Mineralogical data on bat guano deposits from three Romanian caves

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INTRODUCTION

Phosphate minerals are a common feature in caves containing bat guano accumulations, where they form as a result of the interaction of guano derived solutions with the cave bedrock or with secondary (chemical or detrital) cave deposits. Reviews of phosphate minerals occurring in caves were published by Hill and Forti (1997) and Onac and Forti (2011a). Up to now, more than 100 phosphate minerals have been identified in caves (Onac, 2012), five of which are considered as commonly occurring: hydroxylapatite, brushite, ardealite, taranakite and variscite (Hill and Forti, 1997; Onac, 2012). The mechanisms responsible for phosphate formation in caves include digestion, dissolution, double replacement and redox reactions (Onac and Forti, 2011b). When solutions percolating through guano deposits interact with the limestone bedrock, they usually produce Ca-rich phosphates (brushite and hydroxylapatite) (Hill and Forti, 1997). If clay minerals are present on the flowpath, minerals such as leucophosphate, taranakite, variscite etc. may form (Hill and Forti, 1997). Leucophosphate, variscite and taranakite are stable under acidic, wet conditions, whereas hydroxylapatitite indicates an alkaline environment (Onac and Veres, 2003; Onac, 2012). Moreover, phosphate alteration or dehydration processes may sometimes be at the origin of new minerals: if there is a decrease in humidity and an increase in temperature at the site, brushite and francolinite may dehydrate to monetite and taranakite respectively (Hill and Forti, 1997; Onac and Veres, 2003). In such conditions, the study of phosphate minerals may offer information about the environmental conditions.

The aim of this study was to describe the minerals from three Romanian caves containing bat guano accumulations: Gaura cu Muscă, Gaura Haiducească, and Ziditǎ Cave, and the environmental conditions in which they have formed. Of these three caves, only Gaura cu Muscă was previously studied with respect to its mineralogy, and a phosphate association consisting of vashegyite, crandallite, and ardealite was described (Onac et al., 2006).

CAVE SETTINGS, LOCATION AND DESCRIPTION

The three caves studied are located in two different Romanian mountain massifs: Locvei Mountains, SW Romania (Gaura cu Muscă and Gaura Haiducească) and Metaliferi Mountains, W Romania (Ziditǎ Cave) (Fig. 1).

Abstract. Mineralogical studies performed on crusts, nodules and earthy masses from the Romanian caves Gaura cu Muscă, Gaura Haiducească and Peștera Ziditǎ have revealed the presence of three different phosphate associations. The minerals have been identified by means of X-ray diffraction, scanning electron microscopy, and energy dispersive spectroscopy. Five phosphates have been identified in the samples, with hydroxylapatite the only common mineral in all the three caves. Brushite, taranakite, leucophosphate and variscite are the other phosphates identified. Associated minerals include gypsum, calcite, quartz, and illite-group minerals. Aside from differences in the lithology, the occurrences of the different phosphate minerals indicate variable pH and relative humidity conditions near or within the guano accumulations.

Keywords: guano, cave phosphate associations, Gaura cu Muscă, Gaura Haiducească, Ziditǎ Cave, Romania
Gaura cu Muscă and Gaura Haiducească caves are formed in the karst rocks of the Reșița-Moldova Nouă Synclinorium, an area where limestones cover more than 800 km² (Iurkiewicz, 2010). This sector includes parallel massifs separated by valleys or karstic plateaus (Bucur, 1997). Geologically, the synclinorium belongs to the Getic Domain, a structural unit of the South Carpathians (Balintoni, 1997; Balintoni et al., 2009). Limestone deposition in the area occurred discontinuously from the Triassic to the Lower Cretaceous.

Zidită Cave (also known as Mada or Dacilor) is located in the SE part of the Metaliferi Mountains, in the upper watershed of the Geoagiu River where the mesozoic limestones crop out as faulted karstified alignments or isolated blocks (Povară and Horoi, 1993; Orășeanu, 2010). The Geoagiu River flows into the Mada Gorges, separating the Balșa Tithonian limestone block (3 x 1.5 km) in two massifs, Pleșa Mare (E) and Dosu (W) (Mantea and Tomescu, 1986; Cocean, 1988).

Gaura cu Muscă Cave (GM)

Gaura cu Muscă Cave (GM) opens in the Upper Jurassic limestones (Bleahu et al., 1976) from the left bank of the Danube, 3 km downstream the locality of Coronini, Caraș-Severin County (SW Romania). The entrance is located at 92 m asl and is easily reached following a footpath spotted right from the DN 57 road, built along the left side of the Danube Gorge, near the border of Romania and Serbia. This active cave was inhabited since the Hallstatt period and was fortified during the XV-XVI and XVIII-XIX centuries (Boroneanț, 2000). The cave is 254 m long and was firstly mapped by Negrea and Negrea (1969) (Fig. 2a). The Dry Passage (40 m long) opens from the entrance, behind the fortification and contains clay sediments and wood fragments (Negrea and Negrea, 1979). The stream is flowing through the main gallery of the cave (the Water Passage) and deposits banks of gravel, sand and clay. In the Bats Room fresh guano accumulates due to the presence of a Myotis capaccinii colony (Coroiu, pers. comm.). The Water Passage is shortcut by a ~20 m long fossil gallery (Bats Passage), which is flooded when the stream level is high. A sequence consisting of alternating guano and silt-clay layers is deposited on the floor of this gallery. Another fossil gallery (Clay Passage) is located towards the end of the cave and hosts a Rhinolophus euryale colony (Coroiu, pers. comm.). Mineralogical samples were collected from the Bats Room and Bats Passage and consist of ochre to dark brown earthy material interlayered within horizons of fossil guano.

