P. Audra and F. Hobléa – The first cave occurrence of jurbanite [$Al(OH\ SO_4) \cdot 5H_2O$], associated with alunogen [$Al_2(SO_4)_3 \cdot 17H_2O$] and tschermigite [$NH_4Al(SO_4)_2 \cdot 12H_2O$]: thermal-sulfidic Serpents Cave, France. *Journal of Cave and Karst Studies,* v. 69, no. 2, p. 243–249.

THE FIRST CAVE OCCURRENCE OF JURBANITE [$Al(OH\ SO_4) \cdot 5H_2O$], ASSOCIATED WITH ALUNOGEN [$Al_2(SO_4)_3 \cdot 17H_2O$] AND TSCHERMIGITE [$NH_4Al(SO_4)_2 \cdot 12H_2O$]: THERMAL-SULFIDIC SERPENTS CAVE, FRANCE

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Abstract: Serpents Cave, located in the French Alps, contains a sulfidic-thermal (41 °C) karst spring. Degassing of the sulfidic vapor produces diverse sulfate minerals. The reaction with the limestone host-rock produces gypsum, anhydrite, sulfur, and magnesium calcite. The reaction with an artificial material (aluminum door) produces alunogen, tschermigite, and jurbanite. Microbial activity is suspected in the genesis of sulfur and tschermigite. Aluminum sulfates have usually been reported in mines, in volcanic settings, and in rock-shelters in phyllites. Some of these alum minerals such as tschermigite are rarely observed in caves, and jurbanite is identified here for the first time in a cave. Serpents Cave is therefore an important site for sulfate minerals in caves, even if the aluminum sulfates should be considered border minerals because they originate from sulfur vapor reaction with artificial media.

Introduction

The chemistry of development of hypogenic caves by the oxidation of sulfur compounds to sulfuric acid, with the resulting corrosion and gypsum replacement of limestone, has only relatively recently been defined (Morehouse, 1968; Egemeier, 1981). The replacement corrosion process occurs according to the following reactions: (1) H_2S originating from degassing oxidizes, (2) then sulfuric acid reacts with the limestone rock to produce gypsum ($CaSO_4 \cdot 2H_2O$) as a by-product, and finally (3) CO_2 can again dissolve the limestone rock according to the classical reaction of limestone dissolution.

$$H_2S + 2O_2 \Rightarrow H_2SO_4 \tag{1}$$

$$H_2SO_4 + CaCO_3 + H_2O \Rightarrow CaSO_4 \cdot 2H_2O + CO_2 \tag{2}$$

$$CaCO_3 + CO_2 + H_2O \Rightarrow Ca(HCO_3)_2 \tag{3}$$

Sulfidic hypogenic caves have been studied in the Guadalupe Mountains, USA (Hill, 1987), in the Frasassi Caves, Italy (Galdenzi and Menichetti, 1995; Forti, 1996), and in France (Audra, 2005; Audra et al., 2002, 2007; Audra and Häuselmann, 2004; Audra and Hofmann, 2004). The active participation of microbial processes was identified in Movile Cave, Romania (Sarbu et al., 1996), in the Frasassi Caves, Italy (Sarbu et al., 2002), and in Villa Luz Cave, Mexico (Hose and Pisarowicz, 1999).

Aix-les-Bains is a thermal resort in Savoy, France, located between the Bourget Lake shore and the foot of the Bauges massif at the front of the Northern French Prealps overthrust. Serpents Cave, a water-table cave, harbors the Alum Spring, a sulfidic and thermal spring (about 41 °C). Since the early mention of sulfidic origin of the cave by Martel (1935), it has been studied to define the origin of the thermal flow-path (e.g., Carfentan et al., 1998); it is only recently that Serpents Cave has been studied for its karst processes (Hobléa, 1999). Within the cave, sulfidic degassing produces replacement-corrosion with a H_2S-rich corrosive atmosphere and deposition of gypsum.

