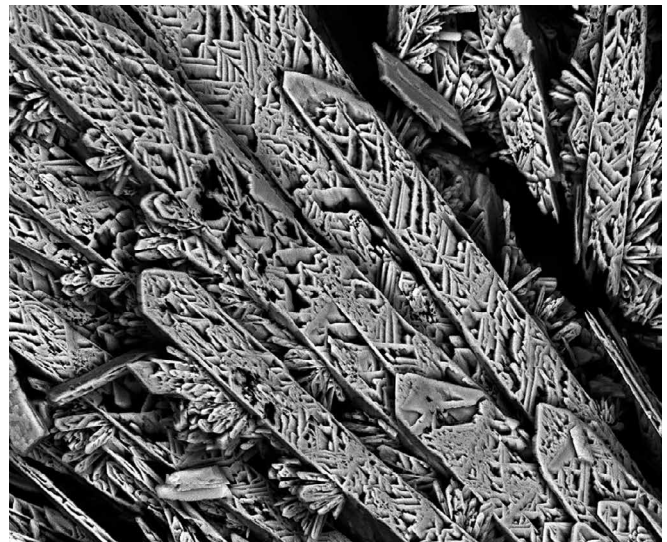


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# SPELEOTHEMS IN CAVITIES DEVELOPED IN MAGMATIC ROCKS

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Four types of natural cavities in magmatic rocks are known: (1) developed along fracture planes, (2) associated with residual block fields, (3) tafone, and (4) lava tube. These openings are the only access for the runoff toward inside the rocky massif. The water flows always of low velocity (trickles) weather the rock forming small fissural regoliths that are moved by the water and then deposited, giving rise to granular detrital accumulations (primary speleothems) of openwork texture. The porous system of these sediments is the temporal refuge for different microorganisms (bacteria, algae, fungi, testate amoebae, spores, diatoms, collembola and mites, etc.), which inhabit the cavity during the humid stage. Their organic activity provides the water with metabolic compounds able to solubilise ions, mainly Si, of the rock without changes in pH which in the dry stage will precipitate by oversaturation as opal-A and other authigenic minerals that will not only contribute to cement the primary speleothems but also to form the secondary speleothems. The shape of the speleothems, either cylindrical or planar, is mainly defined by the way of the water circulation at low velocity by dripping, capillarity, foam-drops like textures or by laminar flow. The relationship between the microbiological activity and the processes of weathering, dissolution and sedimentation justifies their name as biospeleothems.

## 1. Introduction

The speleothems studied in this paper are formed during the water circulation at low velocity (trickles) through the fissural system of massifs of igneous rocks. In the water/rock contact the physical weathering produces a heterometric detrital aggregate of mineral grains which are first moved by the water as a hydro-suspension (slurry) and then deposited on the walls, floor or ceiling of the cave. These types of speleothems may be considered as residual materials because they derive from the rocky substratum of the cavity, but other authigenic species are associated with them, i.e. generated in the same cave at room temperature as amorphous opal, evansite, bolivarite, struvite, pigotite, taranakite, allophane, hematite, goethite. The most common mineral species among these is the amorphous opal (called coralloid in the old works (Caldcleugh 1829; Swarzewski and Keller 1937), though here the term opal-A is used (Vidal Romani et al. 2010). An additional feature of the silica hydrogel from which the opal-A speleothems are formed is that it may be the base for the formation of new authigenic mineral species called whiskers (Twidale and Vidal Romani 2005). Whiskers twined crystalline aggregates of mineral species such as halite, gypsum, siderite, cerussite, plumbean aragonite, malachite, etc., though this list is growing every day more. However, in the caves developed in basic igneous rocks (gabbros, diorites, peridotites, basalts), the amorphous opal speleothems are not very frequent, other minerals, also authigenic, as the carbonates of Ca, Mg, Fe, Pb, etc. being habitual. All these minerals were described in caves of very different rock types and varied geographic-climatic environments: temperate humid, arid to cold regions (Spain, Portugal, Azof speleothems in cavities in magmatic rocksores Islands, United Kingdom, Germany, Poland, Czech Republic, Sweden, Finland, Corea), tropical (Brazil, Venezuela, Madagascar), arid (South Australia, Argentina, Nigeria, Botswana, Mexico, U.S.A., etc) (Willems et al. 1998, 2002; Twidale and Vidal Romani 2005; Vidal Romani et al. 2010).

## 2. Morphological features of the speleothems

Speleothems are not only differentiated by their mineralogical composition but also by their morphology. For example, carbonates or whiskers associated with the amorphous opal speleothems are always presented as crystals of high idiomorphy in spite of their small size. On the contrary, the amorphous mineral species are adapted to the relief of the surface on which they deposit, and their morphology is related to the features of the dynamics of the fluid, which originates the speleothem.

