Carpathian Journal of Earth and Environmental Sciences, August 2014, Vol. 9, No. 3, p. 25 - 32

MINERALOGY OF BAT GUANO DEPOSITS FROM HUDA LUI PAPARĂ CAVE (TRASCĂU MOUNTAINS, ROMANIA)

Tudor TĂMAŞ[1,2], Oana MIHEŢ[1] & Alexandra GIURGIU[1]
[1]*Department of Geology, Babeş-Bolyai University, M. Kogălniceanu 1, 400084 Cluj-Napoca, Romania,*
e-mail: tudor.tamas@ubbcluj.ro; alexa.giurgiu@yahoo.com; oana_mihet@yahoo.com
[2]*"Emil Racoviţă" Institute of Speleology, Clinicilor 5, 400006, Cluj-Napoca, Romania*

Abstract: Several guano deposits found in the passages of Huda lui Papară cave (Trascău Mts, Romania) have been sampled to elucidate their mineralogical composition. The samples were studied by means of X-ray diffractometry (XRD), environmental scanning electron microscopy (ESEM) and energy dispersive X-ray analysis (EDS). Four phosphate minerals, belonging to three different types of deposits, have been identified in the samples: hydroxylapatite, ardealite, brushite and taranakite, associated with gypsum, calcite, and minerals of detrital origin (kaolinite, vermiculite, muscovite) and quartz. The phosphate minerals resulted from the interaction of acid solutions derived from the guano deposits with the limestones, calcite speleothems and/or detrital sediments in various conditions of pH and relative humidity.

Keywords: guano, speleothems, cave phosphates, Huda lui Papară, Romania

1. INTRODUCTION

Huda lui Papară, a 5.2 km cave located near Sălciua, in Alba county, Romania, is the longest cave discovered in the Trascău Mountains (Apuseni Mountains, Romania). The cave is well known due to its formidable entrance portal, over 35 m high, but also because it hosts one of the largest bat hibernation colonies in Romania and probably in Europe, according to Coroiu et al., (2006) and Coroiu & David (2008). Mentioned as early as 1839 (Bleahu et al., 1976), the cave was first explored in the ′50s, the length attained at the time being 2020 m (Balogh, 1969). Later (1979 – 1984), cavers from the Polaris Caving Club from Blaj established a total length of 5.2 km (Luduşan, 1983).

The first mention of the minerals from Huda lui Papară belongs to Balogh (1969), who noted especially calcite speleothems, but also crusts composed of apatite and gypsum. Balogh and the later explorers mention bat guano accumulations in particular places along the cave, however no detailed study has been attempted on these accumulations. The purpose of this paper was to describe the minerals associated with the bat guano accumulations and to assess the environmental conditions in which they have formed.

2. CAVE DESCRIPTION AND SAMPLE LOCATION

Detailed descriptions of Huda lui Papară cave have been published by Balogh (1969) and more recently by Luduşan (1983) on the cave website (*hudaluipapara.com*). The cave is located near the commune of Sălciua (Alba County), in a Tithonian limestone stripe from Creasta Bedeleului (Bedeleu Ridge), in the Trascău Mountains. (Fig. 1a). The cave entrance (Fig. 1b), situated at 567 m a.s.l., has the shape of a gothic portal, 35 m high and 4 to 6 m large (Balogh, 1969). The dislevelment from the entrance to the opposite end of the cave is +123 m (Luduşan, 1983). The cave consists of a large active passage, around 1200 m long, with a relatively simple morphology, and an intricate maze of smaller fossil passages (Luduşan, 1983, Viehmann & Kovacs, 1990). Of the total length of the cave, more than three kilometres (not discussed in this study) are represented by these fossil passages, discovered by the Polaris Blaj Caving Club (Luduşan, 1983).

