HYPOGENE SULFURIC ACID SPELEOGENESIS AND RARE SULFATE MINERALS (FIBROFERRITE, JAROSITE SUBGROUP) BAUME GALINIERE CAVE (ALPES-DE-HAUTE-PROVENCE, FRANCE)

Philippe Audra[1], Fernando Gázquez[2], Fernando Rull[3], Jean-Yves Bigot[4], Hubert Camus[5]
[1]Polytech Nice – Sophia, University of Nice – Sophia Antipolis, 930 route des Colles, 06903 Sophia-Antipolis, France & Innovative City – IMREDD, Nice, France, audra@unice.fr
[2]Water Resources and Environmental Geology Research Group, Dept. of Hydrogeology and Analytical Chemistry – University of Almería, Crta. Sacramento s/n, 04120 La Cañada de San Urbano, Almería, Spain, f.gazquez@ual.es
[3]Unidad Asociada UVA-CSIC al Centro de Astrobiología, University of Valladolid. Parque tecnológico Boecillo, 47151 Valladolid, Spain, rull@fmc.uva.es
[4]Association française de karstologie (AFK), 21 rue des Hospices, 34090 Montpellier, France, catherine.arnoux@clubinternet.fr
[5]CENOTE, 1 chemin de Valdegour, 30900 Nîmes, France, camus.hubert@laposte.net

The oxidation of sulfide sources (H_2S gas, pyrite, hydrocarbons) produces sulfuric acid that strongly reacts with bedrock, causing limestone dissolution and complex interactions with other minerals. This type of cave development, known as sulfuric acid speleogenesis, is a subcategory of hypogenic speleogenesis, where aggressive water rises from depth. It also produces uncommon minerals, mainly sulfates. Baume Galinière is located in Southern France, in the Vaucluse spring watershed. This small maze cave displays characteristic features such as corrosion notches, calcite dikes and iron crusts, and sulfate minerals. Thirteen minerals were identified, including elemental sulfur, calcite, quartz, pyrite, goethite, gypsum, fibroferrite, plus all of the six members of the jarosite subgroup (jarosite, argentojarosite, ammoniojarosite, hydroniumjarosite, natrojarosite, plumbojarosite). The Baume Galinière deposits are the first documented cave occurrence of argentojarosite and the second known occurrence of plumbojarosite, hydronium jarosite, ammoniojarosite, and fibroferrite. Together with other hypogenic caves in the Vaucluse watershed, Baume Galinière Cave owes its origin in buried conditions to deep water rising along major faults, mixing with meteoric water at the contact of the karst aquifer and overlying impervious cover, and causing pyrite deposition. Sulfuric acid speleogenesis occurred later after base level drop, when the cave arrived in shallow phreatic then in vadose zone, with oxidation of pyrites involving sulfidic gases. Attenuated oxidation is still occurring through condensation of incoming air from outside. Baume Galinière Cave records the position of the paleo-cover and documents its retreat in relationship to valley incision caused by uplift and tilting of the Vaucluse block during Neogene.

1. Introduction

Sulfuric acid speleogenesis involves the dissolution of limestone by sulfuric acid derived from H_2S that degasses from hypogenic water fed by deep sources (Egemeir 1983). The source of acidity may be hydrocarbons, sulfides or sulfates, or may be a result of volcanism. Cave development is due to strong acid corrosion, which also resulted in production of secondary sulfate minerals and development of microbial activity evidenced by the presence of poolfingers (Melim et al. 2001). These minerals are mainly gypsum and rare sulfate minerals, depending on the composition of the hypogenic water and the host carbonate rock. Sulfuric acid caves develop near the water table, where mixing of meteoric water and hypogenic water allows oxidation processes. Such caves record position of the water table contemporaneous with their development and are good markers of geomorphological evolution. Baume Galinière is a cave located at the edge of the Vaucluse Plateau, close to the margin of impervious beds that overlie the karst aquifer. The cave contains masses of pyrite that are of hypogenic origin. The speleogenetic history of the cave points toward the oxidation of these pyrite masses during a vadose phase as a result of meteoric water seepage. Oxidation is ongoing under the influence of air convection between the surface atmosphere and the cave, which results in seasonal condensation and evaporation. Beside the classical products of sulfide oxidation, such as gypsum and iron oxihydroxides, some unusual sulfates are present. These minerals occur as colorful crusts or foam-like silky masses. Mineral analyses have been performed, using XRD, Raman, SEM imaging, and stable isotopes. In this paper, we present details of mineralogy of Baume Galinière. Discussion focuses on mineral genesis and on cave genesis in relation to the geomorphological evolution of the region. In addition to the presence of rare sulfate cave minerals, Baume Galinière also records successive stages of regional geomorphological evolution. The area is an important place to study the evolution of the Vaucluse area landscape.