The following types of speleothems in cavities in magmatic rocks are distinguished:

### 2.1. Cylindrical speleothems

They are associated with water movement either by dripping or capillarity. There are different types as follows:

Stalactites s.s.: they are formed on the upper part of rock fissures (the ceiling or eaves of cavities) when the weight of the drop overcomes the superficial stress (then dripping is produced).

Grass-shaped speleothems: multiple associations of very thin (maximum 1 mm) cylindrical forms and associated with the ceiling, walls or floor of cavities. These speleothems grow by deposition associated with capillary movements of the water through the agglomerate mass of clastic accumulations of angular grains soaked with water.

Anti-stalactites: These individual speleothems (Vidal Romani and Vilaplana 1984) grow by capillary movements of the water from a clast grain mineral agglomerate soaked in water. They are usually thicker (up to 4 mm of diameter) and reach longitudinal developments between 4 and 10 mm.

Stalagmites s.s.: these speleothems are infrequent in the igneous rock caves. They are formed by the precipitation of the substances dissolved or dragged by the water which fall from the stalactites s.s.



Club-like stromatolites s.l.: they are formed by the growth of biofilms of blue-green algae while there is humidity inside the cave. When the environment dries, the algae transform into the substratum of the new generation of algae that will grow in the following humid stage.

## 2.2. Planar speleothems

They may normally appear associated on any flat, low relief surface (either ceiling or floor) but even in subvertical surfaces as far as they do not overpass the threshold of dripping, which is given by the stress adherence of the water to the cave rocky surfaces. Different types of planar speleothems are distinguished:

Flowstone, rimstones and microgours: they are continuous covers of the cave rocky surface with variable thicknesses and may also hide the rock micro rugosity. They are disordered accumulations of mineral clasts pushed by the water layer during the humid phases marked by lineal accumulations with sinuous shape behind the ones that may even hold water temporarily. Flowstones, rimstones and associated pool (microgour) are associated with flat (either ceiling or floor), gentle-sloped and inclined or even subvertical surfaces when the flow speed does not overpass the threshold of water-rock superficial adherence in the trickles.

Water drop structures: they are similar to the foam-like structures formed on the upper part of the beach when an advance front of the water layer is individualized into small drops. They are associated with the ceiling of the cavity where the water is divided into small drops, which, by superficial stress, attract a thin coat of clasts of minerals that the water evaporation will cement as opal-A allowing the conservation of the morphology of the drop.

## 3. Methods

Different analytical techniques have been used to study these speleothems: ICP Mass Spectroscopy, XRD, XRF, and mainly SEM; all of them, but the last, are destructive analytical methods. Though SEM gives morphological information (texture, structure, morphometry of grains), it also gives data of elemental composition with the backscattered X-R. From the first works (Caldcleugh 1829) these speleothems were considered to be formed by water dripping ignoring the existence of other types of speleothems. In this work, the information obtained by Stereoscopic Microscopy is included, allowing to establishing the complete sequence of formation of speleothems.

## 4. Results and discussion

The following stages are distinguished in the formation of speleothems: (1) accumulation of the granular material coming from the fissure regolith and transported by water; (2) first colonisation by microorganisms as bacteria, algae, fungi, amoebae, collembola and mites; (3) formation, dissolution and precipitation of amorphous opal; and (4) formation of whiskers from the silica hydrogel. The activity

of these microorganisms promotes the dissolution of Si, mainly, (Ehrlich 1996) providing with low molecular weight organic acids (mainly oxalates) with chelant ability without pH changes (McMahon and Chapelle 1991; Barker et al. 1997). Later, the dissolved Si precipitates as amorphous opal  $\text{SiO}_2 \cdot 15(\text{H}_2\text{O})$ , 100 times more soluble in water converting the generation of speleothems into a continuous process always depending on the water circulation through the fissure system. Each time it rains again, the re-circulation of water through the fissural system of the rocky massif produces the re-dissolution of the amorphous opal and its later re-precipitation. This phase in the evolution of the speleothem is favourable for the growth of authigenic minerals of small size, whiskers, which are located on the points where water accumulates; for the cylindrical speleothems on their final edge and for the planar speleothems or flowstone in the places where the water accumulates in the microgour or pool. The mineralogy of these whiskers is very varied: gypsum, carbonates, halides, though the most common is gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). In some cases, whiskers appear as isolated individuals except for gypsum which always gives nice twinned crystalline associations in physical continuity, with deposits of opal-A. Some authors attribute the presence of S necessary for the formation of gypsum to the activity of microorganisms (Franklin et al. 1994; Welch and Ullman 1996) which are able to produce sulphate oxides from oxidation of organic matter, this latter invariably associated with the zones where the speleothems are observed (Vidal Romaní et al. 2003). Some authors (García Ruíz and Miguez 1982) achieved to reproduce the process in laboratory using a silica hydrogel base to obtain the growth of crystals of different substances in very low concentrations. In the cavities of igneous rocks, gypsum whiskers are normally found, but also, in accordance with our own observations, whiskers of calcite, aragonite, plumboaragonite and phosphates are also formed. Some authors (Van Rosmalen and Marcheé 1976) explain the diverse morphology of the gypsum whiskers formed from silica hydrogel by the presence of different additives or impurities. The lowest abundance of opal-A speleothems is symptomatic in cavities (e.g., lava tube) (Woo et al. 2008) developed in basic igneous rocks (syenites, granodiorites, diabases, etc.) and their physical association with calcite crystals obviously formed (Beinlich and Austrheim 2012) by combination of  $\text{CO}_2$  dissolved in water with brucite or other carbonates existing in the rock. At pressure and room temperature, Si does not form stable crystalline structures but minerals of low temperature (opal-A) slowly evolve toward more stable polymorphs of silica as opal-CT (Bustillo 1995). Notwithstanding, the first essays to date opal-A speleothems by OSL (Sanjurjo and Vidal Romaní 2011) seem to indicate that at least in some climatic environments the transition Opal-A to Opal-CT may be delayed many thousands of years.

