

RARE SULFATES (MIRABILITE, EUGSTERITE) IN THE DRY MICROCLIMATE OF CHAMOIS CAVE (ALPES-DE-HAUTE-PROVENCE, FRANCE)

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The Chamois Cave (Alpes-de-Haute-Provence, France) opens at 1,360 m asl. above the Coulomp spring, which is fed by the Grand Coyer massif (2,693 m). The cave develops 10 km and gives access to the Underground Coulomp, one of the largest underground rivers in France. As any mountain cave, the air is cold, between 4 °C (highest part receiving air breathed in at 2,000 m altitude) and 8.5 °C (lowest confined part) where the river temperature is 6 °C. In this low part of the cave, a tributary (Thenardier Gallery) displays a fossil level covered with various decorations. On the ceiling, calcite helictites [CaCO₃] are surrounded with hydromagnesite [Mg₅(CO₃)₄(OH)₂·4H₂O]. The lower part of the walls and the fine sediment on the ground are covered with sulfates: gypsum [CaSO₄·2H₂O], mirabilite [Na₂SO₄·10H₂O], and eugsterite [Na₄Ca(SO₄)₃·2H₂O]. The two last minerals are common in salars depressions, lava tube and in cave developing under semi-arid condition, and not so frequent in temperate caves. Their presence in Chamois Cave is explained by the microclimate (RH 88%, T = 8.5 °C). The lowest part of the cave is under dry conditions because of the air subsidence that causes warming without moisture renewal since percolation are rare. Moreover, the Thenardier Gallery is confined between a sump upstream and a temporary sump downstream. Such a low RH allows developing of these minerals under evaporation effect. S comes from the weathering of pyrites that are present in limestone and Na from the weathering of sandstones in sediments. These evaporative conditions makes the Chamois cave an exceptional one, since mirabilite is not frequent in temperate caves and eugsterite is mentioned only for the second time in cave.

1. Introduction

Caves are well known for their decorations, where calcite is the dominant mineral precipitated by CO₂ degassing. Some minerals, such as sulfates, are due to evaporation process. Gypsum is a common species; however some sulfate minerals are more rarely encountered, especially in temperate and wet caves. Several mineralogical species in caves are partly or entirely due to evaporation processes. If calcite [CaCO₃] generally precipitates through CO₂ degassing, precipitation can be boosted by evaporation allowing supersaturation. When evaporation continues, the Ca/Mg ratio lowers, allowing the successive deposition of aragonite, huntite [CaMg₃(CO₃)₄], then hydromagnesite [Mg₅(CO₃)₄(OH)₂·4H₂O]. Such gradation is typical in confined or ventilated parts of caves where strong evaporation occurs, making calcite stalactites covered with aragonite frostwork generally developing on wind side, and hydromagnesite cotton ball growing at the tip of aragonite needles where the solution reaches the highest saturation. Sulfates are frequent and highly soluble minerals, which consequently can develop only in dry conditions. Gypsum [CaSO₄·2H₂O] is the most frequent. In especially dry conditions, magnesium sulfates such as epsomite [MgSO₄·7H₂O] or sodium sulfates, such as mirabilite [Na₂SO₄·10H₂O] and thenardite [Na₂SO₄] can develop with decreasing level of hydration. Eugsterite [Na₄Ca(SO₄)₃·2H₂O] was only once identified in a cave, in Turner Avenue, Mammoth Cave (Benington 1959; visible in White 2005, photo. 2B, p. 290), but the name was later given from another locality. It occurs as acicular crystals inside a water-clear mirabilite stalactite (White oral comm.).

The evaporation gradient pumps out the solutions present inside the rock toward the cave wall. Sulfates crystals grow

by extrusion (Hill and Forti 1997). In cold caves, percolations can only be saturated with respect to calcite and aragonite. Consequently, other mineral forms depend on processes other than degassing, i.e. concentration of the solution by evaporation (Harmon et al. 1983).