2. A sulfuric cave at the border of the Vaucluse Plateau

Baume Galinière Cave is located in Provence (South-East France), at the foot of Ventoux Plateau, which roughly corresponds to the Vaucluse spring catchment (Fig. 1).

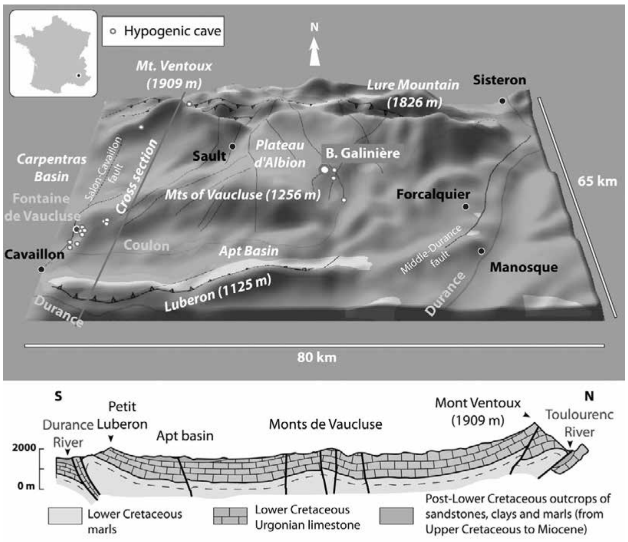

Figure 1. Structural characteristics of the Vaucluse plateau (geology after Blavoux 2010). The block is composed of thick Lower Cretaceous Urgonian Limestone. It is gently undulant and bounded to the north and south by overthrusts resulting from alpine crustal shortening. Hypogenic caves are located on the periphery of the plateau along primary fault lines (Audra et al. 2013).

To the north, the Lure crest rises to 1,826 m. Elevation decreases to the south toward the Durance River at about 300 m above sea level. Topographic relief is caused by an Urgonian (Barremian-Bedoulian) monocline containing. 1,000 m thick limestone that has been carved by karst processes that formed poljes, gorges, dolines, and some avens. To the north, the Lure crest corresponds to a north-verging overthrust. To the south, the limestone monocline gradually plunges under a thick cover of clastic formations ranging from Upper Cretaceous to Oligocene (successively Gargasian marls, Albian sandstone, Cenomanian sand, then Eocene-Oligocene clay, marls and marly limestone; Blanc et al. 1973). The boundary of this cover follows an irregular line caused by erosional retreat that exposed Urgonian limestone and allowed the development of surface karst features. Additionally, the plateau is cut by several N-S faults that form horsts and grabens, such as the Oppedette graben, which is still filled with Cenozoic cover and is surrounded by higher karst surfaces.

Baume Galinière Cave is at the top of the northern slope of a 200 m deep valley, in the uppermost part of the Urgonian limestone. The entrance is a few meters below Albian sandstone cover, close to a local fault. Baume Galinière is a horizontal maze cave less than 200 m long (Fig. 2). Passages are commonly between 0.5 and 2 m high and wide, with two main routes forming a loop around the entrance chamber. Two chimneys rise above the maze, the highest reaching overlying sandstone cap rock. Vadose flow features and sediments are absent, except at one spot corresponding to a small collapse undermining the overlying cover. Typical sulfuric acid corrosion features and mineral byproducts are present (Audra 2007; Audra et al. 2009). Walls are deeply etched or weathered. The floor, which is devoid of sediment, displays smooth surfaces and deeply entrenched rills caused by corrosive laminar or concentrated flow. Numerous niches, pockets, and bell holes result from the intense corrosion. A horizontal notch records the position of a pool once filled with corrosive water. Above, some odd-shaped voids may be replacement pockets. Feeder channels occur as narrow fissures where aggressive water rose from depth, whereas blind chimneys were upper outlets truncated at the contact with the overlying sandstone caprock.

Several minerals are present and have a specific distribution in the cave. A fissure rising along the chimney to the sandstone caprock is filled with iron oxihydroxides and calcite spar. Iron occurs as dikes and crusts, with centimeter-long pool fingers in some places. Calcite spar lining the fissure is mostly scalenohedral.