Chevalley Aven and Serpents Cave belong to the same system (Fig. 1) (Hobléa, 1999; Gallino, 2006). Chevalley Aven is a blind chimney developed above the water table, made of stacked spheres arranged in a bush-like pattern, originating mainly from condensation-corrosion (Audra et al., 2007). Chevalley Aven contains gypsum as crust, flowstones, stalactites and stalagmites, made by replacement corrosion originating from the thermal pool which is degassing H_2S. Biofilm develops on the walls where condensation moisture occurs. The active Alum thermal spring flows into the cave at the upstream head. The thermal characteristics of the spring are responsible for major condensation-corrosion activities as evidenced by the development of spherical ceiling cupolas.

The discharge of Alum Spring ranges from 8 to 42 L s^{-1}; the temperature oscillates seasonally between 33.5 and 46.6 °C due to some mixing with meteoric water (Muralt, 2003). Water has a high concentration of calcium,

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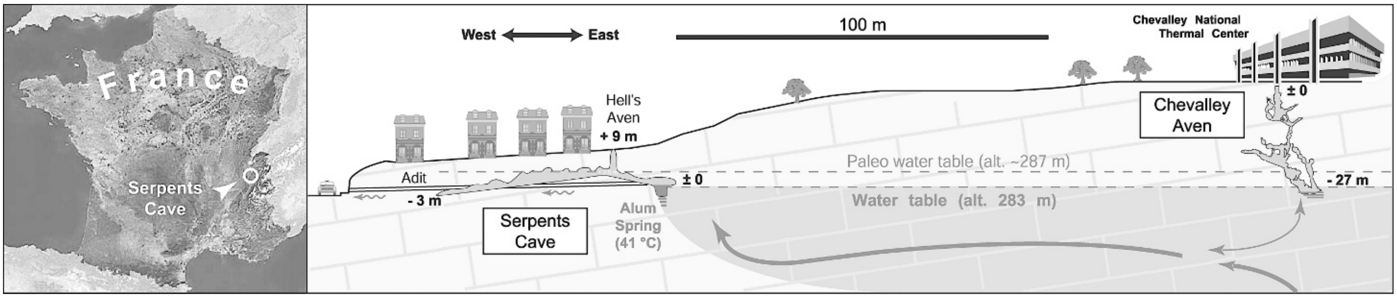

Figure 1. Profile of the Aix-les-Bains thermal-sulfidic cave system (survey SC Savoy, EDYTEM). Chevalley Aven is a blind chimney developed above the water table; Serpents Cave is a water table cave. The active Alum thermal spring flows into the cave at the upstream head (Audra et al., 2007).

sulfate, and secondary sodium, magnesium, and silica (Table 1). The temperature, high silica and salt contents, and presence of trace elements suggest a deep artesian flowpath (about 2000 m) confined under the Bourget Lake syncline, where Triassic evaporites are leached (Carfantan et al., 1998). The water is flowing out turbulently from the Alum spring and produces a CO_2 and H_2S degassing, this last being evidenced by the characteristic rotten egg smell together with a thick coating of replacement gypsum covering walls around the spring pool (Fig. 2). The spring also brings up microbial soft flakes.

In this paper, we describe the processes responsible for the formation of sulfates in the Serpent sulfidic-thermal cave. To examine the products of the corroding activities, we carried out X-ray diffraction (XRD) of the corrosion products. The results of our studies indicate not only the classical sulfate minerals deposited through replacement-corrosion, but we also identify aluminum sulfates growing on an artificial door that encloses the spring. Some of these alum minerals such as tschermigite are rarely observed in caves, and jurbanite is identified here for the first time in a cave. Finally, we discuss the role of the artificial aluminum of the door in the formation of the aluminum sulfates, which for this reason, are considered as border minerals.

MATERIALS AND METHODS

SAMPLE SITE DESCRIPTION

Distribution of Gypsum and Aluminum Sulfates Around the Sulfidic-Thermal Spring

The Alum Spring thermal siphon (37–41 °C) is isolated from outside contamination by a glass partition framed with aluminum (Fig. 2). This door separates two types of microclimatic conditions. The inside temperature is about 37 °C, and humidity at saturation produces condensation on the glass; outside of the door, the temperature is about 24 °C, and the atmosphere is less saturated with vapor, thus allowing some evaporation. Degassing in the Alum Spring produces sulfidic vapor which reacts with the surroundings (inside and outside).