These types of microenvironments developed in the porous system of the speleothems either cylindrical or flowstones with their small gours where water is kept temporarily are a very suitable environment for the development of microorganisms which develop their vital cycle while water remains. Their disappearance by evaporation during the dry stages causes the precipitation of amorphous opal dissolved

in it fossilizing the microorganisms or their remains that are immediately coated by opal-A. Each time the rain provides the fissural system with water, life regenerates, at least partially, in the speleothem producing the germination of the latent or resistance forms developed in diatoms, spores, algae, testate amoebae, etc, which live and develop in the micro speleological system. At the same time, other organisms (mites and collembola) use the speleothem as physical support to move and feed on organic matter. The growth processes of the speleothems are superposed to the ones of the development of microorganisms in these cavities causing subtle differences between life and sedimentation, justifying the name of biospeleothems given to these deposits.

## 5. Conclusions

The partially open fissure systems of granitic massifs through which water circulates at very slow speed (trickles) are natural environments with which different types of neomineralizations are associated: opal-A, gypsum, the most frequent minerals. These biominerals or biospeleothems are formed indirectly due to microbiological processes (as a consequence of reactions produced by the metabolic products derived from the organic activity). Si and Al are the most abundant elements in the granitic rocks and thus mainly prevail in the infiltration water. The oversaturation by water evaporation or/and the pH changes cause the precipitation of the elements and solubilised compounds originating the speleothems of granite systems. Opal-A (Si) is the most important type of speleothem quantitatively and the most diversified morphologically. The organisms (bacteria, algae, fungi) that live and are developed in these speleothems are active while the speleothem is wet. When water flow diminishes or evaporates, the organisms react developing resistance spores staying until the next humid period when they germinate again. Mites and collembola also have activity in the speleothem using the content in organic matter of the same speleothem for their subsistence. The last stage in the speleothem development is where S of organic origin is combined with the Ca of the plagioclases, and using the substratum of amorphous silica (silica gel) gypsum crystals develop with an excellent idiomorphism and are present widely in the opal-A.

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## References

Barker WW, Welch SA, Banfield JF, 1997. Biogeochemical weathering of silicate minerals. In: *Geomicrobiology: interactions between microbes and minerals* (Banfield, J. F. and Nealson KH, eds.). Washington: Mineralogical Society of America, 391–428.