Pyrite bodies are present, surrounded by gypsum crusts and iron oxihydroxides. The inner and dryer parts of the cave are partly covered by evaporitic sulfate minerals, mostly gypsum, displayed as saccharoid crusts on ceilings and grey to yellow minute crystals on walls. Foam-like masses of a green color, silky appearance and a ribbon-like texture correspond to an uncommon mineral, fibroferrite. Additionally, some iron oxihydroxide stalactites are present. Currently, the cave is entirely dry, due to its perched position at the top of the limestone, to the presence of the sandstone caprock, and to the absence of connections to the

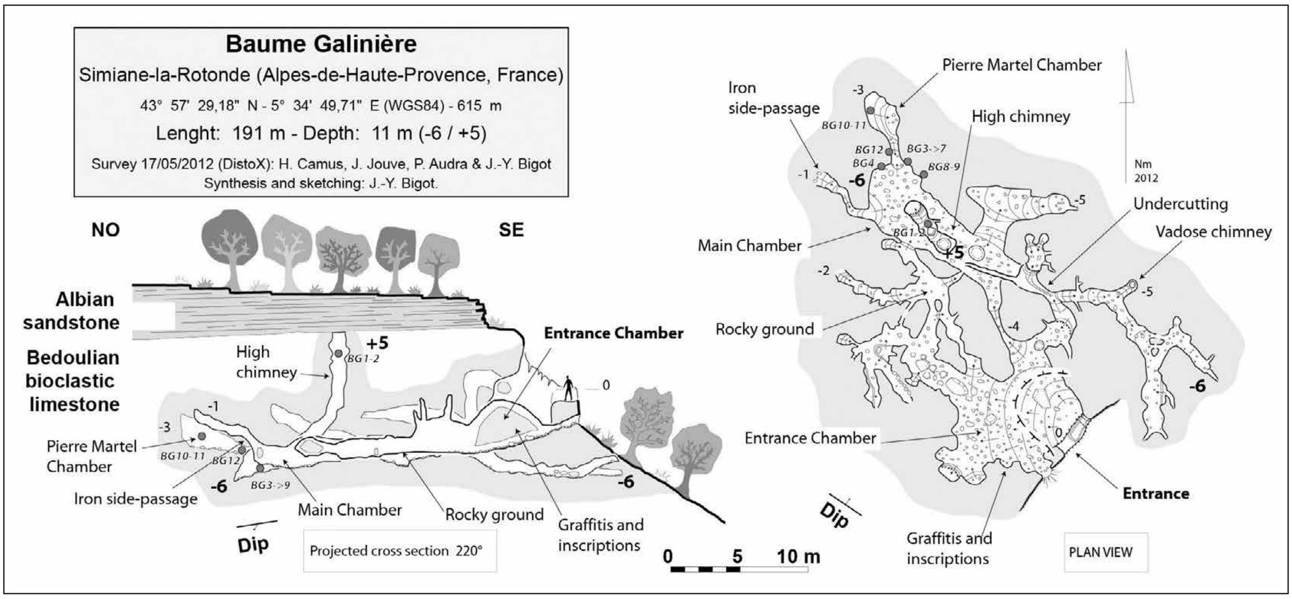

Figure 2. Baume Galinière Cave survey. Red dots indicate sampling locations.

surface. Consequently, the atmosphere is extremely dry and under the influence of thermobarometric exchange with the outer atmosphere. Since the cave is horizontal, we suppose that convection drives the cave climate: cold air entering in winter mainly favors evaporation whereas cooling of warm summer air favors condensation.

3. Methods

In May 2012, the cave survey was completed, documented with pictures, and 13 samples were taken for mineralogical analysis (Fig. 3; the locations of the sampling sites are shown on Fig. 2). Samples are labeled BG1 through BG13.

(i) **Calcite-iron oxihydroxides association**: ferruginous pool fingers hanging under ghosts of calcite scalenohedra (BG1); calcite scalenoedra covered with iron oxihydroxides (BG2); calcite scalenohedra (BG11). (ii) **Sulfidic deposit with oxidized aureole**: mass of pyrite (BG3a) with a white to yellow gypsum crust (BG3b); core of greyish-blue mass (BG5) with an inner yellow-white aureole of gypsum (BG6) and an outer red aureole of iron oxihydroxides (BG7). (iii) **Gypsum crystals associated with colored crusts:** yellow gypsum crystals (BG4); grey gypsum crust (BG10); large grey gypsum crystal (BG12). (iiii) **Foam-like mass** (BG8), located on gypsum crust with yellow surface (BG9).

Mineral identification was carried out using X-ray powder diffraction (XRD) and micro-Raman spectroscopy. The spectra obtained were compared with those reported by Frost et al. (2006) from natural jarosites and our database. Oxygen and hydrogen isotopes were measured on calcite scalenohedra (details in Dublyansky and Spötl 2009). Scanning Electron Microscopy (SEM) was use to observe microbial traces on ferruginous pool fingers.

4. Results

Analytical results of the samples (mineralogy, stable isotopes) are presented in Fig. 3. Thirteen minerals were identified: one native element (sulfur), one carbonate (calcite), one silicate (quartz), one sulfide (pyrite), one hydroxide (goethite), eight sulfates (gypsum, fibroferrite plus six members of the jarosite subgroup (jarosite, argentojarosite, ammoniojarosite, hydronium jarosite, natrojarosite and plumbojarosite). The mineralogical analysis by micro-Raman spectroscopy revealed the presence of up to five different minerals of the jarosite subgroup in the samples (Tab. 1). For space reasons, the Raman spectra are not displayed here and will be discussed in a future paper.

