses corrélatoire et spectrale. CNAM.

Santoro, L., Boni, M., Rollinson, G.K., Mondillo, N., Balassone, P., Clegg, A.M., 2014. Mineralogical characterization of the Hakkari nonsulfide Zn(Pb) deposit (Turkey): The benefits of QEMSCAN®. Minerals Engineering, 69, 29–39. https://doi.org/10.1016/j.mineng.2014.07.002

Schwertmann, U., 1993. Relations between iron oxides, soil color, and soil formation. In: Bigham, M., Ciolkosz E.J. (Eds.), Soil color. Soil Science Society of America, San Antonio, 51–69. https://doi.org/10.3390/ijms24021114

Skarpelis, N., Argyraki, A., 2009. Geology and origin of supergene ore at the Lavrion Pb-Ag-Zn deposit, Attica, Greece. Resources Geology, 59, 1–14. https://doi.org/10.1111/j.1751-3928.2008.00076.x

Smailer, S.M., White, W.B., 2013. The luminescent humic substances in speleothems. Applied Geochemistry, 36, 132–139. https://doi.org/10.1016/j.apgeochem.2013.06.002

Triantafyllou, A., Mattielli, N., Clerbois, S., Da Silva, A.C., Kaskes, P., Claeys, P., Devleeschouwer, X., Brkojewitsch, G., 2021. Optimizing multiple non-invasive techniques (PXRF, pMS, IA) to characterize coarse-grained igneous rocks used as building stones. Journal of Archaeological Science, 129, 105376. https://doi.org/10.1016/j.jas.2021.105376

Turner, K., 2002. Chromophores producing blue speleothems at Cliefden, NSW. Helictite 38(1), 3–6.

Van Beynen, P., Bourbonniere, R., Ford, D.C., Schwarcz, H.P., 2001. Causes of colour and fluorescence in speleothems. Chemical Geology, 175, 319–341. https://doi.org/10.1016/S0009-2541(00)00343-0

Verhaert, M., Bernard, A., Dekoninck, A., Lafforgue, L., Saddiqi, O., Yans, J., 2017. Mineralogical and geochemical characterization of supergene Cu–Pb–Zn–V ores in the Oriental High Atlas, Morocco. Mineralium Deposita, 52, 1049–1068. https://doi.org/10.1007/s00126-017-0753-5

Vlieghe, M., Rochez, G., Pire-Stevenne, S., Felten, A., Dechamps, M., Mouchet, S.R., Cecchet, F., Bruguier, O., Galéra, J.-L., Lima-Mendez, G., Llirós Dupré, M., Yans, J., 2025. Polymetallic interactions of Zn-Pb-Cu in blue/green-colored speleothems from Malaval Cave (France). Geochemistry, 85, 126285. https://doi.org/10.1016/j.chemer.2025.126285

Vlieghe, M., Rochez, G., Pire-Stevenne, S., Storme, J.Y., Dekoninck, A., Vanbrabant, Y., Namur, O., Zhang, Y., Van Ham-Meert, A., Donnadieu, J.P., Berbigé, M., Hasbroucq, J.L., Yans, J., 2023. Ni-rich mineral nepouite explains the exceptional green color of speleothems. Scientific Reports, 13, 1–8. https://doi.org/10.1038/s41598-023-41977-7

White, W., 2006. Identification of cave minerals by Raman spectroscopy: new technology for non-destructive analysis. International Journal of Speleology, 35(2), 103–107. https://doi.org/10.5038/1827-806x.35.2.6

White, W.B., 2019. Speleothems. In: White, W.B., Culver, D.C., Pipan, T. (Eds.), Encyclopedia of caves (3rd Ed.). Elsevier, London, p. 1006–1017. https://doi.org/10.1016/b978-0-12-814124-3.00117-5

White, W.B., 1997. Color of speleothems. In: Hill, C.A., Forti, P. (Eds.), Cave minerals of the world. National Speleological Society, Huntsville, p. 239–244.