- Beinlich A, Håkon Austrheim H, 2012. In situ sequestration of atmospheric CO<sub>2</sub> at low temperature and surface cracking of serpentinized peridotite in mine shafts. *Chemical Geology*, 332–333, 32–44.
- Bennett PC, 1991. Quartz dissolution in an organic-rich aqueous system. *Geochimica et Cosmochimica Acta*, 55, 1781–1797.
- Blyth AJ, Baker A, Collins MJ, Penkman KEH, Gilmour MA, Moss J S, Genty D, Drysdale RN, 2008. Molecular organic matter in speleothems and its potential as an environmental proxy. *Quaternary Science Reviews*, 27, 905–921.
- Brady PV, Walther JV, 1990. Kinetics of quartz dissolution at low temperatures. *Chemical Geology*, 82, 253–264.
- Bustillo MA, 1995. Una nueva ultraestructura de ópalo CT en silcretas. Posible indicador de influencia bacteriana. *Estudios Geológicos*, 51, 3–8.
- Caldcleugh A, 1829. On the geology of Rio de Janeiro. *Transactions of the Geological Society*, 2, 69–72.
- Cañaveras JC, Sánchez-Moral S, Soler V, Saiz-Jiménez C, 2001. Microorganisms and microbially induced fabrics in cave walls. *Geomicrobiology Journal*, 18, 223–240.
- Ehrlich HL, 1996. *Geomicrobiology*. 3<sup>rd</sup> ed. Marcel Dekker, Inc., New York, 719.
- Franklin SP, Ajas AJr, Dewers, TA, Tieh T.T, 1994. The role of carboxylic acids in albite and quartz dissolution: An experimental study under diagenetic conditions. *Geochimica et Cosmochimica Acta*, 58(20), 4259–4279.
- García-Ruiz JM, Miguez F, 1982. Condiciones de formación del primer precipitado en la técnica del gel de sílice. *Estudios Geológicos*, 38, 3–14.
- Kröger N, Deutzmann R, Sumper M, 1999. Polycationic peptides from diatom biosilica that direct silica nanosphere formation. *Science*, 286, 1129–1131.
- McMahon PB, Chapelle FH, 1991. Microbial production of organic acids in aquitard sediments and its role in aquifer geochemistry. *Nature*, 349, 233–235.
- Sanjurjo Sánchez, J, Vidal Romani JR, 2011. Luminescence dating of pseudokarst speleothems: a first approach. 2nd Conference on Micro-raman and luminescence studies in the Earth and Planetary Sciences (CORALS II). May 18–21, Madrid, Spain.
- Swarzlow CI, Keller WD, 1937. Coralloid Opal. *Journal of Geology*, 45, 101–108.
- Twidale CR, Vidal Romani JR, 2005. Landforms and geology of granite terrains. Balkema, London, 351.
- Van Rosmalen GM, Marcheé WGH, 1976. A comparison of gypsum crystals grown in silica gel and agar in the presence of additives. *Journal of Crystal Growth*, 35, 169–176.
- Vidal Romani J.R, Vilaplana JM, 1984. Datos preliminares para el estudio de espeleotemas en cavidades graníticas. *Cadernos do Laboratorio Xeolóxico de Laxe*, 7, 35–324.
- Vidal Romani JR, Bourne, J A, Twidale CR, Campbell EM, 2003. Siliceous cylindrical speleothems in granitoids in warm semiarid and humid climates. *Zeitschrift für Geomorphologie*, 47(4), 417–437.
- Vidal Romani JR, Sanjurjo J, Vaqueiro, M, Fernández Mosquera D, 2010. Speleothem development and biological activity in granite cavities. *Geomorphologie: relief, processus, environment*, 4, 337–346.

- Welch SA, Ullman WJ, 1996. Feldspar dissolution in acidic and organic solutions: Compositional and pH dependence of dissolution rate. *Geochimica et Cosmochimica Acta*, 60(16), 2939–2948.
- Willems L, Compere P, Sponholz B, 1998. Study of siliceous karst genesis in eastern Niger: microscopy and X-ray microanalysis of speleothems. *Zeitschrift für Geomorphologie*, 42(2), 129–142.
- Willems L, Compère P, Hatert F, Pouclet A, Vicat JP, Ek C, Boulvain F, 2002. Karst in granitic rocks, South Cameroon: cave genesis and silica and taranakite speleothems. *Terra Nova*, 14, 355–362.
- Woo KS, Choi DW, Lee KC, 2008. Silicification of cave corals from some lava tube caves in the Jeju Island, Korea: Implications for speleogenesis and a proxy for paleoenvironmental change during the Late Quaternary. *Quaternary International*, 176–177, 82–95.

# EVOLUTION OF GUANO UNDER DIFFERENT ENVIRONMENTAL CONDITIONS: A MINERALOGICAL APPROACH

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The phosphate minerals from three Romanian caves that host bat guano deposits have been investigated. The XRD and SEM analyses have revealed the presence of seven phosphates (brushite, francoanellite, hydroxylapatite, leucophosphite, taranakite, vashegyite and variscite) along with the more common gypsum, calcite and various allochthonous clay minerals. The occurrence of these phosphate minerals highlights the decomposition and various reactions that take place between the phosphate-rich solutions leaching out from the guano and different cave sediments and/or bedrock. The variation of the environmental conditions in the vicinity and within the guano accumulations is responsible for the type of mineral that is being precipitated. The abundance of specific phosphates indicates changes of the pH (from acidic to alkaline) and moisture (both wet and dry conditions) in all the three caves.

## 1. Introduction

Phosphates represent the second largest group among cave minerals (after sulfates), 55 out of over 300 being found in different cave settings (Hill and Forti 1997; Onac 2012). The most abundant phosphate minerals are hydroxylapatite, brushite, ardealite, taranakite and variscite, whereas the rest are rare and form only if particular conditions are present. The occurrence of phosphate minerals is related to the accumulation of significant bat guano or bone accumulations. The clay minerals from detrital sediments in caves are a source for aluminum, silica, potassium, and sodium, which, when combined with the phosphoric acid will increase the chances for precipitation of rare phosphate minerals (Hill and Forti 1997).

The present study provides data on some phosphate minerals identified in three Romanian caves (Zidită [Walled], Gaura cu Muscă, and Gaura Haiducească; Fig. 1) that host important guano deposits. The aim of the paper is to emphasize that the phosphate solutions leaching from underneath the guano have reacted with the bedrock and

other cave sediments under different environmental conditions precipitating a variety of phosphate minerals.