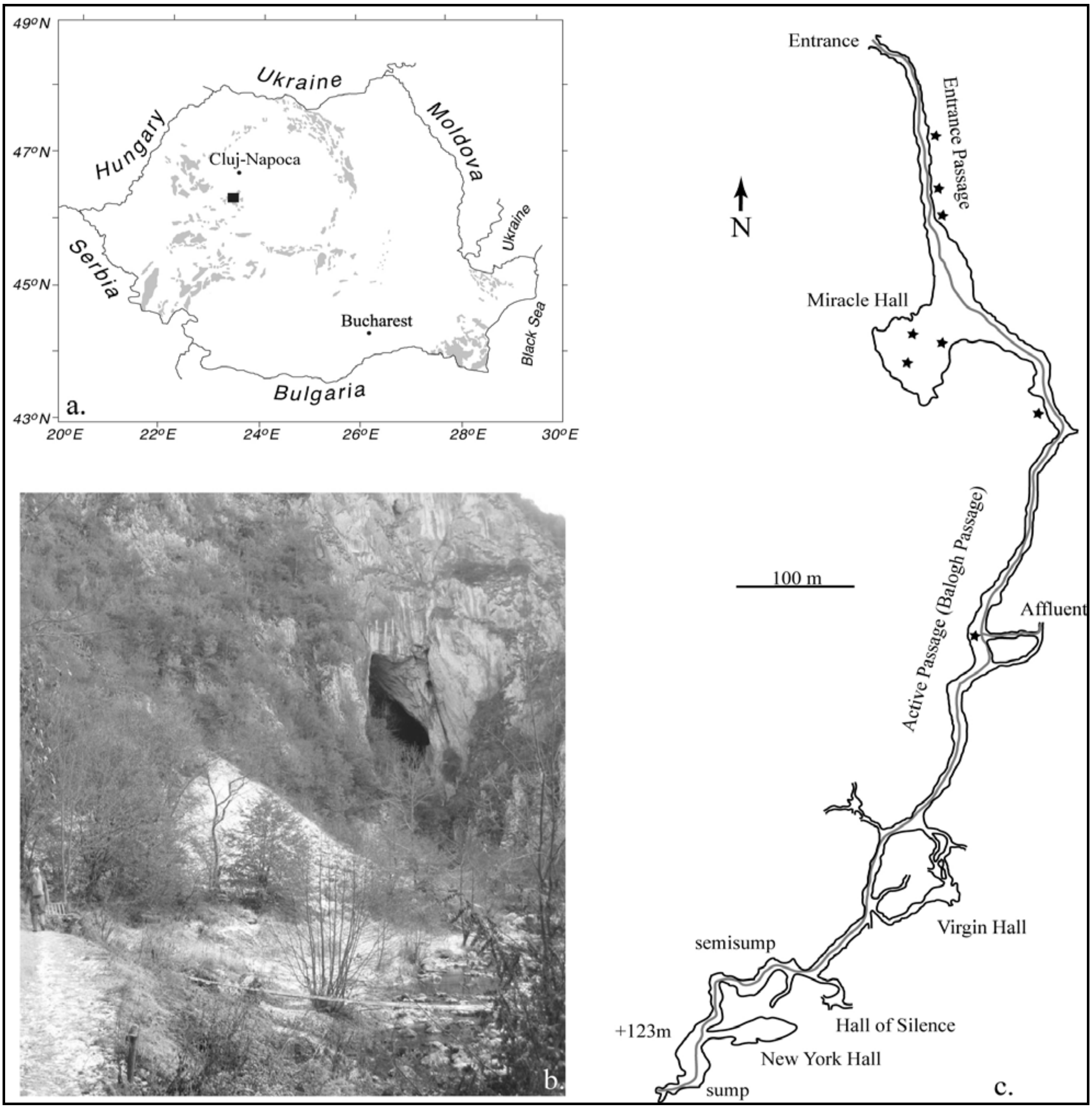

Figure 1. a. Location of Huda lui Papară cave on the map of Romanian karst areas; b. Huda lui Papară cave entrance; c. Simplified cave map (after Balogh, 1969) with the location of samples.

The entrance passage to the cave is relatively steep and fragmented by numerous breakdown boulders and waterfalls. It has only a few speleothems; of note are several old and corroded stalactites and flowstones as well as centimetric crusts, covered by guano of both bats and birds, formed above the level of the cave river. The 8 samples collected from this part of the cave consist of crusts and earthy masses located close to recently deposited, dry, bird and bat guano accumulations. The junction with the Miracle Hall is reached after ca. 300 m. This chamber (Fig. 1c) is 50-80 m large and up to 100 m high at the junction with the active passage and hosts numerous stalactites and flowstones, as well as crusts and earthy masses. The filling of the chamber consists predominantlly of silts and clays, probably marking old flooding stages. Although there are mentions (i.e. Balogh, 1969) of impressive guano deposits inside the Miracle Hall, they are insignificant at the sediment surface. We collected several earthy crusts from various locations in the chamber. A small guano deposit, ca. 20 cm thick, was discovered in a dig on the slope in the upper part (Figs. 1c, 2). This deposit contains various lenses and nodules of phosphate minerals, milimetric to centimetric in size.

Figure 2. The guano deposit from the Miracle Hall, Huda lui Papară cave. The white dashed lines delimit the approximate extent of the guano sequence. White spots inside the deposits are nodules consisting of phosphate minerals.