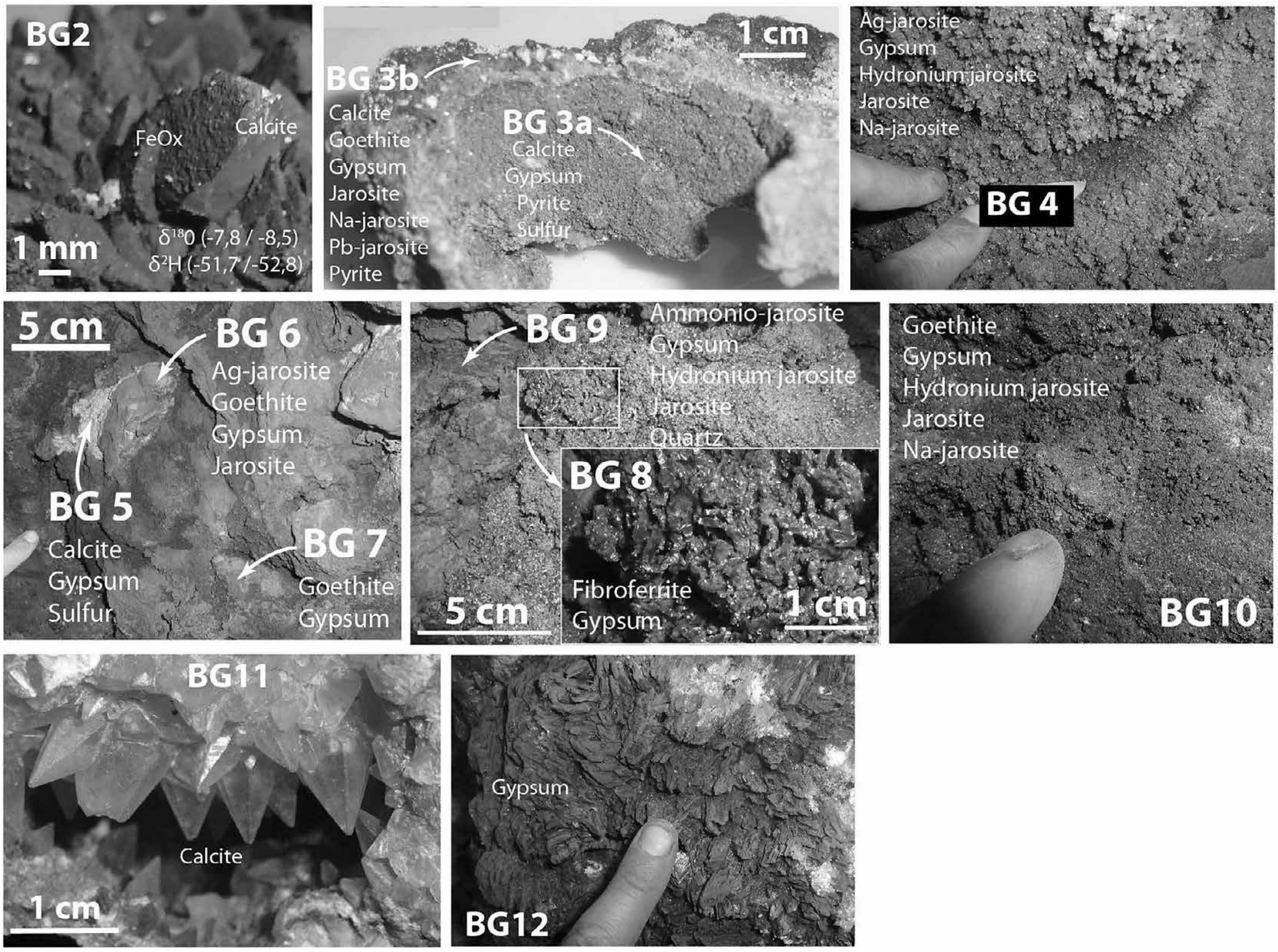

Figure 3. General results of the mineralogical analysis (XRD, micro-Raman spectroscopy), and stable isotopes. Thirteen minerals were identified: One native element (sulfur), one carbonate (calcite), one silicate (quartz), one sulfide (pyrite), one hydroxide (goethite), eight sulfates (gypsum, fibroferrite, and six members of the jarosite subgroup (jarosite, argentojarosite, ammoniojarosite, hydronium jarosite, natrojarosite, plumbojarosite).

Table 1. Results of the mineralogical analysis by micro-Raman spectroscopy. Percentages represent the occurrence of each mineral in each sample regarding the total number of spots analyzed (n).