## 2. Cave settings

The Gaura cu Muscă is a 254 m long active cave developed in Upper Jurassic limestones and opens in the left bank of the Danube near the village of Moldova Nouă (Caraş-Severin county, SW Romania). The guano deposits in this cave are related to the presence of large bat colonies (*Myotis myotis* and *Rhinolophus ferrumequinum*) (Negrea and Negrea 1979). The samples collected for this study were taken from the Bats Passage, a short fossil gallery that shortcuts the Water Passage (Fig. 2a) and consist of ochre to dark brown earthy material interbedded within horizons of fossil guano deposits.

The second cave, Gaura Haiducească, is developed in the Lower Cretaceous (Barremian-Aptian) limestones of the Locvei Mountains and is located north from the town of Moldova Nouă. The cave, explored and mapped on 714 m until 1976 (Bleahu et al. 1976) is presently a hydrological traverse 1,370 m long and consists of three well individualized sectors: a large entrance room (Great Hall, 180 m long, 60 m large and 25 m high) in its upstream part, a small median passage, temporary active but which sometimes may get completely flooded, and a larger downstream active passage leading to the “spring” entrance (Lurkiewicz et al. 1996). The phosphate samples were collected from the slopes on the southern side of the Great Hall (Fig. 2b), where they occur as white to yellowish-brown nodules, lenses, and earthy aggregates within a significant guano accumulation.

Zidită Cave (also known as Dacilor) is an old cave fortress in the Metaliferi Mountains (SE part of the Western Carpathians) developed in Upper Jurassic limestones. The cave is a fossil maze with a total length of 547 m (Fig. 2c) and has several guano accumulations. The largest of them, possibly belonging to a *Rhinolophus* colony, is a 1.5 m guano deposit located in Bat Room, near the end of the cave



Figure 1. Gaura cu Muscă (GM), Gaura Haiducească (GH), and Zidită (PZ) caves on the Romanian karst map.



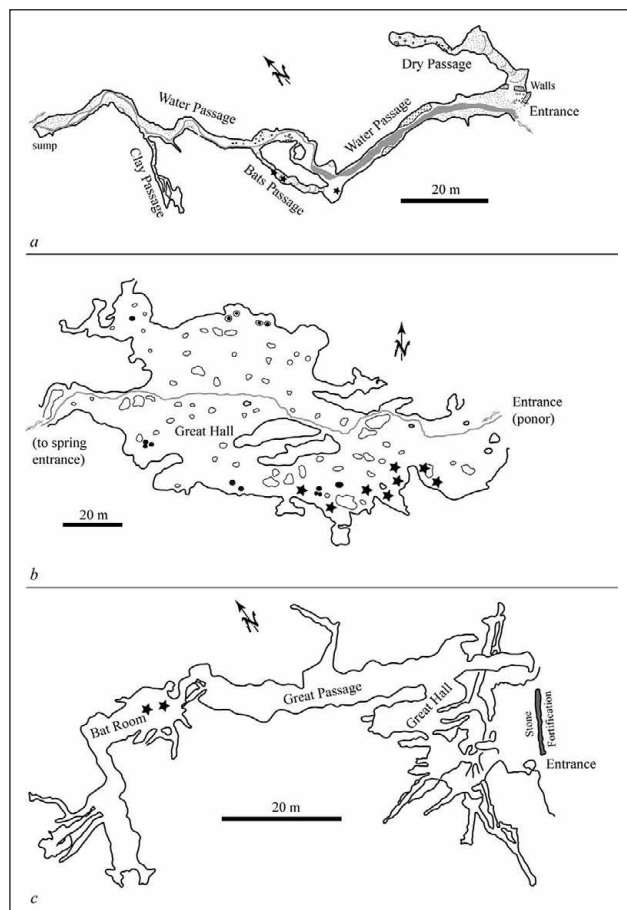


Figure 2. Maps of the studied caves with location of samples (stars): a. Gaura cu Muscă (simplified from Bleahu et al. 1976); b. The Great Hall from Gaura Haiducească (simplified from Bleahu et al. 1976); c. Zidită Cave (map by Proteus Hunedoara Caving Club, used with permission).

(Fig. 2c). All the samples taken from this cave were collected from the vicinity of this large deposit and consist of crusts formed on limestone blocks and on clay deposits from the room floor.

### 3. Methods

The X-ray diffractions were performed using a Siemens D5000 diffractometer operated at 40 kV and 30 mA. The instrument employs  $\text{CuK}\alpha$  radiation. The step-scan data were continuously collected over the range of  $5^\circ$  to  $75^\circ 2\theta$ , using a step interval of  $0.05^\circ 2\theta$ . Counting time was 1 second per step. The scanning electron microscopy was performed on a Hitachi S-3400N equipped with a Bruker Energy Dispersive Spectroscopy (EDS) microanalyzer system. All analyses were carried out using instruments at the Serveis Científicotècnics (Universitat des les Illes Balears, Palma de Mallorca, Spain).