Upstream from the junction with the Miracle Hall, the active passage is narrower, with a less steep slope, and the sediments deposited by the cave river consist of cobble and sand terraces. During winter, the large bat hibernation colonies are presently located in this sector. (Fig. 1c). During the summer, due to the location of the maternity colonies above the cave river, the guano accumulations are small and only the ones that happen to form on terraces above the cave stream are preserved. One such deposit has been sampled from this sector; it consists of a small guano pile, 50 cm high, formed on a sandy bank on the left side of the passage, at the contact with a limestone breakdown boulder. The samples consist of white and yellow nodules and milimetric crusts, formed at the surface of the guano deposit and at the contact with the limestone block.

The upstream sector of the cave, from the semisump to the terminal upstream sump (Fig. 1c), has a slope and filling deposits similar to the entrance sector. Several breakdown piles need to be climbed up to reach a short horizontal passage occupied by a lake, ended with a sump situated at a mere 18 m from the ponor at the surface. No guano deposits were found in this part of the cave.

3. BIRDS, BATS, CAVE CLIMATE AND GUANO ACCUMULATIONS

The upper parts of the cave entrance passage represent a good nesting site for birds, especially pigeons, and in some places along the river banks, small deposits of bird guano are present. Most importantly, Huda lui Papară cave is an important hibernation site for bats. Coroiu et al., (2006) identified eight species using the main passage of the cave for hibernation: *Rhinolophus ferrumequinum*, *Rh. hipposideros*, *Myotis myotis/blythii*, *Plecotus auritus*, *Miniopterus schreibersii*, *Nyctalus noctula*, *Barbastella barbastellus* and *Pipistrellus pipistrellus*. Due to the size of the entrance, cold air from outside reaches up to 450 m inside the cave during winter, this being the main reason for the high mortality of bats recorded during extremely cold periods (Coroiu & David, 2008). In spite of this, the number of bats hibernating in the cave has been estimated at around 120000 in 2012. In the rest of the cave the air temperature is relatively constant all year long and has values of 10°C - 11.5°C on the active passage and surprisingly, 13°C - 20°C in the Miracle Hall (Balogh, 1969; Bleahu et al., 1976). Due to its fast transit across the cave, the cave river temperature is strongly influenced by the outside temperature and shows considerable seasonal variations, usually between 3°C - 4.5°C in winter and 10°C in summer (Iepure, 2002).

As mentioned above, guano accumulations are produced during summer under the maternity colonies of *Miniopterus schreibersii*, *Myotis myotis/blythii* and *Rhinolophus euryale* (Coroiu et al, 2006). Most maternity colonies are located above the underground river and thus only a few small accumulations are preserved.

4. ANALYSIS METHODS

Samples discussed in this study include 32 pieces of crusts, efflorescences and earthy masses collected from the vicinity of, and from within the guano deposits described in the previous chapters. The samples were studied by X-ray diffractometry (XRD), environmental scanning electron microscopy (ESEM) and energy dispersive spectroscopy (EDS). X-ray diffractions were performed with a Bruker D8 Advance diffractometer with Bragg-Brentano geometry, $CoK\alpha_1$ with λ = 1.78897, Fe filter and a one-dimensional detector, at the Department of Geology, Babeş-Bolyai University Cluj-Napoca, using corundum (NIST SRM1976a) as internal standard. The data were collected on a 5 - 64° 2θ interval, at a 0.02° 2θ, with the measuring step of 0.2 seconds. The identification of the mineral phases was performed with the Diffrac.Eva 2.1 software from Bruker AXS, using the PDF2 (2012) database. Scanning electron microscopy was performed at Serveis Cientificotècnics (Universitat des les Illes Balears, Palma de Mallorca, Spain) using a Hitachi S-3400N instrument equipped with a Bruker AXS Flash 4010 EDS, and at the Electron Microscopy Centre, Babeş-Bolyai University, Cluj-Napoca using a Jeol JSM 5510LV device.

5. RESULTS

The analyses performed on samples taken from Huda lui Papară cave highlight four authigenic phosphate minerals (ardealite, brushite, hydroxylapatite and taranakite), along with gypsum, calcite, muscovite, quartz and clay minerals (kaolinite and vermiculite). The phosphate minerals can basically be grouped in four different associations, depending on the type of the deposit that was sampled (data on the samples are summarized in Table 1). The crusts collected from the entrance passage have a monomineral composition and consist either of hydroxilapatite (dark brown or blackish) or of brushite (white, yellow) and show only one phase of evolution. The crusts collected from the Miracle Hall have similar characteristics.