The stability of extremely soluble sulfates is closely dependent on cave climate conditions. Consequently, they grow seasonally when cave air is dry and re-dissolve when moisture increases. Epsomite melts under the breath or the heat of carbide lamp (Hill and Forti 1997). Below 70% of relative humidity (RH), mirabilite spontaneously dehydrates to thenardite (Onac 2012), which in turn is stable at 5–40% RH. Phase diagram (T – RH) of sodium sulfates are available from Flatt (2002), and discussed by Rodriguez-Navarro et al. (2000) for non-equilibrium conditions.

Cave sulfate minerals can have several origins (White 2005): interstratal evaporites in limestone rock (gypsum, anhydrite), oxidation of pyrite present in the limestone or in the caprock (e.g., sandstone at Mammoth Cave, Kentucky), oxidation of hypogenic H₂S corroding and replacing the limestone (Lechuguilla Cave, New-Mexico; Polyak and Provencio 2001), or brines such as in the Naica mine geodes (Mexico; Forti 2010). The geochemistry of the solution shall contain the elements necessary for Na-Ca-sulfate salt precipitation, i.e. Na, sulfate ion, etc. Studies on soil and salt pans evidenced the need of Na/Ca ratio > 4, pH > 5, and rapidly changing local environments and variations in redox, pH, and rates of availability of S and other elements (Fitzpatrick et al. 2005). In caves, percolation through limestone containing pyrites and strong evaporation could mimic such conditions.

Gypsum forms bulk crystals (on soil, dentate gypsum, gypsum

needles), crusts (granular or fibrous), and fibers (gypsum flowers, angel hairs, cotton) (White 2005). The highly soluble sulfates have habitus similar to gypsum, but different crystal structures; epsomite and mirabilite form crusts and in the driest conditions flowers may be present (White 2005). On the field, highly soluble minerals can be easily distinguished from gypsum, since they display ice-clear crystals and salty taste. However, their visual identification is difficult, even if epsomite has a bitter taste only, whereas mirabilite taste is bitter and salty (Hill and Forti 1997).

The highly soluble sulfates are generally found in extremely dry environments, such as salar depressions. In cave, they are mostly encountered in young volcanic caves still influenced by fumaroles and residual heat, and in warm and dry limestone caves (Guadalupe Mountains caves in New-Mexico, Cup-Coutunn Cave in Turkmenistan, Bahamas islands) (Hill and Forti 1997). However, they are also found in limestone and gypsum caves in which the temperature is below 20 °C. The first occurrence of thenardite, growing together with mirabilite, was in an Italian cave with temperature below 15 °C (Bertolani 1958). Thenardite (or mirabilite?) is present in “alpine” caves such Picos de Europa (Spain) (Hill and Forti 1997), and mirabilite occurs in a similar environment in Gamslöcher-Kolowrathöhle, Salzburg Alps (Bieniok et al. 2011). In even colder caves, they are present in Norway (Onac and Lauritzen unpubl.) and in the Canadian Rockies: in Castleguard Cave, during winter, outside air entering the cave abruptly warms to about 25 °C, at the origin of an 83% RH. The seasonal reversing of the draught considerably changes the moisture conditions of both extremities of the cave, so that dry conditions are only permanent in the central part of the cave where sulfates are present, such as mirabilite and epsomite (Harmon et al. 1983). The wide range of temperatures, from volcanic to arctic settings, shows that RH is the key-factor. Sulfated solution submitted to strong evaporation alone can form highly soluble sulfate minerals.

In this paper, we present the Chamois cave in Southern French Alps, where sulfate minerals have been identified by X-rays, including gypsum, mirabilite, and eugsterite, together with hydromagnesite associated to calcite. We discuss the conditions of their occurrence, originating from the composition of the host rock and of the allogenic sediments, from the low rate of percolation, and mainly

from the microclimatic conditions with low RH allowing strong evaporation.