### 4. Results

*Brushite*  $[\text{Ca}(\text{PO}_3\text{OH}) \cdot 2\text{H}_2\text{O}]$  occurs only in Zidită Cave as a white-ivory paste-like material. It is a common cave mineral, which is isostructural with gypsum and is stable under acidic ( $\text{pH} < 6$ ) and damp conditions (Hill and Forti 1997). It results from the reaction of carbonate bedrock or calcite/aragonite speleothems with the phosphoric acid derived from guano deposits (Fiore and Laviano 1991).

*Francoanellite*  $[\text{K}_3\text{Al}_5(\text{PO}_3\text{OH})(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}]$  was identified in Gaura cu Muscă and Gaura Haiducească along with taranakite and illite-group minerals (Nickel and Nichols 2009). The likely process that leads to the formation of francoanellite is the mechanism proposed by Hill and Forti (1997), which suggests dehydration of taranakite formed by the reaction between the clay-rich sediments and guano solutions under acidic conditions.

The EDS spectrum of sample 1563 (Gaura Haiducească) shows characteristic peaks for O, P, and Zn suggesting the possibility that hopeite or another Zn-rich phosphate may occur in this cave. More investigations are needed to fully confirm the presence of any Zn-phosphate.

*Hydroxylapatite*  $\text{Ca}_5(\text{PO}_4)(\text{OH})$ , was identified in Gaura cu Muscă and Zidită caves as light- to dark-brown or even black thin crusts, which overlay the limestone bedrock. It most occurrences is closely associated with gypsum. The presence of hydroxylapatite indicates a slightly alkaline environment as this mineral generally forms through the reaction of phosphatic solutions derived from guano with limestone when the pH is above 6 (Fiore and Laviano 1991; Dumitraş and Marincea 2008).

*Taranakite*  $[\text{K}_3\text{Al}_5(\text{PO}_3\text{OH})_6(\text{PO}_4)_2 \cdot 18\text{H}_2\text{O}]$  forms 3–7 cm thick earthy white masses in Gaura cu Muscă and Gaura Haiducească caves. Under ESEM, taranakite appears as platy, pseudohexagonal crystals (Fig. 3). The interaction between bat guano and clay (which provide the Al ions) in acidic conditions is at the origin of taranakite.

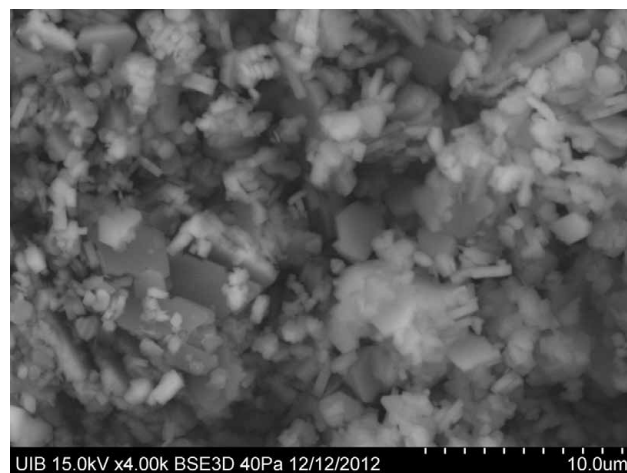


Figure 3. ESEM microphotograph of taranakite crystals (sample 1563; Gaura Haiducească).

*Variscite*  $[\text{AlPO}_4 \cdot 2\text{H}_2\text{O}]$  was found in Gaura cu Muscă in an interbedded guano/clay sequence. We attribute the formation of variscite to the reaction between the phosphate-rich leachates derived from guano and the underlying clay sediments (Onac et al. 2004). Another mineral earlier described from this cave is *vashegyite* (Onac et al. 2006). It occurs as dull white nodules within a highly phosphatized clay horizon interbedded and covered by guano. The underground stream regularly floods the entire deposit, thus permanent damp conditions prevail most of the time.

*Leucophosphite*  $[\text{K}(\text{Fe}^{3+})_2(\text{PO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}]$  is a rare phosphate mineral and forms through the reaction between  $\text{H}_3\text{PO}_4$  (derived from leached guano) and clay minerals in the presence of iron hydroxides. The XRD, SEM, and EDS

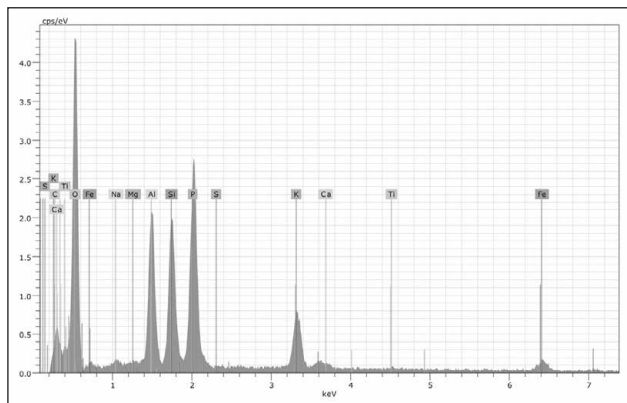


Figure 4. The EDS analysis of leucophosphite (sample 1569; Gaura cu Muscă Cave).

analyses of the sample 1569 reveal the presence of this phosphate in Gaura cu Muscă. Illite-group minerals and iron-rich phases provide the K and Fe ions, respectively. These elements were documented by EDS microanalyses (Fig. 4).