In the particular case of the guano deposit dug in the Miracle Hall (Fig. 2), a ^{14}C dating for its bottom gave an age of ca. 10000 years BP. A profile through this deposit shows at least two main phases of guano deposition, marking different periods when bat colonies were located in the chamber, possibly separated by an invasion of cave water. The mineral association in the phosphatic speleothems sampled consists of ardealite, brushite, taranakite and gypsum, along with kaolinite, vermiculite, quartz and muscovite of detrital origin.

In contrast, the guano deposit studied on the active passage was recently formed and cannot have a long evolution, due to the notoriously high water levels that can be attained by the cave river. At the surface of this deposit, brushite, ardealite and gypsum form tiny crusts, white and yellowish white in color. Probably due to the air circulation along the active passage, intense evaporation has favoured precipitation of secondary minerals at the surface of the deposit; there were no secondary minerals identified at the bottom of the guano pile, at the contact with the sandy sediments.

5.1. Phosphate minerals

Hydroxylapatite *[$Ca_5(PO_4)_3(OH)$], hexagonal.* Hydroxylapatite is a common cave phosphate and was described from various cave occurences (e.g. Fiore & Laviano 1991; Marincea et al., 2004; Diaconu et al., 2008; Tămaş & Ungureanu, 2010. The samples described as „apatite" by Balogh (1969) probably also consist, in fact, of this common cave mineral. Out of the samples analyzed by our study, the XRD data reveal that only one consists of hydroxilapatite (Fig. 3). The X-ray diffractogram shows the mineral has low crystallinity, based on the low, broad, and poorly defined reflections.

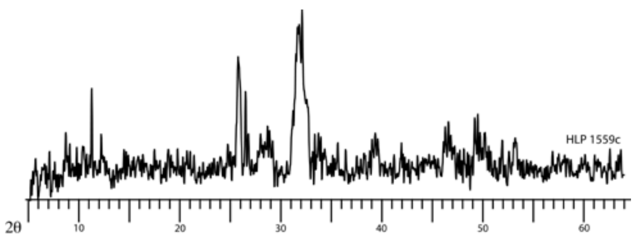

Figure 3. X-Ray diffraction of the hydroxilapatite sample

Table 1. Guano deposits sampled from Huda lui Papară cave: type, location and mineral composition of speleothems

Location	Type of deposit	Speleothems sampled	Mineral association
Entrance Passage	milimetric guano deposits	crusts, earthy crusts	brushite or hydroxilapatite, (+/- calcite)
Active Passage, upstream Miracle Hall	dry guano deposit (0.5 m thick)	efflorescences/thin crusts at guano surface	ardealite, brushite and gypsum
Miracle Hall	milimetric guano deposits	crusts, earthy crusts	brushite, (+/- calcite)
	guano deposit (30 cm thick) covered by detrital sediments	Crusts, nodules inside the guano deposit or at the contact with detrital sediments	brushite, ardealite, taranakite, gypsum, associated with detrital quartz, kaolinite, vermiculite, muscovite

Ardealite $[Ca_2(SO_4)(HPO_4)\cdot 4H_2O]$, *monoclinic*. This phosphate mineral, first described from Cioclovina Cave, Romania (Halla, 1931; Schadler, 1932) occurs within or close to one guano sequence from the active passage as white nodules or powdery masses with smooth silky aspect, generally associated with brushite (Fig. 4). The mineral was identified by X-ray diffraction. In the clay levels from the guano deposit dug in the Miracle Hall, ardealite is found along with taranakite, gypsum and calcite.

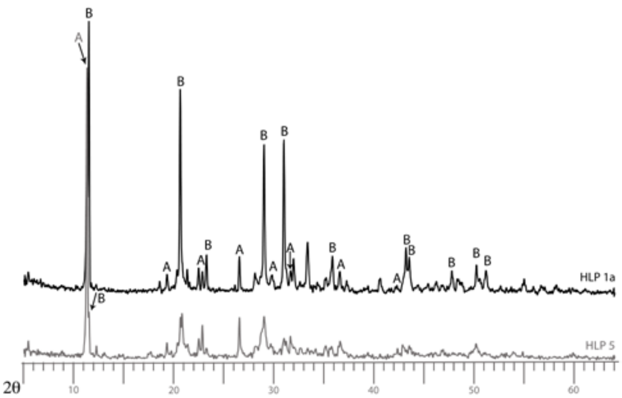

Figure 4. XRD. Ardealite (A) and brushite (B) in two samples from the guano deposit dug in the Miracle Hall: in sample HLP 1a, brushite is dominant, whereas in HLP5 ardealite is the main mineral