2. Cave and context

The Chamois Cave (Castellet-lès-Sausses, Alpes de Haute-Provence, France) opens at 1,360 m asl. in Grand Coyer, between the upper segments of the Var and Verdon valleys (Audra et al. 2009). The Chamois cave develops more than 10 km for a depth of 326 m (+284/-42) (Fig. 1). It gives access to a 1 km segment of the Underground Coulomp, the largest underground river in France (1 m³/s). This underground river gives origin to the Coulomp spring, the largest in the Southern Alps, which pours out below the cave in a scenery waterfall. A sequence of thick marly limestone from Upper Cretaceous (Turonian-Coniacian-Santonian) begins with thick bedded limestones, where the cave develops, at the top of black marls. This sequence is covered in unconformity by the Cenozoic “nummulitic trilogy” (nummulitic limestone, Priabonian blue marls, and Annot sandstones). Decorations are abundant especially in the dry fossil passages: flowstones, aragonite bushes on wall exposed to the draft, gypsum crosses and needles on black marls.

3. Sampling and methodology

The Thénardier Gallery is the lower segment of the Hormones gallery, from which it is isolated by a sump. Access is from Underground Coulomp, through a temporary sump that only opens after a long dry period. As a consequence, this gallery is confined most of the year. A dry and well-decorated level develops 15 m above the temporary course of the active level. Spots of calcite helictites ringed by hydromagnesite develop on bare walls (Fig. 2). Gypsum of different fabrics (Fig. 3) and other sulfate minerals (Fig. 2) cover some parts of the walls and of the soil, which is covered with fluvial sediments made of pebbles, gravels and fine dusty sands. The sulfate minerals other than gypsum are distinguished by ice-clear crystals and a salty taste. All crystals have been sampled in hermetic bottles (numbered from 0 to 9), in order to keep them in dry condition. To preserve this exceptional site we only sampled broken small fragments from each given mineral.

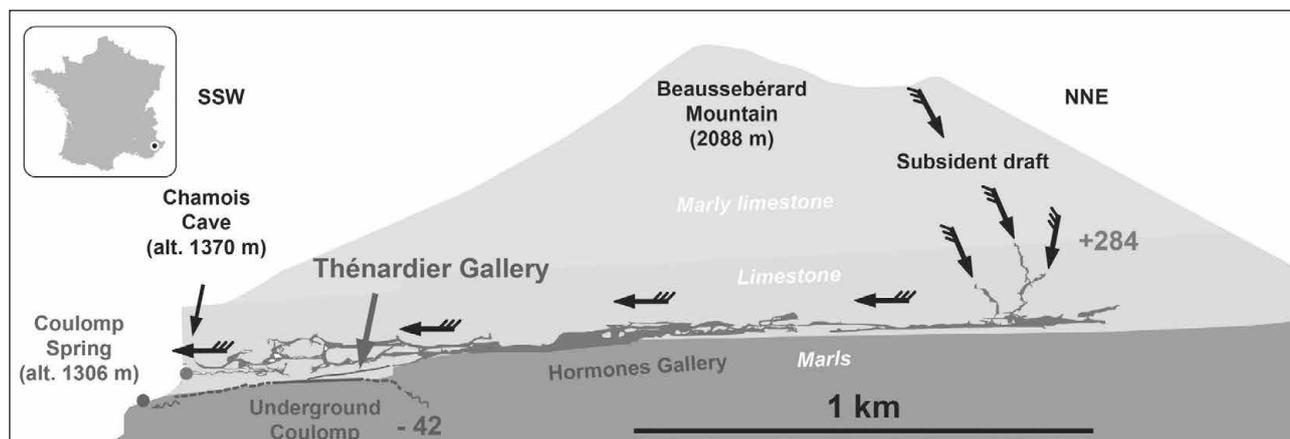


Figure 1. Cross section of the Chamois Cave, showing its development below a narrow ridge, at the contact of a marly basement and in a limestone covered with a thick sequence or marly limestones. Strong draft entering at high altitude crosses the cave system towards the cave entrance. The Thénardier gallery is a tributary of the river, the Underground Coulomp, which is most of the time confined between sumps.

