

Sequence of secondary phosphates deposition in a karst environment: evidence from Măgurici Cave (Romania)

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Abstract: Măgurici Cave hosts a diverse assemblage of minerals. The phosphatization of illite and montmorillonite clay rich sediments, located on the cave’s floor, lead to the formation of taranakite and francoanellite. Mineral assemblages precipitated at the boundary between limestone bedrock and guano deposits are dominantly hydroxylapatite, brushite, ardealite, and monetite. A number of sulphate minerals (gypsum, bassanite, mirabilite, and cesanite) were precipitated along with the phosphates, strengthen the physico-chemical conditions of the depositional environment. The major parameters controlling the environments under which these mineral assemblages were deposited are: pH, relative humidity, alkali content, and Ca/P ratio.

In addition, this study presents the second worldwide reported occurrence of phosphammite discovered in a cave environment. This rare mineral occurs as small transparent crystals within the guano deposit, precipitated in an early stage from the liquid fraction of guano.

Key-words: phosphates, cave minerals, depositional environment, Măgurici Cave, Romania.

Introduction

Phosphates are the largest group of cave minerals. Presently, 56 species have been found in different cave settings (Onac, 2003). They occur whenever a cave contains fresh or fossil guano or significant accumulations of bone breccias. Depending on whether the percolating water passing through guano reacts with carbonate rocks or clay minerals, Ca or Mg-rich and Al-rich phosphates will be formed by alteration of these materials. Unlike other cave minerals (*e.g.*, carbonates), the phosphates do not form spectacular speleothems, but occur as crusts, nodules, lenses, and earthy or powdery masses (Hill & Forti, 1997). Our emphasis here is on the mineralogy of secondary phosphates, in an attempt to understand their depositional environment.

Geographic and geologic setting

The Măgurici Cave is located in northwestern Romania, approximately 100 km north of the town of Cluj, in the north central part of the Someș Plateau (Fig. 1, inset). The cave developed along the Eocene/Oligocene boundary in a 40 to 60-m thick, fossiliferous limestone unit belonging to the *Culmea Cozlei* Group. This carbonate unit is essentially unfolded, the monocline gently deepening towards the southeast (Rusu, 1977). Among the other lithologic units

overlying the *Culmea Cozlei* limestone, a bituminous black shale formation (*Ileanda* Unit) is the most important, being the source of sulphates in the cave (Onac & Todoran, 1987).

The overall pattern of the Măgurici Cave is that of a linear passage cave. For purposes of discussion, the cave is divided into four sections: the Entrance Passage, the Bat Gallery, the Clay Passage, and the Guano Gallery (Fig. 1). The floor of the Entrance Passage comprises boulders and rubble fallen from the roof and walls. Throughout the rest of the cave the floor comprises argillaceous sediments of unknown thickness. The main guano deposits are at the far end of the cave, reached through several tight clefts and low passages (Fig. 1). Isolated bat colonies have formed small guano deposits along the Bat Gallery and Clay Passage. Dry powdery guano covers the cave floor, some limestone blocks and parts of the walls except in the Guano Gallery, where most of the organic sediment is fresh and damp. Throughout the sampled part of the cave, the relative humidity ranges from 85 to 100% while the mean temperature remains constant year-round in the range of 9 to 10.2°C (Borda, pers. comm.). A temperature increase of 5 to 6°C was measured within both fresh and fossil guano deposits.

For the purpose of this research, 34 samples were collected throughout the cave. Most of the samples (28) come from the Guano Gallery and Clay Passage. The locations of the main sampling points are shown on Fig. 1.