Brushite $[Ca(PO_3OH)\cdot 2H_2O]$, *monoclinic.* Brushite (Fig. 5, 6) is a common phosphate mineral in caves containing organic material (Hill & Forti, 1997; Onac, 2012) and is the most frequent phosphate encountered in the samples from Huda lui Papară Cave. Typical brushite occurences in this cave are on limestone breakdown or calcite speleothems located close to the guano deposits, where it forms whitish, usually monomineral crusts. Brushite crystals are prismatic to tabular (010) and are clustered in aggregates with a foliated aspect as shown by the ESEM images (Fig. 5). In the Miracle Hall, brushite forms nodules, in association with ardealite, taranakite and gypsum (Figs. 4, 7). On the guano deposit from the active passage however, brushite occurs on the surface of guano accumulations as white - yellowish white crusts consisting of submillimeter crystals, most likely formed from calcium phosphate solutions through evaporation.

Taranakite $[K_3Al_5(PO_3OH)_6(PO_4)_2\cdot 18H_2O]$, *trigonal*. This mineral appears in the vicinity and within the interlayered deposit of guano and clay from the Miracle Hall, potassium and aluminium from its composition being sourced by phyllosilicates such as kaolinite or muscovite. It occurs as white nodules in association with ardealite and brushite (Fig. 7). Under ESEM, taranakite exhibits pseudohexagonal crystals flattened after the (0001) crystal face (Fig. 8).

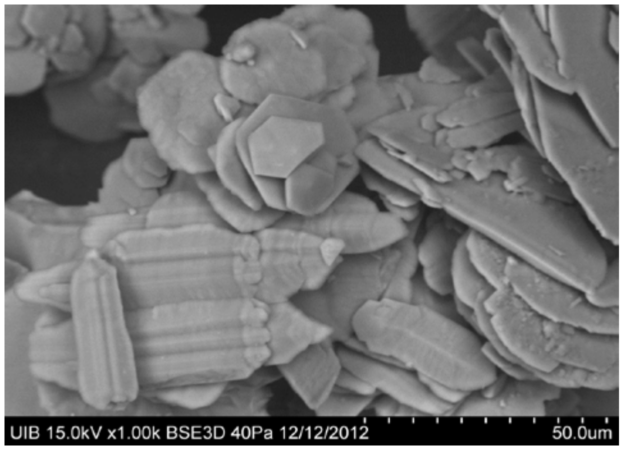

Figure 5. ESEM. brushite crystals (tabular, monoclinic), associated with taranakite (pseudohexagonal) in the guano deposit from the Miracle Hall.

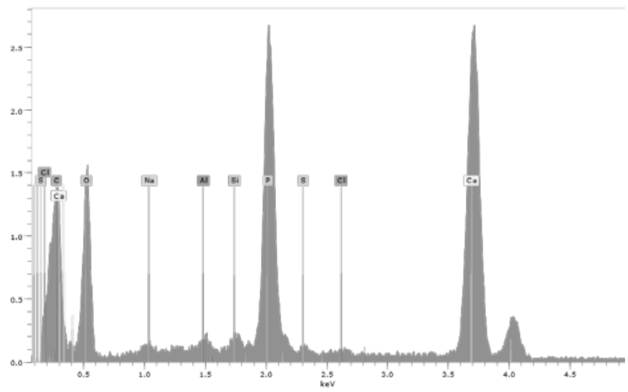

Figure 6. EDS spectrum of a sample containing brushite as a main mineral.

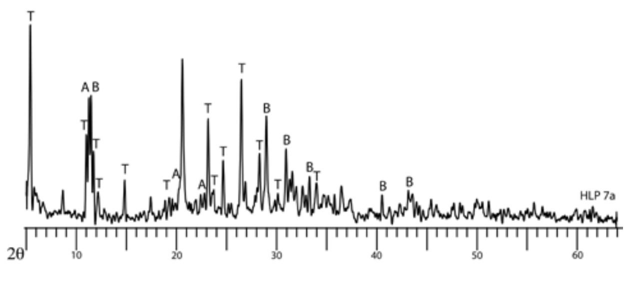

Figure 7. X-ray diffraction of a phosphate nodule containing taranakite (T), brushite (B) and ardealite (A).

5.2. Other minerals

Calcite $[CaCO_3]$, the most common mineral in caves, occurs in the form of common speleothems, such as stalactites, stalagmites and popcorn all along the cave, as described by Balogh (1969). In our study, several crusts collected from the entrance passage, in the vicinity of guano deposits, analyzed by XRD, consist of low-Mg calcite.