## 5. Conclusions

Bat guano deposits and the related minerals from three Romanian caves were studied and the analyses have revealed the presence of seven phosphates along with calcite, gypsum, and illite-group minerals. The occurrence of phosphate minerals highlights the decomposition of bat guano in time and the variation of the environmental conditions (mainly changes in pH and moist vs dry) in the vicinity and within the accumulation.

The results suggest diverse interactions between the solutions from bat guano and the limestones and clay sediments from the cave. The reaction with limestone is responsible for the formation of Ca-rich phosphates whereas the precipitation of taranakite, variscite, or leucophosphite normally suggests the existence of a clay mineral precursor (Dumitraş et al. 2002). Francoanellite has formed by the partial dehydration of taranakite. The occurrence of Ca-rich phosphates indicates variations of the pH and moisture within and below the guano deposit as well as an increase in Ca/P ratio towards apatites (Onac and Vereş 2003) in all three caves.

The described phosphate minerals provide information about the environment in which they have formed. In Zidită Cave brushite is the most common phosphate mineral suggesting an overall acidic and damp depositional environment. In Gaura Haiducească the same acidic environmental conditions but much wetter are inferred from the abundance of taranakite. Phosphate minerals from Gaura cu Muscă show different abundances, with taranakite, variscite, vashegyite, and francoanellite indicating a wet, acidic environment (in the proximity of the guano deposits). The hydroxylapatite occurs mainly at distant locations from the large guano accumulations in sections of the cave where only small-size colonies are hibernating (Negrea and Negrea 1979). Its presence indicates slightly alkaline and drier conditions.

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## References

- Bleahu M, Decu, V, Negrea Ş, Pleşa C, Povară I, Viehmann I, 1976. Peşteri din România. Bucureşti, 415 (in Romanian).
- Dumitraş D, Marincea Ş, 2008. Apatite-(CaOH) in the fossil bat guano deposit from the “Dry” Cioclovina Cave, Şureanu Mountains, Romania. *Canadian Mineralogist*, 46, 431–445.
- Dumitraş D, Marincea Ş, Diaconu G, 2002. Leucophosphite and taranakite in the bat-guano deposit from Lazului Cave (Mehedinţi Mountains). *Romanian Journal of Mineral Deposits*, 80, 23–25.
- Fiore S, Laviano R, 1991. Brushite, hydroxylapatite, and taranakite from Apulian caves (southern Italy): New mineralogical data. *American Mineralogist*, 76, 1722–1727.
- Hill C, Forti P, 1997. Cave minerals of the world. National Speleological Society, Huntsville, Alabama.
- Iurkiewicz A, Constantin S, Bădescu B, 1996. Sisteme carstice majore din zona Reşiţa – Moldova Nouă. A.S. Exploratorii Reşiţa, 70 (in Romanian).
- Negrea A, Negrea Ş, 1979. Peşterile din Defileul Dunării şi fauna terestră. In: Orghidan T. & Negrea Ş. (Eds.) – *Speologia*, Bucureşti: Editura Academiei RSR: 30–75 (in Romanian).
- Nickel EH, Nichols MC, 2009. IMA/CNMNC list of mineral names. <http://www.MaterialsData.com>
- Onac BP, 2012. Minerals. In: William B. White and David C. Culver, (Eds.), *Encyclopedia of Caves*. Academic Press.
- Onac BP, Vereş DS, 2003. Sequence of secondary phosphates deposition in a karst environment: evidence from Măgurici Cave (Romania). *European Journal of Mineralogy*, 15, 741–745.
- Onac BP, Kearns J, Breban R, Cîntă Pânzaru S, 2004. Variscite (AlPO<sub>4</sub>·2H<sub>2</sub>O) from Cioclovina Cave (Şureanu Mountains, Romania): A tale of a missing phosphate. *Studia UBB Geologia*, 49 (1), 3–14.
- Onac BP, Zaharia L, Kearns J, Vereş D, 2006. Vashegyite from Gaura cu Muscă Cave. *International Journal of Speleology*, 35 (2), 67–73.



# A CONTRIBUTION TO THE MINERALOGY OF MONTE GUISI CAVE (SW SARDINIA, ITALY)

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This note presents a preliminary mineralogical study of the skarn-hosted Monte Guisi Cave in SW Sardinia (Italy).