Inside the Door. Where temperature and humidity are high, vapor condenses along walls and limestone replacement

Table 1. Main physical and chemical data from the Alum spring, Serpents Cave, Aix-les-Bains.

Physico-chemistry	Values	Reference
Temperature	33.5–46.6 °C	Muralt, 2003
Discharge	$8–42\ L\ s^{-1}$	Muralt, 2003
Conductivity	$576–691\ \mu S\ cm^{-1}$	Hobléa, 1999
pH	6.5	Hobléa, 1999
TDS	$496\ mg\ L^{-1}$	Muralt, 2003
HCO_3^-	$262\ mg\ L^{-1}$	Muralt, 2003
SO_4^{2-}	$60–230\ mg\ L^{-1}$	Muralt, 2003
Cl^-	$15–30\ mg\ L^{-1}$	Muralt, 2003
Na^+	$20–40\ mg\ L^{-1}$	Muralt, 2003
Ca^{2+}	$100–150\ mg\ L^{-1}$	Muralt, 2003
K^+	$3–6\ mg\ L^{-1}$	Muralt, 2003
Mg^{2+}	$10–25\ mg\ L^{-1}$	Muralt, 2003
SiO_2	$22–26\ mg\ L^{-1}$	Muralt, 2003
H_2S	$5\ mg\ L^{-1}$	Iundt et al., 1987
Trace Elements	Al, Fe, Mn, Pb, B, Sr, Sn, Sb, Ba, Li	Iundt et al., 1987

Figure 2. The Alum sulfidic-thermal spring, in Serpents Cave. The thermal siphon (37–41 °C) is isolated from outside contamination by a glass partition framed with aluminum. Note floating microbial mats at the water surface and gypsum replacement crust on the wall. Studied minerals form on the frame of the glass door.

occurs. Consequently, the walls are covered with a several-centimeter thick gypsum crust. XRD analysis shows the presence of anhydrite, together with gypsum (Fig. 3). In some places, the gypsum crust is covered with a thin (<1 mm) yellowish coating. It corresponds to native sulfur, together with magnesium calcite (Fig. 4). Sulfur crystals are not visually distinguishable. The elemental sulfur may originate from sulfate reduction through microbial activity (Barton and Luiszer, 2005). The magnesium calcite precipitation may be of hydrothermal origin, possibly influenced by microbial activity.

Outside the Door. The gypsum crust quickly disappears at about 1 m from the door because of seepage plus dissolution by condensation from cold surface air entering the cave. However, a peculiar crust has developed on the aluminum frame of the glass door, especially close to the contact between the rubber joint, the glass, and the aluminum (Fig. 5). It occurs as a soft crust, mainly pure white, but sometimes transparent or tinted in grey or brown. The taste, bitter and astringent, is typical of alum. XRD analyses described below show the presence of gypsum with three aluminum sulfates: alunogen, jurbanite, and tschermigite (Fig. 6).

Method

X-ray powder diffraction (XRD) patterns were recorded on a Philips diffractometer using Cobalt radiation (λ = 1.79 Å) 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° 2θ using a step interval of 0.05° 2θ and a counting time of 2.5 s.

Results

Mineralogical Characteristics of the Jurbanite and Associated Hydrous Aluminum Sulfates

The Alum Spring in Serpents Cave owes its name to the alum mineral, which is a generic term for hydrous sulfates of aluminum and an alkali. Three of these alum minerals evidenced by XRD (Fig. 6), alunogen, tschermigite, and jurbanite, are presented here. Information about the minerals is provided by Jolyon and Ida (2006) for a general presentation, and Hill and Forti (1997) for cave minerals.