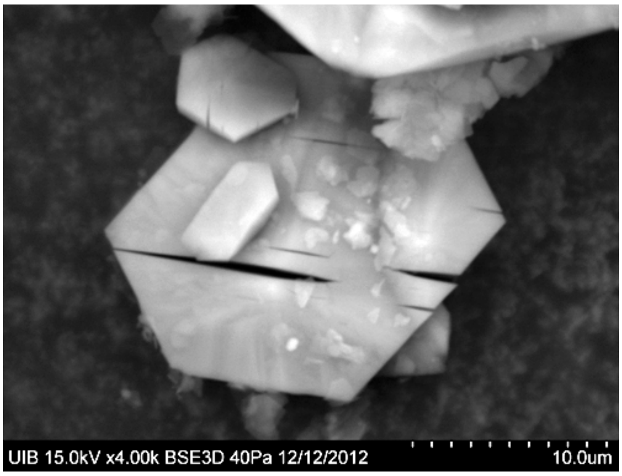

Figure 8. ESEM. Detail of platy taranakite crystals.

Gypsum [$CaSO_4 \cdot 2H_2O$], monoclinic, is a common mineral within cave phosphate deposits (Hill & Forti, 1997). In Huda lui Papară it occurs as whitish crusts within the guano deposit from the Miracle Hall, and as powdery crusts on top of the guano deposit from the active passage. The crusts are composed of small blocky crystals generally 5 to 8 μm in size (Fig. 9). Gypsum may have originated most likely from the oxidation of the organic matter inside the guano deposit.

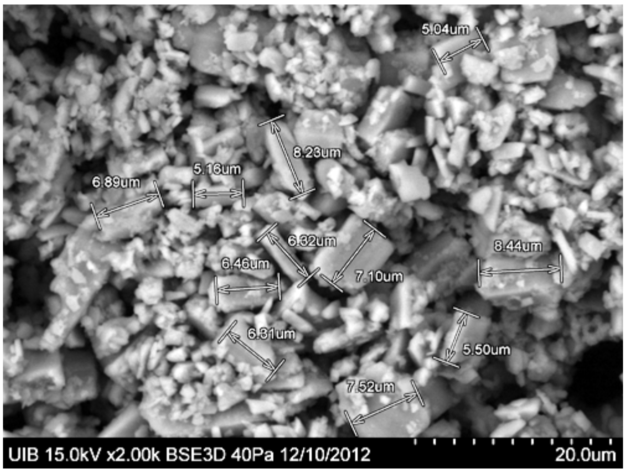

Figure 9. ESEM. Gypsum crystals in the guano deposit from the Miracle Hall.

Kaolinite [$Al_2(Si_2O_5)(OH)_4$], *vermiculite* [$(Mg, Fe^{3+}, Al)_3(Si,Al)_4O_{10}(OH)_2 \cdot 4H_2O$], quartz and muscovite, all of detrital origin, were found by means of X-ray diffraction in the samples from the guano deposit located in the Miracle Hall.

6. DISCUSSION AND CONCLUSIONS

The precipitation of phosphate minerals is a common process which takes place in caves where organic material deposits, such as guano or bones, occur (Hill & Forti, 1997; Onac, 2012). Chemical analyses carried out by Hutchinson (1950) on bat guano revealed significant amounts of phosphorus and sulfur, which are further concentrated by the water passing through bat guano remains. The interaction of these acidic guano-derived leachates with the underlaying carbonatic rocks results in the formation of calcium phosphates (ardealite, brushite, and hydroxylapatite) (e.g., Onac & Vereş, 2003; Marincea et al., 2004). When clay minerals are involved in the reaction they release Al^{3+} ions and taranakite may form (Murray & Dietrich, 1956).

Four phosphate minerals, belonging to three different types of guano deposits, are reported in this study. They are: 1. hydroxylapatite, in monomineral crusts from the Entrance passage; 2. brushite, in monomineral crusts from the Entrance passage and from the Miracle Hall; 3. brushite + ardealite + taranakite ± gypsum, in the guano deposit dug in the Miracle Hall; 4. brushite + ardealite ± gypsum in crusts and efflorescences covering the guano deposit from the active passage of the cave. These phosphates largely indicate environmental conditions (pH and relative humidity, the latter also influenced by evaporation) within and nearby the guano accumulations from different locations in Huda lui Papară Cave.

Hydroxylapatite forms from solutions with an alkaline pH (Fiore & Laviano, 1991). The results of the experiments carried out by Abbona & Baronnet (1996) on solutions having [Ca]=[P]=5 mM and pH=7.94 show the direct precipitation of hydroxylapatite from an amorphous phase, with no other intermediate crystalline phases occurring. It formed in an area where the pH reached high values (>7) necessary for its formation. The sample position on the entrance passage of the cave also suggests rapid evaporation of the solution due to air currents.