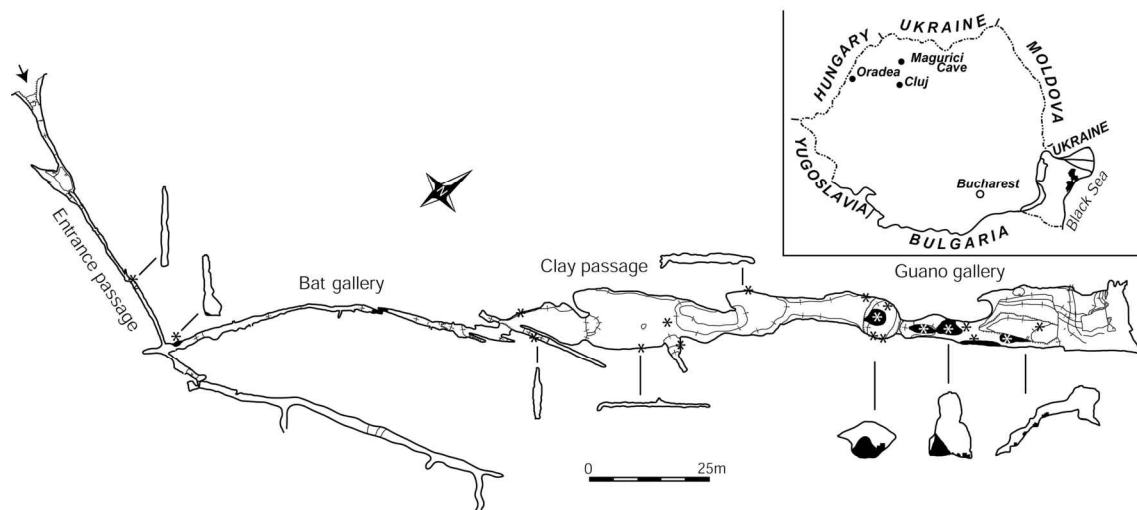


Fig. 1. Locality map, plan and cross-section through Măgurici Cave. (* = the main sampling points). Note that profiles scale is half of the map scale.

Analytical methods

X-ray powder diffraction (XRD) patterns were obtained from all samples using a Philips PW1800 diffractometer operated at 45 kV and 40 mA. The instrument employs Ni-filtered $\text{CuK}\alpha$ radiation. The step-scan data were continuously collected over the range of 3 to $90^\circ 2\theta$, using a step interval of 0.01° or $0.025^\circ 2\theta$. Counting time was 30 seconds per step, and a NaF internal standard was employed. The lattice parameters obtained by least-square refinement of the XRD data were calculated using the UnitCell Program (Holland & Redfern, 1997).

A Stemi 2000-C (Zeiss) (up to 50x magnification) binocular microscope was used to inspect and characterize the earth-like samples and small crystal aggregates. Observations on selected samples were also conducted on a Hitachi 3500N scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer that provided us with the specimens' chemical composition.

Minerals occurrence and characterization

Crystals

Sparse, colourless, and transparent anhedral crystals (0.5 mm in size) having a glassy luster (Fig. 2) were collected from the lower part of a dry decomposed bat guano deposit occurring in the first part of the Guano Gallery. The XRD patterns of these crystals revealed the presence of phosphammite, $(\text{NH}_4)_2\text{HPO}_4$, a rare ammonium orthophosphate. The only previously documented record of phosphammite from a cave is from Toppin Hill Cave, Australia (Bridge, 1973). The XRD data and the unit cell of the Măgurici specimen showed a striking similarity to that of artificial $(\text{NH}_4)_2\text{HPO}_4$ as recorded in the ICDD file 29-111 (Table 1). This similarity indicates an almost pure compound. The complete set of data is available by request from the senior