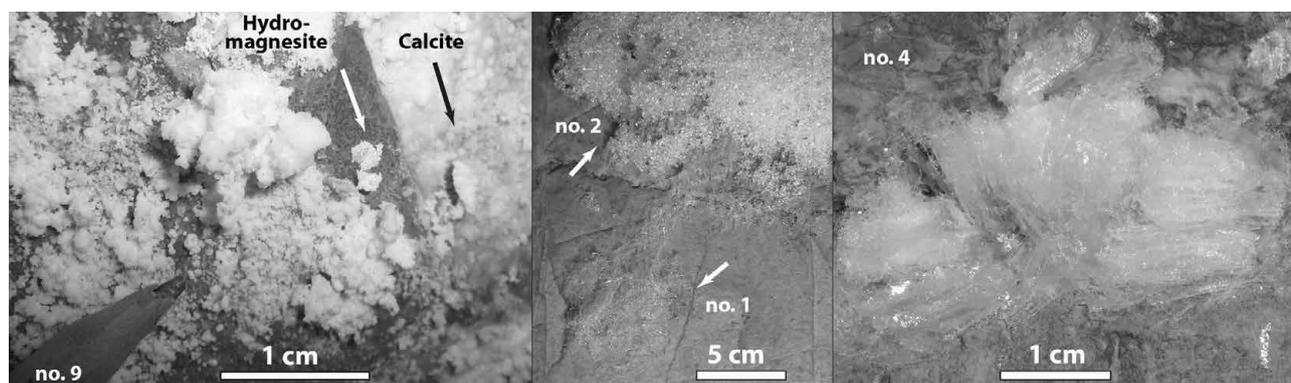


Figure 2. Left picture: calcite spot occurring as wall coating originating from small percolation along a fissure, ringed by hydromagnesite cotton-like bundles [sample no. 9]. Central and right pictures: diverse mirabilite crystal fabrics. Candy floss-like filaments [sample no. 1]; melting snow-like isometric crystals [sample no. 2]; ice clear blades forming a flower [sample no. 4].

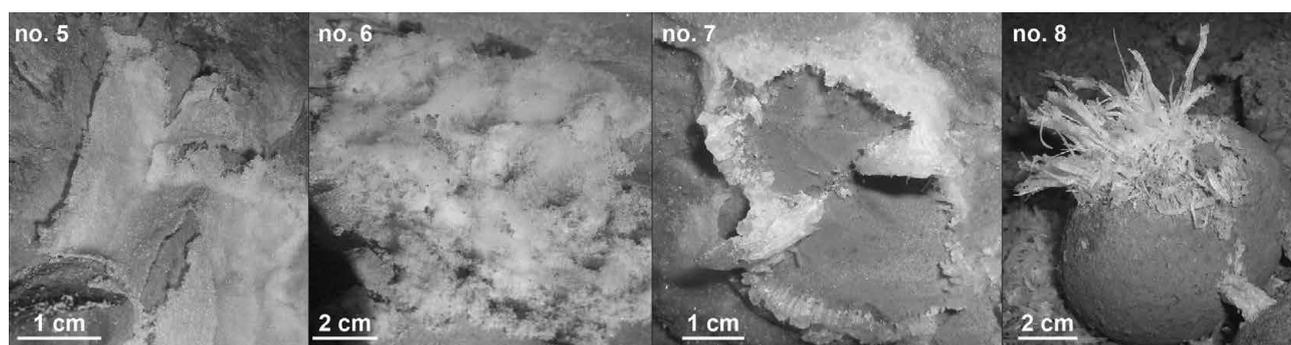


Figure 3. Diverse fabrics of gypsum crystals: wall crust [sample no. 5]; saltpeter-like fibers growing on dry silts [sample no. 6]; gypsum flower ringed by transparent crust [sample no. 7]; gypsum crosses on sandstone pebble [sample no. 8].