Sample No.	Number (n) of analyzed spots	Jarosite	Hydronium jarosite	Argento-jarosite	Plumbo-jarosite	Natro-jarosite
BG3b	11	36%	–	–	54%	10%
BG4	10	10%	20%	50%	–	20%
BG6	7	14%	–	86%	–	–
BG9	9	–	100%	–	–	–
BG10	10	40%	20%	–	–	40%

Oxidation of sulfide produces suites of variably soluble efflorescent sulfate salts (Hammarstrom et al. 2005). In Baume Galinière, sulfide is present as **pyrite** [FeS_2], and is the original sulfide deposit. It is displayed in decimetric masses of small pyrite crystals (< 1 mm). It may not be considered as a true cave mineral, since it was deposited by hydrothermal solution in vugs before the cave developed. **Calcite** [$CaCO_3$] is found as detrital grains of limestone host rock inside sulfide deposits or in the weathering aureole. Other minerals result from reactions between the pyrite, the surrounding limestone, and the clays where sulfuric acid from the oxidation of pyrite is responsible for a strong acidic environment.

Native **sulfur** [S°] is present inside the pyrite deposit and probably results from the oxidation of pyrite. **Goethite** [$FeO(OH)$] is typically displayed as red crusts surrounding oxidized pyrite masses. **Gypsum** [$CaSO_4 \cdot 2H_20$] is displayed in two forms according to its location. On ceilings, the high parts of walls, and around pyrite masses it occurs as saccharoid white crusts. On the lower parts of walls it occurs as macrocrystals which are always tinted yellow, grey or brown.

Jarosite sub-group minerals and **fibroferrite** are present around the pyrite masses in the oxidation aureole. The **Jarosite subgroup** is composed of six sulfate minerals, with the following common composition [$MFe_3(SO_4)_2(OH)_6$], where M = K^+ (jarosite), Ag^+ (argentojarosite), NH_4^+ (ammoniojarosite), Na^+ (natrojarosite), Pb (plumbojarosite), H_3O (hydronium jarosite). Such minerals are commonly found in mines in the oxidized zones of sulfide deposits, formed by sulfuric acid derived from the oxidation of pyrite reacting with clay from the wall rock. **Jarosite** [$KFe^{3+}_3(SO_4)_2(OH)_6$] is named after the type locality, Barranco Jaroso in Southern Spain. It is usually displayed as yellow, amber, or brown crusts. It is not soluble in water, and rather common in sulfuric caves (Fiume – Vento, Italy; Cottonwood, New Mexico, USA). It also occurs in volcanic caves, or in caves in metamorphic rocks where sulfidic ores are present (Hill and Forti 1997). Jarosite may also precipitate subaqueously in shallow, low-pH pools (Hammarstrom et al. 2005). **Ammoniojarosite** [$(NH_4)Fe^{3+}_3(SO_4)_2(OH)_6$] is named from the ammonium ion (NH_4^+) and displays as light yellow to nearly colorless crusts. It has been mentioned only once before, in Cueva Alfredo Jahn, Venezuela, where it brought into the cave by flooding, and the mineral, displayed as light blue spots, forms by evaporation during the dry season (Forti et al. 1998). **Argentojarosite** [$AgFe^{3+}_3(SO_4)_2(OH)_6$] is named from silver (Ag) and displays as pale yellow, yellow, yellow-brown to brown crusts. It is mentioned here for the first time as a cave mineral. **Hydronium jarosite** [$(H_30)Fe^{3+}_3(SO_4)_2(OH)_6$] is named from the hydronium ion (H_30^+) and displays as ochrous, amber to dark brown granular masses or crystalline to earthy crusts. It has been mentioned as a cave mineral only once, in Iza Cave, Romania, where *"goethite and hydronium jarosite formed through the action of percolating water over pyrite that is present as accessory mineral in the crystalline schists"* (Tămaş and Ghergari 2003). **Natrojarosite** [$NaFe^{3+}_3(SO_4)_2(OH)_6$] is named from sodium (natrium) and displays as yellow, golden brown, red-brown crusts. It has been mentioned as a cave mineral only once, in Jungle Pot Cave, South Africa, originating from the oxidation of pyrite from shales combined with Na from a diabase sill (Martini 1984). **Plumbojarosite** [$Pb_{0.5}Fe^{3+}_3(SO_4)_2(OH)_6$] is named from lead (Pb) and displays as golden brown to dark brown crusts or masses. It has been mentioned only from Naica Cave, Mexico, originating from neoformation after the dewatering of the famous geode (Forti 2010). **Fibroferrite** [$Fe^{3+}SO_4(OH) \cdot 5H_2O$] is a hydrated iron sulfate. It displays as fibrous mushroom-like masses of minute acicular crystals. Coalescent needles form ribbons folded by extrusion. The color ranges from pale yellow, yellowish green, greenish gray, nearly white, to translucent, with a typical silky luster. It is soluble in water and forms by evaporation. Consequently it is most stable in arid regions, rarely as volcanic sublimate (Anthony et al. 2003). It has been mentioned only from Grotta Ferrata, Italy, originating from pyrite oxidation and growing over mud associated with goethite and gypsum. Its stability requires strong acid environment (pH < 2). When pH increases due to the buffering effect of limestone reacting with sulfuric acid, fibroferrite becomes unstable and forms iron oxihydroxides (Forti and Salvatori 1988).