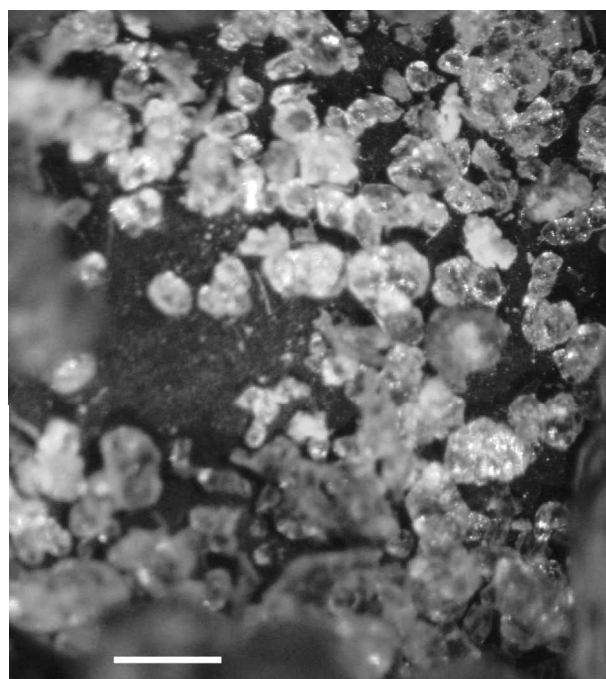


Fig. 2. Phosphammite crystals within bat guano (scale bar: 1 mm).

Table 1. Comparative crystallographic data for phosphammite.

Cell parameters	Phosphammite	
	This paper	ICDD file 29-111
a (Å)	10.736(6)	10.735
b (Å)	6.688(5)	6.689
c (Å)	8.007(4)	8.000
β	109.73(6)	109.72

author. The cell parameters of phosphammite were calculated on the basis of 51 powder reflections in the 2θ range 8 to 75° . As in the other occurrence, phosphammite was precipitated in an early stage, from the liquid fraction of guano.

Crusts and coatings

A distinctive feature of Măgurici Cave is the widespread occurrence of crusts and coatings. Between the cave entrance and the Clay Passage, the walls are coated with fibrous or granular gypsum crusts up to 30 millimetres thick (Onac, 1991). Along the second half of the cave, the ceiling, the walls, and the fallen limestone blocks are covered with ochre to red-brown to black crystalline crusts, a few centimetres in thickness. These crusts are composed of various minerals of the apatite group. Routine XRD indicated that hydroxylapatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ was the main constituent of the crusts. Except for two samples (#1485 and 1486) hydroxylapatite is associated with cesanite; in all the others it appears along with gypsum. Fluorapatite – $\text{Ca}_5(\text{PO}_4)_3\text{F}$ – and carbonate-hydroxylapatite – $\text{Ca}_5(\text{PO}_4)_3(\text{CO}_3)(\text{OH})$ – were also documented in the composition of a light-brown crust covering the limestone bedrock. Each of these three minerals appears in different samples. After removing the diffraction peaks produced by phosphate minerals, the majority of the remaining reflections conform closely to those of quartz, along with lesser amounts of kaolinite. Both of these minerals are allogenic.

Taranakite was confirmed by means of XRD analyses in a number of samples collected from the Clay Passage and Guano Gallery. At these locations, taranakite forms white-dull thin coatings of plastic consistency, covering the clay on the floor in the vicinity of fresh guano deposits.

Earthy masses

The phosphatic-rich solutions emerging from guano combined in various proportions with limestone and clay sediments to produce a phosphate aureole surrounding the guano deposits. The morphology of majority of the phosphate speleothems occurring within this aureole zone are in the form of earthy masses (nodules, lenses or powdery material).