X-ray powder diffraction (XRD) patterns were recorded on a Philips diffractometer using Cobalt radiation ($\lambda = 1.79 \text{ \AA}$) with a secondary graphite monochromator. The diffractometer optic used to record all samples was a front fixed slit of 1° , a scattered radiation slit of 1° after the sample, and a 0.2 mm detector slit. The X-ray tube operating conditions were 40 kV and 40 mA and the step-scan data were continuously collected over the range 3.5 to $78^\circ 2\theta$ using a step interval of $0.05^\circ 2\theta$ and a counting time of 2.5 s. Patterns were matched with reference bibliotheca to identify minerals. Since Na-sulfates are highly instable at normal Temperature (T) and relative humidity (RH) conditions (involving hydration or dehydration resulting in mineral change), we assessed a possible influence of the RH change during X-ray analysis. Some grains of sample no. 2 were exposed to an atmosphere close to vapor saturation during several days, being put in a small beaker, which was placed in a water-filled crystallizer, itself covered with a second beaker. X-ray analysis was immediately done while putting grains directly on the silicon mount. Then a second analysis was done after 50 min. of exposition to drier laboratory atmosphere (45–55 % RH).

While sampling on the field site, T and RH were measured with a Brannan Compact Sling Psychrometer, where temperature is read on a dry bulb thermometer and % RH is later calculated from dry and wet bulb T using a table. Reading precision of T values is expected to be $\pm 0.5^\circ \text{C}$ and calculated RH about $\pm 5\%$. Additionally, a TFA-Dostmann

30.3015 thermo-hygrometer with data logger was settled to record T and RH for the coming year. Precision is 1°C for T and $\pm 3\%$ for RH from 35 to 75 % RH, otherwise $\pm 5\%$.

4. Results

X-ray analysis showed the presence of quartz and calcite in several sample, together with hydromagnesite, gypsum, thenardite, and eugsterite. Table 1 and Fig. 4 resumes the presence of the minerals found in each sample. The hydration-dehydration experiment on sample no. 2 shows mirabilite after exposure to wet atmosphere then thenardite after 50 min. in the drier atmosphere of the laboratory.

Microclimatic values in Thénardier Gallery at the sampling moment were 8.5°C and 88 % RH.

Table 1. The minerals identified with X-rays.

(*): see below for discussion about dehydration.

Minerals	Sample No.									
	0	1	2	3	4	5	6	7	8	9
Quartz	x	x	x	x			x	x		
Calcite	x	x	x	x			x			
Hydromagnesite										x
Gypsum		x	x	x		x	x	x	x	
Thenardite	x	x	x(*)	x	x					
Mirabilite			x(*)							
Eugsterite	x									

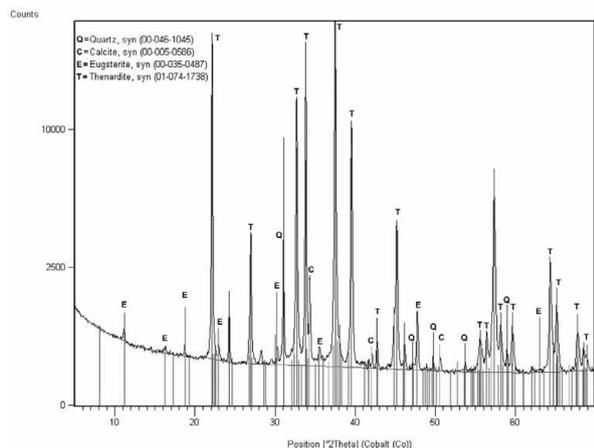


Figure 4. Pattern example for the no. 0 sample.