X-ray diffraction (XRD) and environmental scanning electron microscope (including energy dispersive X-ray spectroscopy microanalysis; EDS) analyses allowed us to identify some uncommon cave minerals such as: cerussite  $\text{PbCO}_3$ , rosasite  $(\text{Cu,Zn})_2(\text{CO}_3)(\text{OH})_2$ , dundasite  $\text{PbAl}_2(\text{CO}_3)_2(\text{OH})_4 \cdot \text{H}_2\text{O}$ , brochantite  $\text{Cu}_4\text{SO}_4(\text{OH})_6$ , cuprite  $\text{Cu}_2\text{O}$ , hemimorphite  $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ , chrysocolla  $(\text{Cu,Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ , shattuckite  $\text{Cu}_5(\text{SiO}_3)_4(\text{OH})_2$ , and plancheite  $\text{Cu}_8(\text{Si}_4\text{O}_{11})_2(\text{OH})_4 \cdot \text{H}_2\text{O}$ . Dundasite and plancheite are for the first time reported as cave minerals. All these species appear to represent oxidation/hydrolysis products of the primarily Pb-Zn and Cu-rich ore mineralization that impregnates the carbonate bedrock.

## 1. Introduction

Caves are natural underground laboratories where the precipitation of minerals can be directly monitored. The caves carved in carbonate rocks (limestone, dolomite, marble) normally display a monotonous mineralogy, with calcite, aragonite, and gypsum being the most common species (Onac 2012). If caves are active/fossil  $\text{H}_2\text{S}$  systems (e.g., Frasassi, Diana, Carlsbad, etc.) or host massive accumulations of guano (Cioclovina, Rastoci, etc.), rich association of sulfates and phosphates will normally be encountered (Galdenzi and Menichetti, 1995; Polyak and Provencio 2001; Onac et al. 2002, 2009). The mineralogical situation changes dramatically when caves are located nearby ore deposits or sometimes within them. Such settings guarantee very diverse and unique assemblages of secondary cave minerals (Maltsev 1997; Onac et al. 2002, 2007; Audra and Hofmann 2004; de Waele and Forti 2005; Forti et al. 2006). These are formed by oxidation/hydrolysis, acid/base, and redox processes (White 1997; Onac and Forti 2011a). The recent focus and more thorough investigations conducted in these last types of caves added a significant number of new minerals (Hill and Forti 1997; Onac and Forti 2011b).

Over the past years, Sardinia, with its countless caves discovered during mining activities, became a focal point for mineralogical research (Naseddu 1993; Forti et al. 2005; Boldoni et al. 2013). This paper reports on the cave minerals precipitated in the unique environment of the Monte Guisi Cave (SW Sardinia), from where all samples were collected (not from mine passages).

## 2. Local geology and mining activities

Paleozoic sedimentary rocks dominate the geology of Sardinia, but igneous and metamorphic rocks are also common. The Variscan deformation phase is responsible for

low-grade metamorphism and several phases of magmatic intrusion, some of which produced at the contact with the carbonate rocks skarn deposits (Boni 2001). The Iglesias-Sulcis region in the SW Sardinia, Italy (Fig. 1) is one of the oldest mining districts in the world, with ore exploitation since Phoenicians times. In the early stages, the mining activities focused on recovering silver, lead, and copper, and later, zinc and barium deposits (Boni 2001). Most of the ores are hosted in the Lower Cambrian carbonate formations of Gonnessa Group. In mining areas such as Monteponi, San Giovanni, or Barega, very spectacular and important (mineralogically speaking) cavities were discovered during the exploration and in the process of extracting the ore. Most of these caves develop in the Lower Cambrian limestones, with some (e.g., Monte Guisi Cave) carved in calcic skarns in which rich Pb-Zn ( $\pm$ Ba) mineralizations of Mississippi-type valley deposits (MVT) occur as veins, breccia cements, void-filling, and diagenetic replacements. The most common ore minerals are sphalerite, galena, and barite with variable amounts of pyrite. Near the surface these minerals oxidize/hydrolyze to form smithsonite, hydrozincite, and cerussite (Aversa et al. 2002).

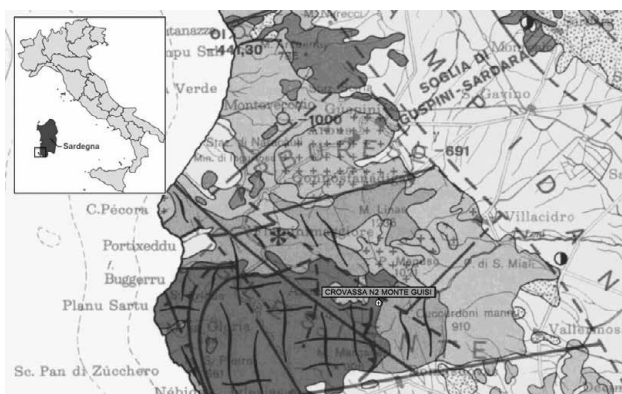


Figure 1. Location of the investigated cave in the Iglesias-Sulcis region, SW Sardinia (Italy). Map from the National Geological Service of Sardinia.