Yellowish white, soft, clay-like, (sometimes powdery) lenses or nodular earthy masses appear within the lower part of the fresh guano that is in contact with the argillaceous floor deposits in the Clay Passage and the Guano Gallery. The pH of the solutions seeping off the guano deposit in all the sampled locations ranges from 6.2 to 6.8. XRD of these samples revealed the presence of taranakite – $\text{H}_6\text{K}_3\text{Al}_5(\text{PO}_4)_8 \cdot 18\text{H}_2\text{O}$. All spectra show sharp diffractions and a strong (006) basal reflection. Under SEM, pseudo-hexagonal thin plates of taranakite are clearly visible. In the close vicinity of the taranakite sampling points, soft and unctuous to the touch, white nodular aggregates (3 to 50 mm in diameter) and earthy masses were collected. Analysis of these samples by XRD indicated the mineral as francoanellite – $\text{H}_6\text{K}_3\text{Al}_5(\text{PO}_4)_8 \cdot 13\text{H}_2\text{O}$. Its XRD patterns exhibit similar d -values with taranakite except at the initial part of the diffraction spectra ($2\theta < 20^\circ$). The difference in water content between the two hydrated phosphates leads to a noticeable variation of the c value (97.6 Å for taranakite and 83.2 Å for francoanellite), whereas the a value is identical (8.70 Å) for both minerals. All francoanellite samples inspected

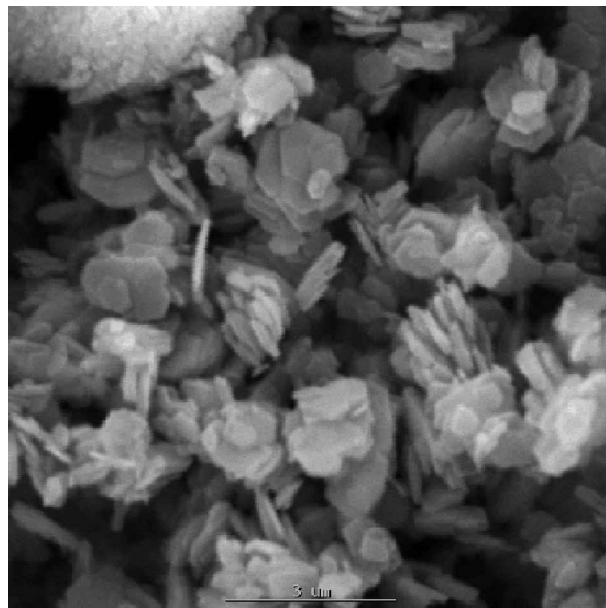


Fig. 3. Pseudo-hexagonal crystals of francoanellite.

by means of SEM revealed the presence of thousands of pseudo-hexagonal crystals (Fig. 3).

Ardealite – $\text{Ca}_2(\text{HPO}_4)(\text{SO}_4) \cdot 4\text{H}_2\text{O}$ occurs as wet, powdery material near the contact of guano with limestone bedrock or fallen blocks. It varies in colour from white, to yellow and from reddish to brown. In most of the samples it was observed together with gypsum crystals and occasionally with minute crystals of mirabilite. In two other locations it occurs mixed with brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). Brushite appeared as a paste-like material varying in colour from white-ivory to yellow-ivory and may occur in up to 40 mm thick lenses within bat guano. The pH values of the micro-environment around brushite locations were below 5.8.

In some ventilated sectors of the cave, reddish-brown and white earthy masses associated with snow white microscopic needles were found underlying dry, decomposed guano and overlying limestone bedrock. The diffraction patterns of such samples showed a mixture of monetite (CaHPO_4) and bassanite ($2\text{CaSO}_4 \cdot \text{H}_2\text{O}$).

Discussion

The occurrence of phosphammite in Măgurici Cave provides evidence that the highly soluble phosphate mineral may persist even in relatively moist environments as long as the temperature within the dry fossil guano deposit is almost twice the annual average within the cave.

