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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.

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

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 (Iurkiewicz 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

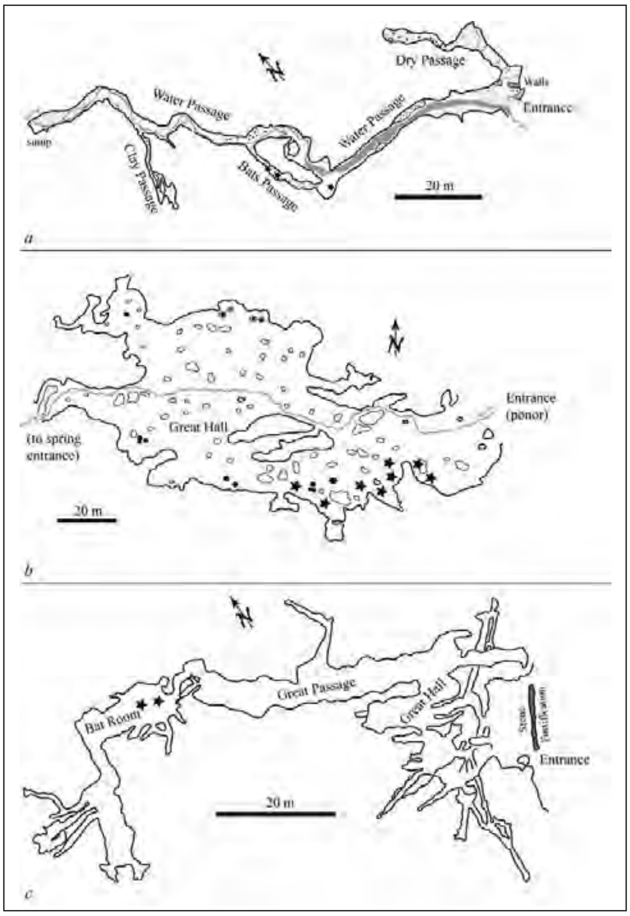

Figure 2. Maps of the studied caves with location of samples (stars): a. Gaura cu Muscă (simplified from Bleahu et al. 1976); b. The Great Hall from Gaura Haiducească (simplified from Bleahu et al. 1976); c. Zidită Cave (map by Proteus Hunedoara Caving Club, used with permission).

(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 Cu*Kα* radiation. The step-scan data were continuously collected over the range of 5° to 75° 2θ, using a step interval of 0.05° 2θ. 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 Cintificotècnics (Universitat des les Illes Balears, Palma de Mallorca, Spain).

4. Results

Brushite [$Ca(PO_3OH)\cdot 2H_2O$] 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 (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 [$K_3Al_5(PO_3OH)(PO_4)_2\cdot 12H_2O$] 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 $Ca_5(PO_4)(OH)$, 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 [$K_3Al_5(PO_3OH)_6(PO_4)_2\cdot 18H_2O$] 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.

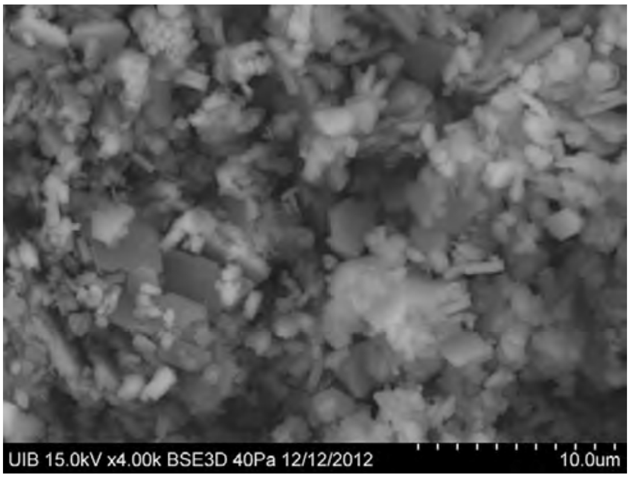

Figure 3. ESEM microphotograph of taranakite crystals (sample 1563; Gaura Haiducească).

Variscite [$AlPO_4\cdot 2H_2O$] 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 [$K(Fe^{3+})_2(PO_4)_2(OH)\cdot 2H_2O$] is a rare phosphate mineral and forms through the reaction between H_3PO_4 (derived from leached guano) and clay minerals in the presence of iron hydroxides. The XRD, SEM, and EDS

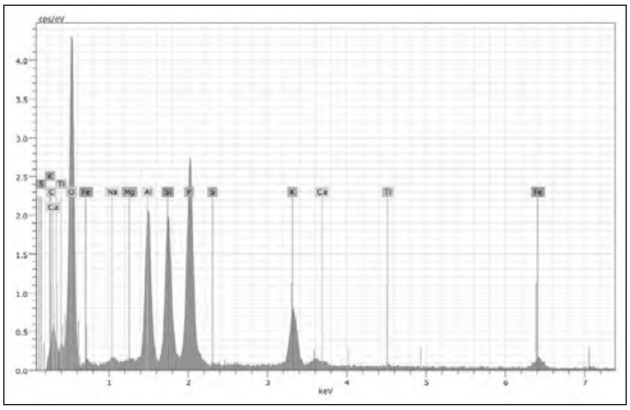

Figure 4. The EDS analysis of leucophosphite (sample 1569; Gaura cu Muscă Cave).

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.

Acknowledgments

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