Brushite forms at a pH of up to 6.2 (Simpson, 1964) and is stable up to a pH of 6.93 in wet environmental conditions (Elliot et al., 1959; Hill & Forti, 1997). The association of ardealite ± brushite ± gypsum was previously reported from caves such as Cioclovina (Schadler, 1932), Măgurici (Onac & Vereș, 2003), Peștera Mare de la Merești (Marincea et al., 2004), Adam's Cave (Diaconu et al., 2010), Majorcan caves (Onac et al., 2005), Jenolan Caves (Pogson et al., 2011) and other locations. Although ardealite contains the sulphate and phosphate ions in

1:1 proportion, this mineral is not a member of the brushite – gypsum system, having the *b*-axis larger than those of the both end-members (Sakae et al, 1978; Pinto et al., 2008; Pinto et al., 2012). An ardealite-like compound may form when the pH is lower than 5.6 and sulphate ions are available, as resulted from the experiments of Rinaudo et al., (1994, 1996). pH values required for the occurence of a brushite + gypsum + ardealite-like association as the one identified in Huda lui Papară Cave more likely range between 5.2 and 5.6, the process evolving in the presence of ~ 55-67 mol% sulphate (Rinaudo et al., 1996). Taranakite, also present in the association, is known to form in highly acidic environments in the presence of alkali ions derived from the clay minerals (Axelrod et al., 1952; Fiore & Laviano, 1991). It may be therefore assumed that the pH within and close to the guano remains from the Miracle Hall was generally acidic, and damp environmental conditions have prevailed. This is sustained by the climate conditions from this particular spot, where temperature is high for a Romanian cave (13°C - 20°C) and no air currents are present, attesting for a higher relative humidity than in the rest of the cave. In contrast, the mineral associations from the Entrance and Active Passage of the cave may point to a similar pH of the solutions, but to completely different relative humidity conditions. All samples from the active passage show that evaporation plays a more important role in their formation. Due to strong evaporation caused by air currents, solutions circulating through the guano pile do not reach the bottom and as a result, phosphatic minerals precipitate at the surface of the guano accumulation.

ACKNOWLEDGEMENTS

The authors wish to thank T. Brad and L. Barbu-Tudoran for help during sample collection. T.T. and A.G. acknowledge financial support from the Romanian National Authority for Scientific Research, grant PCE-2011-3-0588.

REFERENCES

Abbona, F. & Baronnet, A., 1996. *An XRD and TEM study on the transformations of amorphous calcium phosphate in the presence of magnesium.* Journal of Crystal Growth, 165, 98-105.

Axelrod, J. M., Carron, M. K., Milton, C. & Thaver, T. P., 1952. *Phosphate mineralization at Bomi Hill and Bambuta, Liberia, West Africa*. American Mineralogist, 37(11-12), 883-909.

Balogh, E., 1969. *World of Stalactites*. Youth Publishing House, Bucharest, 205 p (In Hungarian).

Bleahu, M., Decu, V., Negrea, S., Pleșa, C., Povară, I. & Viehmann, I., 1976. *Caves from Romania*. Scientific and Encyclopedic Pubishing House, Bucharest, 416 p (In Romanian).

Coroiu, I. & David, A., 2008. *Long-term changes of hibernating bats in Huda lui Papară Cave (Apuseni Mountains, Romania)*. Abstract. XIth European Bat Research Symposium, Cluj-Napoca, Romania, 39.

Coroiu, I., Viehmann, I. & David, A., 2006. *Multiannual dynamics of bats in Huda lui Papară cave during winter*. The First Conference for Bat Protection in Romania, Băile Homorod, 4-5 (In Romanian).

Diaconu, G., Dumitraș, D.G. & Marincea, Ș., 2008. *Mineralogical analyses in two caves from the Perşani Mountains.* Travaux de l'Institut de Spėologie „Emile Racovitza", 45-46, 113-129.

Diaconu, G., Dumitraș, D.G. & Marincea, Ș., 2010. *Mineralogical analyses in various caves from the Băile Herculane Area, The Cerna Passage.* Travaux de l'Institut de Spéologie „Emile Racovitza", 49, 135-148.

Elliot, J. S., Sharp, R. S. & Lewis, L., 1959. *The effect of the molar Ca/P ratio upon the crystallization of brushite and apatite*. Journal of Physical Chemistry, 63, 725-726.

Fiore, S. & Laviano, R., 1991. *Brushite, hydroxylapatite, and taranakite from Apulian caves (southern ltaly): New mineralogical data.* American Mineralogist, 76, 1722-1727.