Hydroxylapatite and carbonate-hydroxylapatite are the most thermodynamically stable phosphate minerals under ordinary cave conditions, occurring on almost all coatings and crusts. These minerals are closely associated with gypsum. Hydroxylapatite is by far the most common phosphate in Măgurici Cave, being the direct product of reaction between bat guano and limestone. The distinctive feature of hydroxylapatite in this cave is its association with cesanite –

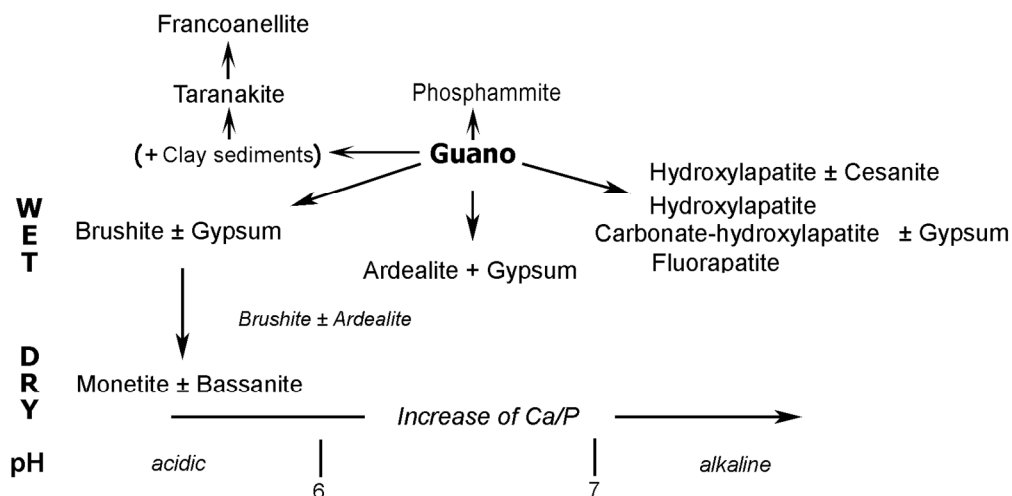


Fig. 4. Mineral paragenesis sequences in Măgurici Cave.

$\text{Na}_3\text{Ca}_2(\text{SO}_4)_3(\text{OH})$, a rare sulphate, documented so far from a single cave location (Onac *et al.*, 2001). This hydroxylated double salt is isostructural with hydroxylapatite, with three Ca^{2+} replaced by three Na^+ and three PO_4^{3-} replaced by three SO_4^{2-} , maintaining charge balance within the structure. Hence, the close association of the two minerals in some of the investigated samples seems to be reasonable. We assume, in the absence of any data on cesanite stability at low temperature, the crystallization sequence is as follows: first precipitated is hydroxylapatite and then cesanite will precipitate from Ca-depleted, Na- and SO_4^{2-} -enriched solutions. The presence of both gypsum and mirabilite in Măgurici Cave may have been crucial to cesanite precipitation.

Fluorapatite crusts seem to represent an intermediate step in the development of hydroxylapatite. This supposition relies on the observation that fluorapatite crusts occur only in the vicinity of bat colonies, where the originally calcite crusts were altered by bat urine to fluorapatite. As a consequence of guano fossilization, the solutions passing through these deposits become depleted with respect to fluorine, being completely replaced by OH^- and thus forming hydroxylapatite.

Millisite, the stable Ca-Al phosphate under acid conditions, was not identified in Măgurici Cave. Therefore, we assume that taranakite precipitated in less acidic (pH 6–7) and poorly drained argillaceous sediments, *i.e.* where phosphorus and the alkali metal ions were not removed from the weathering system. The precipitation of taranakite deposits along well ventilated cave passages has resulted in its partial dehydration to francoanellite, a rare mineral. Until now, it has only been documented from 3 caves in southern Italy (Balenzano *et al.*, 1976). Both minerals are the result of reactions between H_3PO_4 derived from guano and illite and montmorillonite-rich clay sediments. We observed lower clay mineral content in the vicinity of taranakite and francoanellite occurrences.

Brushite is stable under acidic (pH < 6) and damp conditions and is isostructural with gypsum. It is not surprising that ardealite, another acid environment indicator, should

exist in paragenesis, particularly in the view of their frequent association in many caves worldwide (Hill & Forti, 1997). The formation of brushite was interpreted as being the result of reaction between phosphatic solutions and limestone bedrock or blocks buried by guano. This mechanism explains the origin of most of the brushite occurrences in Măgurici Cave, but not its presence as lenses within guano where neither fallen blocks nor limestone bedrock is in direct contact with guano. Therefore, we assume the chemical reaction between phosphatic and bicarbonate-rich solutions may have triggered brushite precipitation within the guano deposits.