Stable isotopes of fluid inclusions ($\delta^{18}O$, δ^2H) were made on tips and bottoms of calcite scalenohedra (BG2). The released water amount (0.39 and 0.54 µL, respectively) provided valuable results. The ratios of $\delta^{18}O$ and δ^2H for tips and bottoms (-7.8/-51.7 and -8.5/-52.8) plot close to the meteoric water line (MWL) (Craig 1961).

SEM imaging of iron pool fingers clearly shows the presence of microbial communities, mainly as filaments growing onto the iron oxihydroxides (Fig. 4). The largest filaments (diam. 5µm, length > 100 µm) must be fungi. Smaller filaments (diam. 2 µm, length 50 µm) and cell-like individuals could be bacteria (H. Barton pers. comm.).

5. Discussion (mineralogenesis and sulfuric acid speleogenesis)

The identification of minerals in the framework of geological and geomorphological context helps understand the genesis of this mineralized cave. Mineralization took place in at least three main phases (Fig. 5).

Early phreatic fissure phase. The initial mineralization phase occurred at depth, below the water table and under the cover of thick marls and sandstones. Chemically reduced water rising from depth along faults carried metallic ions (Fe^{2+}, Pb^{2+}, Ag^+) and sulfur. At shallow depths,

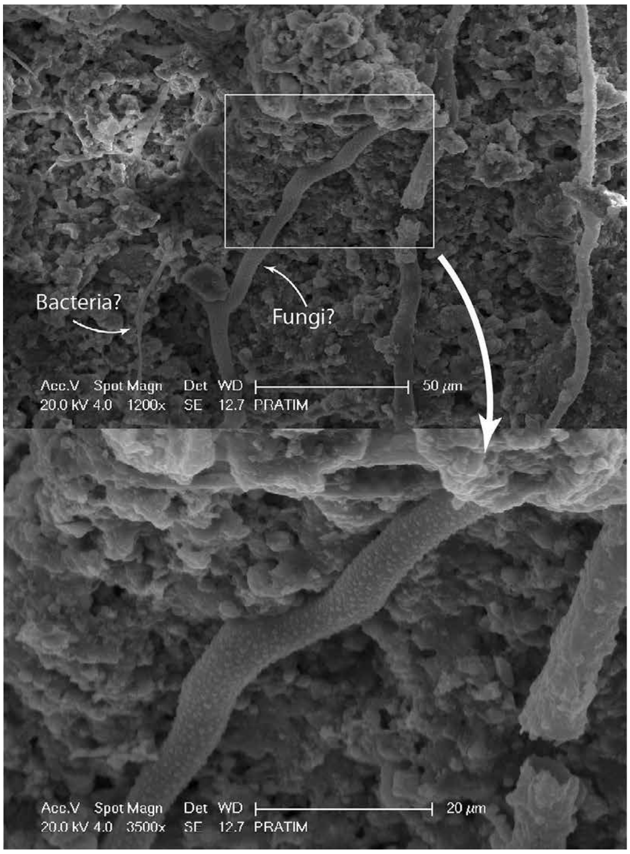

Figure 4. BSE imaging of iron pool fingers. Microbial filaments are developing on iron oxyhydroxides. Largest filaments (diam. 5 µm, length > 100 µm) must be fungi. Smaller filaments (diam. 2 µm, length 50 µm) could be bacteria.

mixing of reduced water with oxygenated meteoric water, probably carried along the sandstone acting as aquifer, changed pH and Eh conditions and led to the deposition of sulfide minerals, mainly pyrite [FeS_2] with traces of Pb and Ag, as masses or sills along fractures. The contact between reduced flow and fresh water from the sandstone aquifer could explain the sulfidic deposits localization where mineralization is concentrated at the top of the limestone just below the sandstone cover. Eventually, calcite with scalenohedral habit was precipitated. This type of calcite is generally associated with a warmer environment than common trigonal rhombohedral calcite spar (Dublyansky and Smirnov 2005). Isotopic ratios ($\delta^{18}O$, $\delta^{2}H$) close to MWL indicate a contribution from surface water. At that time, no cave was present and the corresponding voids were limited to tiny fissures and vugs.