Halla, F., 1931. *Isomorphic relations and double-salt formation between gypsum and brushite.* Zeitschrift für Kristallographie, 80, 349-352 (In German).

Hill, C. & Forti, P., 1997. *Cave minerals of the world*. National Speleological Society, Huntsville, Alabama, 463 p.

Hutchinson, G.E., 1950. *Cave Guano. The Biochemistry of Vertebrate Excretion*. Bulletin of the American Museum of Natural History, 96.

Iepure, S., 2002. *Research on the stygofauna from Huda lui Papară cave (Trascău Mountains, Romania).* Travaux de l'Institut de Spéologie „Emile Racovitza", Cluj-Napoca, 37-38, 133-141 (In French).

Ludușan, V., 1983. *Trascău Mountains*. Romanian caving news. Speotelex, 3, 11 (In Romanian).

Marincea, Ș., Dumitraș, D.G., Diaconu, G. & Bilal, E. 2004. *Hydroxylapatite, brushite and ardealite in the bat guano deposit from Peștera Mare de la Merești, Perșani Mountains, Romania*. Neues Jahrbuch für Mineralogie Monatshefte, 10, 464–488.

Murray, J.W. & Dietrich, R.V., 1956. *Brushite and taranakite from Pig Hole Cave, Giles County, Virginia*. American Mineralogist, 41, 616-626.

Onac, B.P., 2012. *Minerals.* In Encyclopedia of Caves (2nd Edition) (White, W.B., Culver, D.C., Eds.), Chennai: Academic Press, 499-508.

Onac, B. P. & Vereş, D.S., 2003. *Sequence of secondary phosphates deposition in a karst environment: evidence from Măgurici Cave (Romania).* European Journal of Mineralogy, 15, 741–745.

Onac, B. P., Fornós, J.J., Ginés, À. & Ginés, J., 2005. *Mineralogical reconnaissance of caves from Mallorca Island*. ENDINS, 27, 131-140.

Pinto, A.J., Jiménez, A. & Prieto, M., 2008. *Dehydration behaviour of the $Ca(SO_4,HPO_4)\cdot 2H_2O$ solid solution*. Mineralogical Magazine, 72 (1), 283–287.

Pinto, A.J., Carneiro, J., Katsikopoulos, D., Jiménez, A. & Prieto, M., 2012. *The Link between Brushite and Gypsum: Miscibility, Dehydration, and Crystallochemical Behavior in the $CaHPO_4\cdot 2H_2O - CaSO_4\cdot 2H_2O$ System*. Crystal Growth and Design, 12 (1), 445–455.

Pogson, R.E., Osborne, R.A.L., Colchester, D.M. & Cendón, D.I., 2011. *Sulphate and phosphate speleothems at Jenolan Caves, New South Walse, Australia.* Acta Carsologica, 40(2), 239-254.

Rinaudo, C., Lanfranco, A.M. & Franchini-Angela, M., 1994. *The system $CaHPO_4\cdot 2H_2O$ – $CaSO_4\cdot 2H_2O$: crystallizations from calcium phosphate solutions in the presence of SO_4^{2-}*. Journal of Crystal Growth, 142, 184–192.

Rinaudo, C., Lanfranco, A.M. & Boistelle, R., 1996. *The gypsum – brushite system: crystallization from solutions poisoned by phosphate ions.* Journal of Crystal Growth, 158, 316-321.

Sakae, T., Nagata, H. & Sudo, T., 1978. *The crystal structure of synthetic calcium phosphate - sulfate hydrate, $Ca_2HPO_4SO_4\cdot 4H_2O$, and its relation to brushite and gypsum*. American Mineralogist 63, 520-527.

Schadler, J., 1932. *Ardealite, a new mineral, $CaHPO_4\cdot CaSO_4\cdot 4H_2O$*. Centralblatt für Mineralogie, Geologie und Paläontologie, 2, 40-41 (In German).

Simpson, D.R., 1964. *The nature of alkali carbonate apatites*. American Mineralogist, 49, 363-376.

Tămaş, T. & Ungureanu, R., 2010. *Mineralogy of speleothems from four caves in the Purcăreţ - Boiu Mare Plateau and the Baia Mare Depression (NW Romania)*. Studia UBB Geologia, 55(2), 43-49.

Viehmann, I. & Kovacs, H., 1990. *Novel observations on the human - cave impact (a peculiar case of anthropic pollution).* Peştera - Bulletin of the „E. Racoviţă" Cluj-Napoca Caving Club, 3, 146-148 (In Romanian).

Received at: 20. 12. 2013
Revised article: 24. 03. 2014
Accepted for publication at: 28. 03. 2014
Published online at: 05. 04. 2014