Gaura Haiducească (GH)

Gaura Haiducească Cave (Fig. 2b) develops in the Lower Cretaceous limestones from the vicinity of the town of Moldova Nouă, Caraș-Severin County (SW Romania), at 488.5 asl and has two entrances, both located in Poiana Peșterii (Bleahu et al., 1976). It represents the underground capture of the Ogașul Găurii stream (Iurkiewicz et al., 1996), which is reached by following the DC 49 road from the town of Moldova Nouă, Caraș-Severin County (SW Romania), at 488.5 asl and consists of ochre to dark brown earthy material interlayered within horizons of fossil guano.

Zidită Cave (ZC)

Zidită Cave is located close to the Mada village from Hunedoara County (Romania). The cave opens at 410 m asl in the Pleșa Mare limestone massif. This cave was also used for defensive purposes in the medieval period, when its entrance was fortified with a wall, which is visible today.

Zidită Cave, mapped by Proteus Caving Club (Hunedoara, Romania), is a fossil maze with a total length of 547 m consisting of three main sectors: the Great Hall located right after the entrance, the Great Passage in the median part and the Bats Room towards the end of the cave (Fig. 2c). Limestone blocks and clay sediments are common in the entire cave, whereas active stalactites, small rimstone dams and calcite rafts are scarce and may be seen in the median passage. There are several guano accumulations in the median passage (Junction Passage) is only temporarily active, but may be completely occupied by water during floods. In the active Resurgence Passage downstream, another Rhinolophus bat colony is present (Bleahu et al., 1976). This passage leads to the spring entrance of the cave. The samples were collected from the southern slopes of the Great Hall, close to the upstream entrance, and consist of white to yellowish-brown nodules, lenses, and earthy aggregates within the guano sequence or at the contact with the clay sediments.
cave: the largest (1.5 m thick) is located in the Bats Room and probably belongs to a *Rhinolophus* nursery colony. The material sampled for analyses consists of crusts formed on fallen limestone blocks at the contact with this large guano deposit.

**ANALYSIS METHODS**

The 52 mineralogical samples collected from the three caves were analyzed by means of X-ray diffraction, scanning electron microscopy, and electron dispersive spectroscopy. The X-ray diffractions were performed using two instruments: 1. a Siemens D5000 diffractometer with CuKα radiation, (from Serveis Científicotècnics, Universitat des les Illes Balears, Palma de Mallorca, Spain), operated at 40 kV and 30 mA. The step-scan data were continuously collected over the range of 5° to 75° 20, using a step interval of 0.05° 20 with a counting time of 1 second per step, using silicon (NBS 640b) as internal standard. DiffracEVA (8.0) software with the PDF2 database was used to identify the minerals; 2. a Bruker D8 Advance diffractometer with CuKα radiation, Fe 0.01 mm filter and a one-dimensional detector, from the Department of Geology, Babeș-Bolyai University (Cluj-Napoca, Romania). The working parameters are 35 kV and 40 mA. The data were collected between 5° and 64° 20 with a step interval of 0.02° 20 with counting time of 0.5 s/step. Corundum NIST SRM1976a served as internal standard and the DiffracEVA (2.1 ver.) program with the PDF2 database were used to identify the minerals.

Environmental scanning electron microscopy (ESEM) was performed on a Hitachi S-3400N equipped with a Bruker Energy Dispersive Spectroscopy (EDS) microanalyzer system from Serveis Científicotècnics (Universitat des les Illes Balears, Palma de Mallorca, Spain).

**RESULTS**

The analyses of samples collected from the three caves have revealed the presence of five phosphate minerals: brushite, hydroxyapatite, leucophosphate, tamarakite and variscite, along with gypsum, calcite, illite-group minerals and quartz.