Alunogen

Alunogen ($Al_2(SO_4)_3 \cdot 17H_2O$) is a triclinic hydrated aluminum sulfate generally associated with volcanic fumaroles or decomposition of sulfides in coal mines. It appears as a crust made of small white to transparent crystals, but it is often tinted by impurities. In caves, alunogen is a mineral present in volcanic environments,

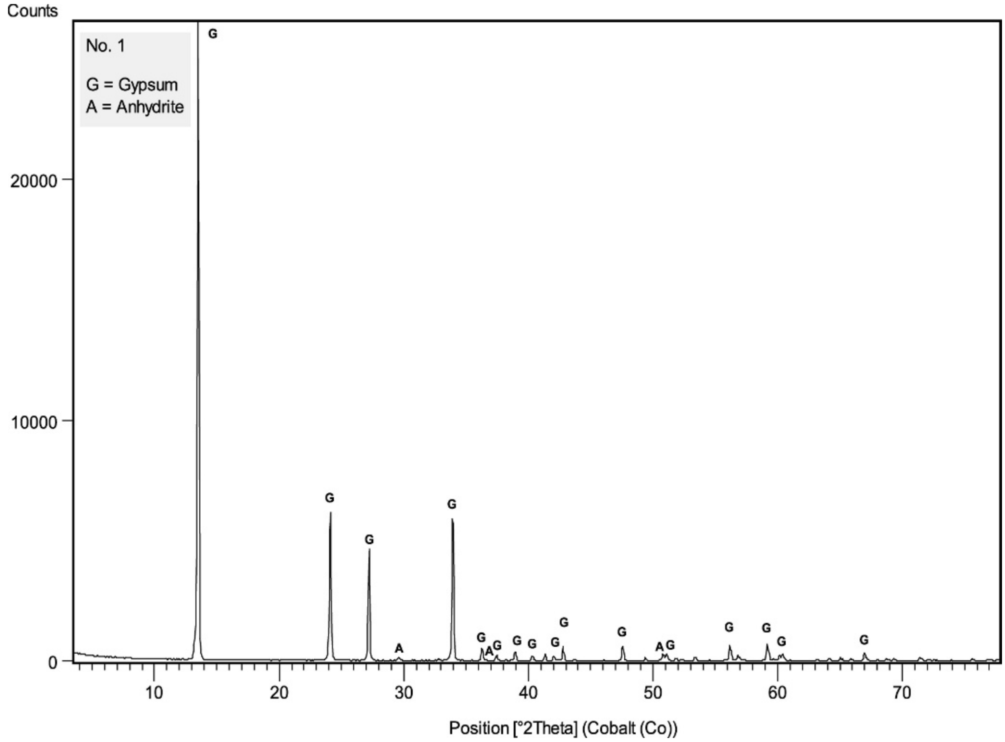

Figure 3. X-ray diffraction diagram of the gypsum crust covering walls inside the chamber isolated by a door. Anhydrite occurs, together with gypsum.