5. Discussion

Slow percolation from wall fissures makes calcite spots that are ringed by distinct aureoles of powder aggregates, which is composed of pure hydromagnesite (Fig. 2). The evaporation of the slow percolation makes the calcite to precipitate first. As evaporation proceeds, the decrease of Ca/Mg ratio progressively brings the residual fluid into the field of hydromagnesite (Harmon et al. 1983). The calcite spot close to the percolation feeder is relatively wet. Centrifuge capillarity strength brings the increasingly saturated solution toward the dry walls where hydromagnesite deposits as a distinct aureole. In Castleguard Cave, Harmon et al. (1983, Fig. 5, p. 506) evidenced that between both end-products (calcite and hydromagnesite), the calcite core also contains transitional mineral species (aragonite, huntite) originating from progressive evaporation and concentration of the solution.

Solutions of carbonates, sulfates, and sodium sulfates account to several origins. Hydromagnesite is mainly present on the walls, i.e. originating from vertical percolations across the limestone vadose zone. Mg is likely to come from slow dissolution of the above Turonian-Coniacian limestone. Sulfates are likely coming from the oxidation of pyrites, present in both Turonian-Coniacian limestone and in Turonian marly basement. The Thenardier gallery develops in massive limestone, but the marly basement crops out less than 200 m upstream. Consequently, sulfates may come both from pyrite in surrounding limestone or from the weathering of fluvial sediments containing marly pebbles that veneer the soil of the gallery. Sulfur isotopes data may precise this relationship with pyrites. For both mirabilite and eugsterite, the Na source is likely to be the fluvial sediments that contain sand and pebbles from Annot sandstones, in which sodium plagioclases (albite) and secondarily perthites are present (Stanley 1961). The weathering of these endogenous minerals would provide the Na present in eugsterite and mirabilite.

The identification of thenardite as cave mineral is a confusing question, since this mineral is unstable outside of the cave atmosphere, which makes it instantaneously evolve to mirabilite, its hydrated form. We made an experience on sample no. 2, where analysis first gave thenardite (conditions in the diffractometer chamber were measured

at 29 °C and 30–35% RH). Then, it was exposed several days to a moist atmosphere, and immediately analyzed, giving mirabilite alone. After 50 min. of exposure to the dry laboratory atmosphere (24 °C and 45–55% RH), the renewed analysis gave thenardite alone. This strongly suggests that the thenardite result is a laboratory artifact and that the mineral present in the cave was mirabilite. A same interpretation arises from other studies base on similar protocol (Bieniok et al. 2011) or without such a control (Harmon et al. 1983). We suspect that the thenardite identified in Picos de Europa (ref. quoted in Hill and Forti 1997) is most probably mirabilite.

The phase diagram of sodium sulfates (Fig. 5, Flatt 2002) also shows that mirabilite is in the field of these caves climates, whereas thenardite can only occur in much warmer and drier environments, such as a laboratory chamber or caves in arid climate. However, in case of strong supersaturation and very low RH (i.e. non-equilibrium conditions possibly encountered in field “reality”), presence of both species is possible during hydration in the stability field of mirabilite (Rodriguez-Navarro et al. 2000).

Since highly soluble sulfates are present in a wide range of temperature, the key-factor for their growth is the dryness of the air, at least seasonally. The Chamois Cave has a special climate due to its topographic and geological setting and to the cave structure. Firstly, most of the cave develops below a narrow crest in a thick sequence of marly limestones dipping perpendicularly to the main passages. As a consequence, most of the infiltration above the cave is guided toward west, and a high cliff to the east (i.e. no catchment) prevents any contribution of the cave itself.