Main vadose phase. Valley entrenchment combined with erosional retreat of the overlying caprock dramatically changed conditions. The water table fell below the sulfidic deposits resulting in vadose conditions and associated oxygenated meteoric seepage. Thinning of the caprock allowed development of soils and vegetation just above the cave. Oxidation of the pyrite masses produced sulfuric acid that dissolved the limestone host rock, resulting in sulfuric acid speleogenetic processes. The earliest sulfuric acid speleogenesis may have occurred in a shallow phreatic environment at the onset of the fall of the water table, when meteoric water was able to flow and be replenished. However, the most active processes occurred in atmospheric conditions after the cave was drained, when seepage water oxidized pyrite masses and produced concentrated sulfuric acid. Most of the cave volume probably developed during this phase, associated with typical sulfuric acid features such as notches along acidic pools, corrosion trenches, *etc*., and sulfate mineral byproducts. Saccharoid gypsum crusts formed on some ceiling and upper wall surfaces where condensation was limited. Otherwise, ceilings and upper walls were etched by condensation corrosion and sulfates in solution were precipitated downwards through evaporation as centimetric gypsum crystals. This sulfuric process produced a low pH environment, and secondary ions combined with iron sulfates to form jarosite subgroup minerals. Hydronium jarosite is produced by seepage on pyrite. Trace amounts of Pb and Ag produced argento- and plumbojarosite, respectively. Weathering of the Albian green sandstone caprock, which contains glauconite group minerals [$(Ka,Na)(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$], may have provided K^+ and Na^+ ions, which in turn produced jarosite and natrojarosite, respectively. Biological activity produced the ammonium ion (NH_4^+), which combined to form ammoniojarosite. Meantime, oxidation of pyrite is boosted by ferro-oxidant bacteria taking energy from oxidation of ferrous ion Fe^{2+} to ferric ion Fe^{3+}, resulting in iron oxihydroxides, mainly goethite. Ferruginous material occurs as massive coatings on calcite spars, as pool fingers, or as powdery masses mixed with gypsum surrounding pyrite masses (Fig. 3).

Still-active seasonal sulfuric mineralogenesis. Currently, the cave is open to the surface allowing convective air exchange. In summer, cooling of air entering the cave favors condensation and thus slow pyrite oxidation and the formation of the associated suite of sulfuric byproducts (gypsum, sulfates ion and iron oxihydroxides). In winter, warming of entering air causes evaporation that concentrates acidic solutions around pyrites and favors evaporitic sulfate development, namely fibroferrite.

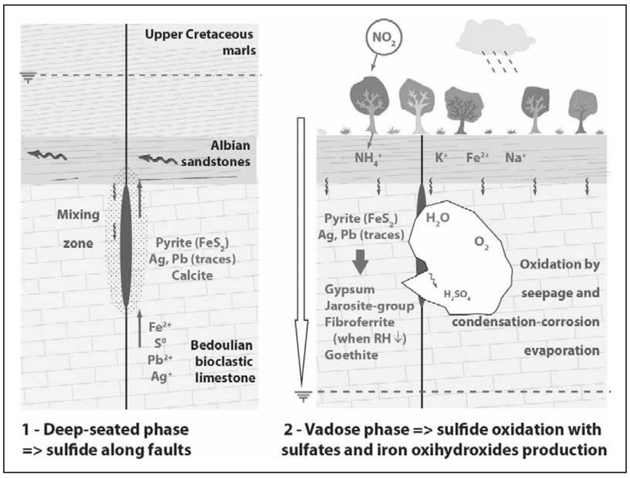

Figure 5. Genesis of minerals in Baume Galinière. First phase in deep-seated conditions, where mixing of hypogenic flow and fresh water produces sulfide deposits (pyrite) along fault below the sandstone aquifer. After a base level drop, vadose seepage oxidizes the sulfide deposits, making sulfuric speleogenesis, with cave development and secondary minerals (sulfates and iron oxihydroxides). Jarosite subgroup minerals appear thanks to the presence of accessories ions originating from traces in the sulfide deposits (Pb, Ag), from sandstone minerals weathering (glauconite), or from biogenic production (ammonium ion). Seasonal changes between condensation and evaporation allow developing of fibroferrite.

Although we did not observe it during our visits, we suspect that fibroferrite follows seasonal cycles of relative humidity (RH), dissolving when wet and regrowing when dry. Evaporation in the vicinity of oxidizing pyrite may be responsible for the deposition of native sulfur, which requires high H_2S concentration in the surrounding atmosphere.