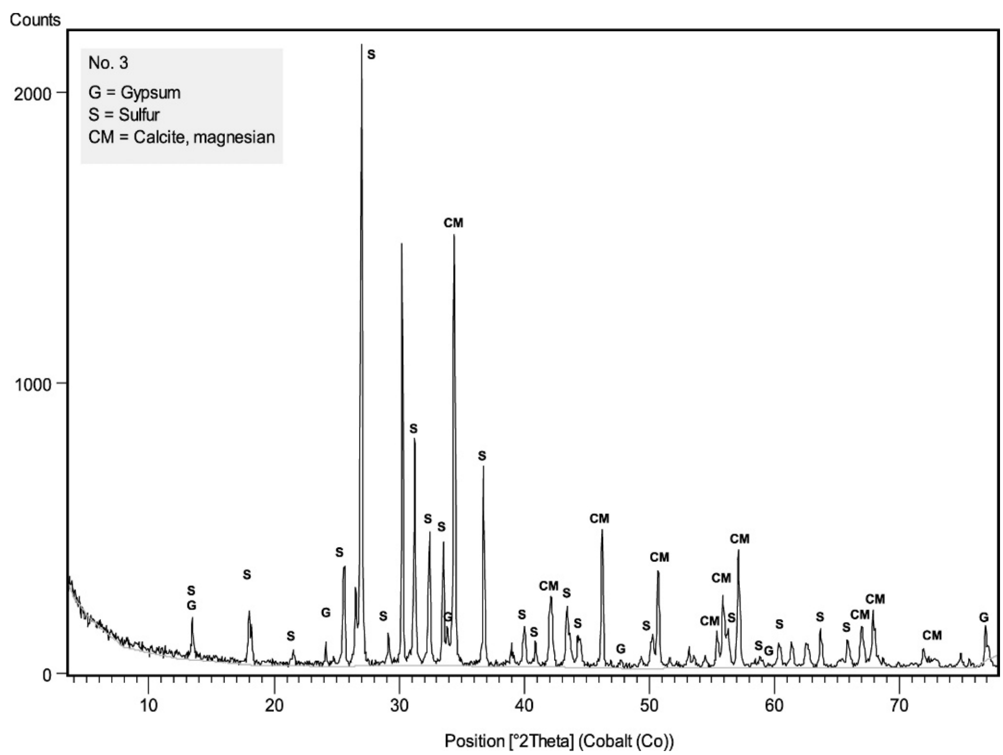

Figure 4. X-ray diffraction diagram of the yellow coating of the gypsum crust. Native sulfur is present, together with magnesium calcite.

Figure 5. Detail of the frame of the glass door. Aluminum sulfate crystals are growing on outer side on aluminum frame, along rubber joints. Outside temperature is 24 °C, inside temperature is 37 °C; humidity at saturation produces condensation on the glass.

either derived from fumarole gases reacting with tuff rock (grotta dello Zolfo, Italy; Bellini, 1901) or from weathering of tuff (Ruatapu Cave, New Zealand; Cody, 1978). It appears that Serpents Cave is the first mention of that mineral in a cave not related to any volcanic influence.

Tschermigite

Tschermigite ($NH_4Al(SO_4)_2 \cdot 12H_2O$) is a cubic ammonium alum that was discovered in 1853 in Cermiky mine in the Czech Republic (called Tschermig at that time, as it was under Austrian domination). It has since been identified in mines or around volcanoes in the Czech Republic, China, Germany, Italy, Hungary, Russia, Slovakia, and the USA. It is reported in Lone Creek Fall Cave, South Africa, as white to yellow sugary efflorescences associated with Lonecreekite, its iron equivalent (Martini, 1983). In Ruatapu Cave, New Zealand, it may be associated with potassium alum (Cody, 1978). In Lone Creek Fall Cave, sulfates are provided by the oxidation of host rock pyrites, ammonia from bat guano, and aluminum from clay. If one excludes Alum Cave Bluff, Tennessee, which is a rock shelter in metamorphic phyllites in the Great Smoky Mountains, Tennessee (Coskren and Lauf, 2000), Serpents Cave is only the third mention of tschermigite in a cave.

Jurbanite

Jurbanite ($Al(OH\ SO_4) \cdot 5H_2O$) is a rare monoclinic hydrated aluminum sulfate. It occurs as short prismatic crystals, commonly in crusts and stalactites, in humid tunnels and in oxidized portions of sulfide deposits in aluminous rocks. It was discovered in 1976 in San Manuel Mine, Arizona (Anthony and McLean, 1976). The name was given by a mineral collector, J. Urban, who first