**Brushite** [(CaHPO₄·2H₂O)] is a phosphate belonging to the monoclinic crystal system and is isostructural with gypsum. This mineral occurs only in Zidită Cave as a white-ivory paste-like material, where the X-ray diffractions have shown its association with hydroxylapatite (Fig 3a.). Under ESEM, brushite crystals are tabular and flattened after the (010) face (Fig. 4). Similar associations consisting of brushite and hydroxyapatite were described, among others, by Fiore and Laviano (1991), Onac and Veres (2003), Marincea et al. (2006), and Tămăș and Ungureanu (2010). Brushite is a common cave mineral, stable under acidic (pH <6) and damp conditions (Hill and Forti, 1997). It results from the reaction of the carbonate bedrock with the phosphoric acid derived from phosphate-rich leachates derived from bat guano and clay minerals in the presence of iron hydroxides (Hill and Forti, 1997). In Gaura cu Muscă, the K and Fe ions were provided by illite-group minerals and iron rich phases, respectively. Leucophosphate was found in several caves in South Africa (Martini, 1987), whereas Cancian and Pricinvalle (1995) described from Femetti Cave (Italy) an association formed at the contact between terra rossa and gypsum. In Romania, Dumitraș et al. (2002) have found tamarakite and leucophosphate in Lazului Cave. **Variscite** [AlPO₄·2H₂O] was revealed by X-ray diffraction in the samples collected from an interbedded guano/clay sequence in Gaura cu Muscă Cave (Fig. 3d). The reaction between phosphate-rich leachates derived from bat guano and the underlying clay sediments is at the origin of this phosphate mineral (Onac et al., 2004).

**DISCUSSION AND CONCLUSIONS**

Phosphate minerals from three caves in Romania have been investigated in order to decipher the local environmental conditions during their formation. The mineral associations are different in the three caves, with hydroxyapatite the only common element in the three associations studied: in Gaura cu Muscă, the minerals identified are tamarakite, leucophosphate, hydroxyapatite and variscite; out of these, only tamarakite and hydroxyapatite are present in Gaura Haiducească, whereas the association from Zidită Cave comprises only brushite and hydroxyapatite. The occurrence of these phosphate minerals highlights the decomposition of bat guano in time and the variation of the environmental conditions (mainly changes in pH and moisture) in the vicinity and within the accumulation. Calcium phosphates (brushite and hydroxyapatite) originate due to the reaction of phosphate rich solutions with carbonate rocks and indicate variations of the pH (acidic, alkaline respectively) and relative humidity of the environment as well as an increase in Ca/P ratio towards apatites (Fiore and Laviano, 1991; Onac and Veres, 2003). The presence of Fe³⁺, K⁺, and Al³⁺ ions derived from clay minerals or iron hydroxides has led to the precipitation of common phosphates.
Brushite occurs in Zidită Cave where it is the most abundant phosphate mineral, indicating a wet and slightly acidic environment. Considering the experiments carried out by Elliot et al. (1959) on urine with low Ca/P ratio it may be assumed that the maximum nucleation pH of brushite was 6.93. Brushite may form at pH > 6 when Mg/Ca ratio is about 4, concentration which supposedly inhibits hydroxylapatite precipitation. According to Abbona and Franchini-Angela’s (1990) experiments, the brushite-hydroxylapatite association forms from initial solutions with low concentration of Ca and P (0.005 M) and initial pH values between 5.5 and 8. This process involves the decrease of pH and starts with the precipitation of unstable mineral phases, which subsequently evolve to more stable ones such as taranakite and variscite, which are stable under acidic environmental conditions, or not so common phosphates such as leucophosphite (Fig. 6).

In Gaura cu Muscă, the phosphate minerals show different abundances and indicate two distinct environments, acidic and alkaline, respectively. Leucophosphite and taranakite form in acidic and damp conditions in the presence of K$^+$ and NH$_4^+$ ions (Axelrod et al., 1952). Variscite is stable in solutions free of K$^+$ and NH$_4^+$ ions and results due to the reaction between bat guano leachates and clay minerals at an acidic pH (Cole and Jackson, 1950; Onac et al., 2004). Hydroxylapatite precipitates in drier conditions, at high Ca/P values and pH > 6.93 (Elliot et al., 1959).

![Fig. 3. X-ray diffractions of: a) hydroxylapatite and brushite (ZC); b) taranakite (GM); c) leucophosphite (GM); d) variscite (GM).](image)

![Fig. 4. ESEM image and EDS spectrum of brushite (ZC).](image)
stable phases. The first to form are brushite and an amorphous calcium phosphate, followed by the conversion of the latter to hydroxyapatite if Mg/Ca < 0.4 or to whitlockite if Mg/Ca > 0.4 (Abbona and Franchini-Angela, 1990). Whitlockite was not found in samples from Zidită Cave and we assume that Mg/Ca ratio in the solutions, which interacted with the organic material was low or 0.

In Gaura Haiducească the pH variation is more or less similar to that from Zidită Cave. The difference between the two caves is given by the presence of taranakite, which indicates the presence of alkali ions derived from the decomposition of illite-group minerals, at acidic and also higher humidity conditions.

The phosphate minerals described 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 tarańakite. Phosphate minerals from Gaura cu Muscă have different abundances, with tarańakite, variscite, and leucophosphite indicating a wet, acidic environment in the proximity of the guano deposits. Hydroxyapatite occurs mainly at distant locations from the large guano accumulations in sections of the cave where only small size colonies are hibernating. Its presence indicates slightly alkaline and drier conditions.

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