The progression of speleogenesis can be traced at the regional scale. Comprehensive data are still missing, but main phases can be traced and assigned to periods when physical conditions were permissive (Fig. 6). Phase 1 of hypogenic rising flow requires a hydraulic gradient and the presence of impervious caprock. Such conditions could have occurred after the first phases of orogenic uplift at the beginning of Miocene. During Phase 2, which corresponds to the main sulfuric acid speleogenetic event, vadose conditions gradually phased in. This occurred after the erosional retreat of the marly caprock and the onset of valley incision. Erosion and caprock retreat caused the water table to fall to depths below the cave. During Phase 3, the cave is open to the surface allowing air exchange in response to seasonal changes in RH. Phase 3 is currently active.

6. Conclusions

Baume Galinière sulfate mineralization resulted from sulfuric acid speleogenesis in successive phases. The first phase of sulfide deposition (pyrite masses) occurred in deep-seated conditions, where hypogene water rising along a fault mixed with meteoric water flowing within an overlying sandstone aquifer. At that time, probably at the beginning of Miocene, the onset of orogenic uplift allowed water to move in a deep loop through the karst aquifer. Impervious caprock cover was present, keeping the karst aquifer in anoxic conditions. Locally there were local, discrete zones where anoxic hypogene water could mix with meteoric water at the contact between the karst aquifer and the overlying sandstone aquifer. Hypogenic flow was probably warm, as shown by the scalenohedral habit of calcite crystals.

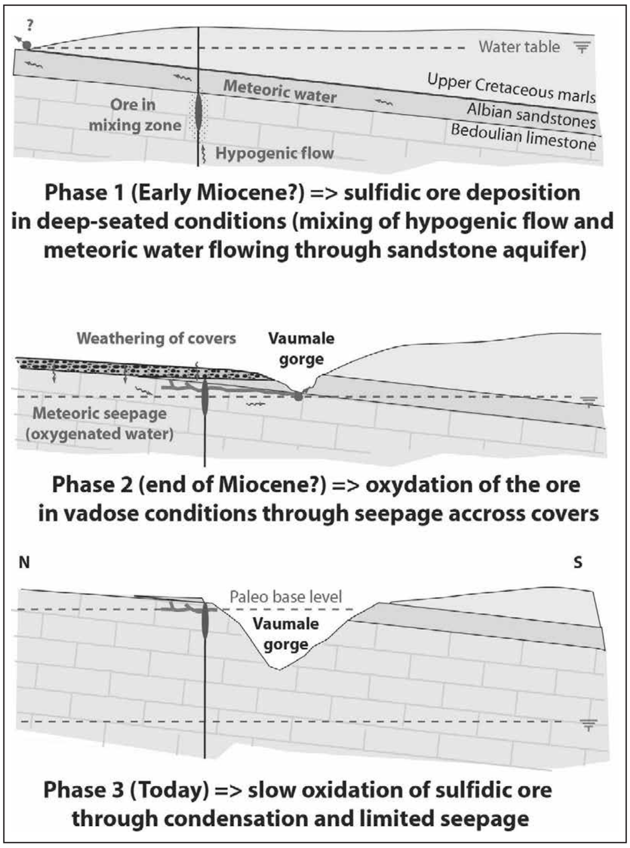

Figure 6. Evolution of Baume Galinière from Miocene. Successive phases, from deep-seated to vadose conditions are related to the retreat and stripping of covering strata related to valley incision.

The second phase of sulfuric speleogenesis corresponds to vadose conditions that were coeval with valley incision. The water table was shallow, and meteoric seepage water reacted with pyrite. Sulfur oxidation released sulfuric acid, which reacted with the carbonate host rock. Typical sulfuric corrosion features developed, with enlargement of voids, including pockets, bell holes, pool notches and entrenchments. Sulfate minerals, mainly gypsum, covered walls as saccharoid crust on ceilings and recrystallized macro-crystals on the lower passage walls. Oxidation of pyrite also produced iron oxihydroxide crusts, masses, and pool fingers on walls around pyrite masses. The oxihydroxides mixed with and tinted the sulfates. Microbial and fungal activity (fungi and probably ferro-oxidant bacteria) developed and is preserved as filaments in the pool fingers. Beside gypsum, rare sulfates crystallized, including all members of the jarosite subgroup. Precipitation of jarosite is mainly due to the weathering of glauconite in the overlying sandstone, which delivered ions by seepage.

The present phase corresponds to the deep entrenchment of the valley and the opening of the cave allowing air exchange corresponding to seasonal changes of RH. Cooling results in condensation that maintains pyrite oxidation and sulfate production. Warming causes evaporation and development of fibroferrite. The development of this cave records the gradual incision of valley and correspondent retreat of impervious caprock, an important milestone for the reconstruction of paleolandscapes. As with similar caves (Audra et al. 2013), Baume Galinière is located at the topographic intersection of a regional fault and the edge of the caprock covering the karst aquifer. The chronology of speleogenesis probably starts at Early Miocene and continues to the present. Dating of successive speleogenetic stages could provide a better understanding of the geomorphological evolution of the Vaucluse region.

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