Under drier conditions, brushite loses water readily, converting to monetite, a mineral that also indicates an acidic depositional environment. The presence of bassanite along with monetite confirms the existence of a rather low relative humidity in those cave sectors where the two minerals occur (Fig. 4). This paragenesis was first documented from a cave in Namibia (Martini, pers. comm.). The anomalous stability of bassanite under cave conditions could be explained by the presence of small amounts of phosphorus found in solid solution with the bassanite. An EDS microanalysis showed about 5% phosphorus that may have replaced part of the sulphur.

Conclusions

The mineral assemblages investigated in Măgurici Cave are diverse (Tab. 2). The phosphatization of argillaceous sediments and limestone leads to the generation of a complex suite of phosphate minerals. Two tendencies were observed: (a) in the presence of excess alkali, the mineral formed initially is taranakite, which partially dehydrates to francoanellite due to a decrease in the water vapour partial pressure (phenomenon restricted to certain locations within the cave), and (b) a sequence of Ca-rich phosphate minerals formed when guano reacts with limestone bedrock or fallen blocks. In the second situation, four main mineral assem-

Table 2. List of minerals identified in Măgurici Cave.

Mineral	Chemical formula	Relative abundance
Ardealite	$\text{Ca}_2(\text{HPO}_4)(\text{SO}_4)\cdot 4\text{H}_2\text{O}$	Common
Brushite	$\text{CaHPO}_4\cdot 2\text{H}_2\text{O}$	Very common
Monetite	CaHPO_4	Rare
Hydroxylapatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	Very common
Carbonate-hydroxylapatite	$\text{Ca}_5(\text{PO}_4)_3(\text{CO}_3)(\text{OH})$	Very common
Fluorapatite	$\text{Ca}_5(\text{PO}_4)_3\text{F}$	Rare
Taranakite	$\text{H}_6\text{K}_3\text{Al}_5(\text{PO}_4)_8\cdot 18\text{H}_2\text{O}$	Very common
Francoanellite	$\text{H}_6\text{K}_3\text{Al}_5(\text{PO}_4)_8\cdot 13\text{H}_2\text{O}$	Rare
Phosphammite	$(\text{NH}_4)_2\text{HPO}_4$	Rare
Bassanite	$2\text{CaSO}_4\cdot \text{H}_2\text{O}$	Rare
Cesanite	$\text{Na}_3\text{Ca}_2(\text{SO}_4)_3(\text{OH})$	Rare
Gypsum	$\text{CaSO}_4\cdot 2\text{H}_2\text{O}$	Very common
Mirabilite	$\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$	Common

blages were documented (Fig. 4). We interpreted their precipitation as a response to changes in the pH and relative humidity of the environment, along with a progressive increase of the Ca/P ratio (Fig. 4). In addition, an interesting observation is that all Ca-rich phosphate minerals appear in paragenesis with different sulphates, each of them strengthens the physico-chemical conditions of the depositional environment.

The coexistence of the described minerals within the phosphate aureole gives information about genetic environments. Brushite and taranakite form under damp conditions from solution with a pH lower than 6. Partial or total dehydration under the same acidic pH results in the precipitation of francoanellite and monetite, respectively. Although ardealite may form over a wide range of relative humidity values, its field of nucleation lies between pH 6.2 and 7. The presence of hydroxylapatite indicates a slightly alkaline environment, which precipitates and is stable under such conditions (Posner *et al.*, 1984). Its abundance when comparing to the other phosphates in this cave clearly suggests that the depositional environment throughout much of the cave extent is slightly alkaline, being acidic or neutral only in the vicinity of guano accumulations.

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