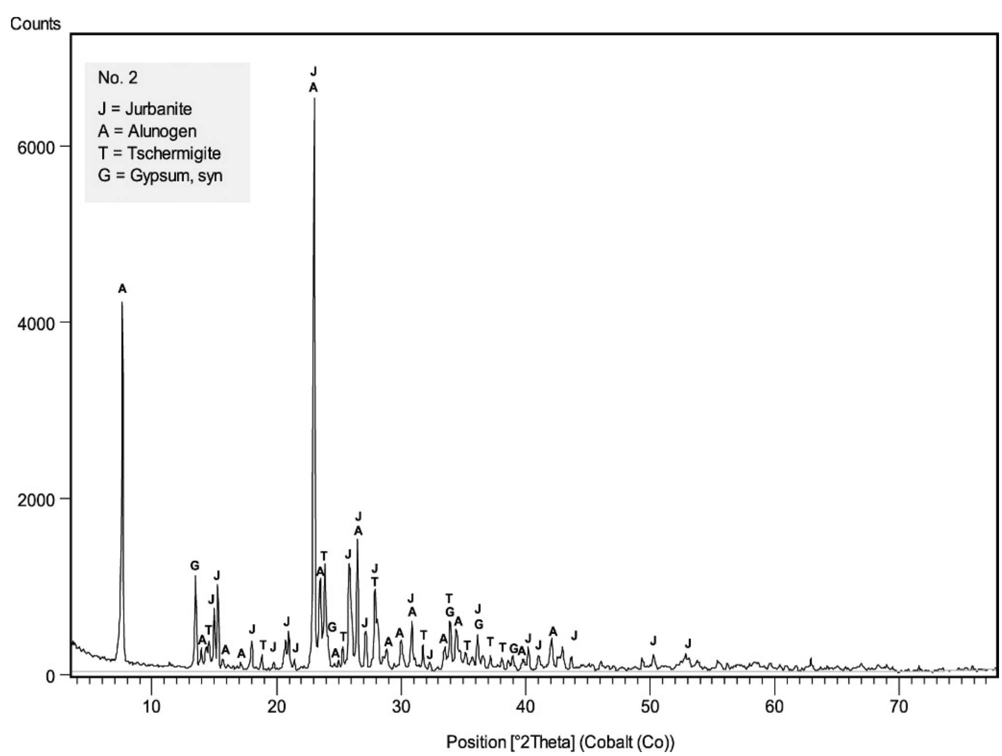

Figure 6. X-ray diffraction diagram of the soft crust growing on the aluminum frame of the door. Together with gypsum, three aluminum sulfates are present: alunogen, jurbanite, and tschermigite.

observed the natural material. Since its discovery, it has been documented in only a few sites worldwide, and exclusively in mines, including Nejedly I Mine, Czech Republic, and Cetine Mine, Italy (Jolyon and Ida, 2006). In addition, jurbanite is suspected to be present in Alum Cave Bluff. Consequently, since Alum Cave Bluff is neither a real cave, nor a karst phenomenon, and since other localities are mines, jurbanite occurrence in Serpents Cave is the first mention in a karst cave.

Discussion

Origin and Possible Anthropic Influence on the Growth of the Aluminum Sulfates

In Serpents Cave, we observe the following association of sulfate minerals originating from the reactions driven by H_2S release from the sulfidic spring:

1. Calcium sulfates such as gypsum and anhydrite over limestone cave walls; and
2. Aluminum sulfates such as alunogen, tschermigite, and jurbanite over the aluminum frame of the door.

Due to their location well above the water, all these minerals are formed by reactions between gases, liquid (condensation), and solids. On the wall, H_2S is dissolved into condensation water, then is oxidized into sulfuric acid by reaction with atmospheric oxygen (Egemeier, 1981). This acid attacks the local media, either the limestone or the aluminum of the door frame. Sulfates for the minerals come from the sulfuric acid. Ammonia could be due to microbial metabolic activity such as nitrification processes involving *Crenarchaeota* which use ammonia as an energy source through oxidation (Weidler et al., 2007). The presence of ammonia could show a biogenic component for the formation of tschermigite and should be confirmed by further studies. The sulfur coating on gypsum crust may also have a microbial origin. Aluminum probably comes from the door frame. For this reason, alunogen, tschermigite, and jurbanite have to be considered here as border minerals since they are formed by a combination of natural processes and human intervention; the aluminum is introduced artificially by the presence of the door. However, in other sites, they are considered as true minerals since there is no human intervention, the aluminum being provided by the host rock or by clay. Similarly, some minerals naturally produced on archaeological stain artifacts were considered as border minerals and consequently accepted by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (Organ and Mandarino, 1970).