Percolations are small and not frequent; the cave owes its origin to allogenic input and to a remote recharge. Secondly, most of the year, a strong draft enters at high altitude and crosses the main passages towards the entrance. During its

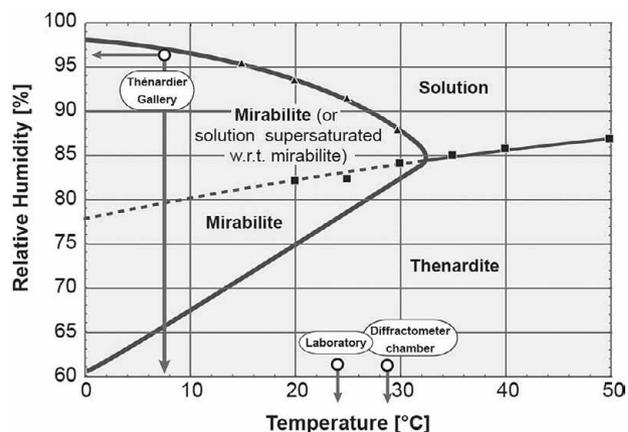


Figure 5. Phase diagram for sodium sulfates. The continuous lines indicate the boundaries of the stable phases. Triangles and squares are experimental data for mirabilite and thenardite, respectively. The discontinuous line corresponds to a solution in metastable equilibrium with respect to thenardite and supersaturated with respect to mirabilite (figure extracted from FLATT 2002 experiments, redrawn). Note that the phase diagram of HILL & FORTI (1997, p. 192) displays the mirabilite-thenardite boundary line, constructed from one field case, in a slightly lower position (i.e. with drier conditions). We plotted the T – RH conditions of the Chamois Cave and of the Laboratory where X-ray analyses have been done, which clearly show that they are in the stability field of mirabilite and thenardite, respectively.

subsidence, it warms up (from 4.3 to 7.1 °C) and dries out (93 to 92% RH), both by compression and by contact with the passage wall which are warmed by geothermic flux since cooling by percolation is very limited [see paper about the Chamois Cave temperature in these Proceedings]. Moreover the Thénardier Gallery has even a more pronounced microclimate (8.5 °C, 88% RH). There is no percolation in the upper dry gallery where sulfates occur. It is confined by sumps most of the year, and especially during wet season. Very similar conditions occur in Gamslöcher-Kolowrathöhle, qualified as “aridity” in the gallery where sulfates are present (Bieniok et al. 2011) and Castelguard Cave (Harmon et al. 1983). Regarding Chamois Cave, we might have expected a strong ventilation to account for the evaporative conditions, but surprisingly Thénardier gallery is a confined passage isolated by sumps during long periods, with at the maximum only slight convection air movements due to local temperature differences.

6. Conclusion

The Chamois Cave (Alpes-de-Haute-Provence, France) harbors unusual highly soluble sulfate minerals, usually found in caves from arid areas or in volcanic caves still under heat influence, but less common in such cold limestone caves (here 8.5 °C). X-ray analyses allow identifying, beside carbonate mineral (calcite and hydromagnesite), calcium sulfate (gypsum), together with highly soluble sodium sulfates, mirabilite and eugsterite. To our knowledge, it is only the second mention of eugsterite as cave mineral. Thenardite also appeared on X-rays, but it is likely an artifact due to dehydration of the cave mineral mirabilite during the analytical process. The origin of sulfate is likely the oxidation of pyrite from the host rock, and the sodium probably comes from the weathering of sodium plagioclases (albite), one of the components of the alluvial deposits coming from Annot sandstones erosion. The main reason for the presence of these sodium sulfates is the dry atmosphere of the Thénardier Gallery, with low RH (88%). Such microclimatic specificities are the result of conditions present in the whole cave (topographic and geologic conditions responsible of scarce percolations, subsiding draft through the cave that warms and dries up thanks to a strong geothermal gradient) and to local conditions of the Thénardier gallery (long isolation periods by temporary sumps). All in all, the main factor for sodium sulfates growth relies on these strong evaporation conditions that are not so frequent in such cold-temperate limestone caves.

Finally, due to the presence of a seasonal sump, we cannot figure of possible period of growth and dissolution of the sodium sulfates. However, a dive project will allow us to observe the site during confinement period and a data logger left last year is currently recording the temperature and humidity cycles. Isotopes analysis could confirm the relationship between pyrites and sulfates.

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