Conclusions

The sulfidic vapor degassing from Alum Spring in Serpents Cave produces sulfate minerals when it reacts with the host rock of the cave. The replacement-corrosion of the limestone wall produces gypsum, anhydrite, sulfur, and magnesium calcite. The reaction of sulfuric acid with the aluminum door produces border minerals in the form of aluminum sulfates: alunogen, tschermigite, and jurbanite. Jurbanite is described within such a cave environment for the first time in this paper. Serpents Cave is an important site for the study of sulfidic karst processes and sulfate minerals in caves. Because microbial communities are present as soft flakes in the phreatic zone and as biofilms on walls where condensation occurs, and because the microbial activity is suspected to influence some mineral precipitation such as native sulfur, magnesium calcite and tschermigite, the Serpents Cave may also be an important site for the study of microbial activity related to karst solution and mineralization processes. Further studies will continue to assess the potential of this cave as a source of information on speleogenetic processes, mineralization, and microbiology.

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References

Anthony, J.W., and McLean, W.J., 1976, Jurbanite, a new post-mining aluminum sulfate mineral from San Manuel, Arizona: American Mineralogist, v. 61, p. 1–4.

Audra, P., 2005, Hydrothermal karst and caves in Southern France: Cave features, related sediments and genesis, Genesis and formations of hydrothermal caves, International Conference on the occasion of the 100th anniversary of the discovery of Pál-Völgy Cave, Budapest 2004, Papers, p. 5–13.

Audra, P., Bigot, J.Y., and Mocochain, L., 2002, Hypogenic caves in Provence (France). Specific features and sediments: Acta Carsologica, v. 31, no. 3, p. 33–50.

Audra, P., and Häuselmann, P., 2004, Hydrothermal origin of two hypogenic karst caves in French Provence: Preliminary results from fluid inclusions: Journées AFK, 2003, Rouen, p. 32–34.

Audra, P., and Hofmann, B.A., 2004, Les cavités hypogènes associées aux dépôts de sulfures métalliques, MVT type (Hypogenic caves associated to sulfidic metal deposits, MVT type): Le Grotte d'Italia, v. 5, p. 35–56.

Audra, P., Hobléa, F., Bigot, J.Y., and Nobécourt, J.C., 2007, The role of condensation-corrosion in thermal speleogenesis: Study of a hypogenic sulfidic cave in Aix-les-Bains, France: Acta Carsologica (in review).

Barton, H., and Luiszer, F., 2005, Microbial metabolic structure in a sulfidic cave hot spring: Potential mechanisms of biospeleogenesis: Journal of Cave and Karst Studies, v. 67, no. 1, p. 28–38.

Bellini, R., 1901, La Grotta dello Zolfo nei Campi Flegrei: Bollettino della Società Geologica Italiana, v. 20, p. 470–475.

Carfantan, J.C., Nicoud, G., and Iundt, F., 1998, L'origine et le parcours des eaux thermo-minérales d'Aix-les-Bains, Savoie (The origin and the path of thermo-mineral waters of Aix-les-Bains, Savoy): Circulations hydrothermales en terrains calcaires, 10e Journée technique du Comité français de l'Association internationales des hydrogéologues, Carcassone, 28 novembre 2003, p. 7–14, AIH-CFH, Orléans.

Cody, A.D., 1978, Ruatapu Cave: New Zealand Speleological Bulletin, v. 6, no. 108, p. 184–187.

Coskren, T.D., and Lauf, R.J., 2000, The minerals of Alum Cave Bluff, Great Smoky Mountains, Tennessee: Mineralogical Record, v. 31, p. 163–175.

Egemeier, S.J., 1981, Cavern development by thermal waters: Bulletin of the National Speleological Society, v. 43, no. 2, p. 31–51.

Forti, P., 1996, Thermal karst systems: Acta Carsologica, v. 25, p. 99–117.

Galdenzi, S., and Menichetti, M., 1995, Occurrence of hypogenic caves in a karst region: examples from central Italy: Environmental Geology, v. 26, p. 39–47.

Gallino, S., 2006, Le karst du dôme anticlinal d'Aix-les-Bains. Nouvelles données sur le panache hydrothermal (The karst of the anticline dome of Aix-les-Bains: New data about the hydrothermal plume): Karstologia, no. 48, p. 29–32.

Hill, C.A., 1987, Geology of Carlsbad Cavern and other caves in the Guadalupe Mountains, New Mexico and Texas: New Mexico Bureau of Mines and Mineral Resources, Bulletin, v. 117, 150 p.

Hill, C., and Forti, P., 1997, Cave minerals of the world, Huntsville, Ala., National Speleological Society, 464 p.

Hobléa, F., 1999, Contribution à la connaissance et à la gestion environnementale des géosystèmes karstiques montagnards: études savoyardes (Contribution to the knowledge and to the environmental management of mountain karstic systems: Savoyan studies) [PhD thesis]: Lyon, University of Lyon, 995 p.

Hose, L.D., and Pisarowicz, J.A., 1999, Cueva de Villa Luz, Tabasco, Mexico: Reconnaissance study of an active sulfur spring cave and ecosystem: Journal of Cave and Karst Studies, v. 61, no. 1, p. 13–21.

Iundt, F., Lopoukine, M., Malatrait, A., and Martelat, M., 1987, Étude du système thermal et minéral d'Aix-les-Bains, Savoie (Study of the thermal and mineral system of Aix-les-Bains, Savoy): Report No. 87-SGN.434 RMA, Orléans, Bureau de recherches géologiques et minières.

Jolyon, R., and Ida, C., 2006, Mindat.org—The mineral and locality database: http://www.mindat.org [accessed August 6, 2006].

Martel, E.A., 1935, Contamination, protection et amélioration des sources thermominérales (Contamination, protection and improvement of thermomineral springs): Congrès international des mines, de la métallurgie et de la géologie appliquée, 7th session, v. 2, p. 791–798.

Martini, J.E., 1983, Lonecreekite, sabieite and clairite, a new secondary ammonium ferric-ion sulphate from Lone Creek Fall Cave, near Sabie, eastern Transvaal: Annals of the Geological Survey of South Africa, v. 17, p. 29–34.

Morehouse, D.F., 1968, Cave development via the sulfuric acid reaction: Bulletin of the National Speleological Society, v. 30, no. 1, p. 1–10.

Muralt, R., 2003, Processus hydrogéologiques et hydrochimiques dans les circulations d'eaux thermales à Aix-les-Bains, Savoie [Hydrogeological and hydrochemical processes in the thermal water flow in Ains-les-Bains, Savoy]: Circulations hydrothermales en terrains calcaires, 10^{e} Journée technique du Comité français de l'Association internationales des hydrogéologues, Carcassone, 28 novembre 2003, p. 65–72, AIH-CFH, Orléans.

Organ, R.M., and Mandarino, J.A., 1970, Romarchite and hydroromarchite, two new stannous minerals: The Canadian Mineralogist, v. 10, p. 916.

Sarbu, S.M., Kane, T.C., and Kinkle, B.K., 1996, A chemoautotrophically based groundwater ecosystem: Science, v. 272, p. 1953–1955.

Sarbu, S.M., Galdenzi, S., Menichetti, M., and Gentile, G., 2002, Geology and biology of Grotte di Frasassi (Frasassi caves) in central Italy, an ecological multi-disciplinary study of a hypogenic underground karst system, *In* Wilkens, H., Culver, D.C., and Humphreys, W.F., eds., Subterranean Ecosystems, Elsevier, New York, p. 369–378.

Weidler, G.W., Dornmayr-Pfaffenhuemer, M., Gerbl, F.W., Heinen, W., and Stan-Lotter, H., 2007, Communities of *Archaea* and *Bacteria* in a Subsurface Radioactive Thermal Spring in the Austrian Central Alps, and Evidence of Ammonia-Oxidizing *Crenarchaeota*: Applied and Environmental Microbiology, v. 73, no. 1, p. 259–270.