MINERALOGICAL ANALYSES IN TWO CAVES FROM THE PERŞANI MOUNTAINS

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Abstract. After diffractometric X-ray analyses through the powder method, made on sampling tests from two caves in the Perşani Mountains karst, mineral associations made up of calcite, magnesium calcite, aragonite, dolomite, brushite, hydroxylapatite, carbonate-hydroxylapatite, gypsum and α-quartz were emphasized. Tables are presented with the resulting data from the diffractometric analyses, including the computed parameters of the elementary cells of each mineral species. The materials are discussed comparatively with the existent data in the literature. In the final chapter there is a discussion upon the mineralogenesis of the determined species.

Key words: cave minerals, carbonates, phosphates, sulfates, silicates, Perşani Mountains.

Résumé. À la suite des analyses diffractométriques en RX par la méthode en poussière, effectuées sur des échantillons prélevés de deux grottes, localisées dans le karst des Monts Perşani, ont été mises en évidence des associations minéralogiques constituées de calcite, aragonite, dolomite, brushite, hydroxylapatite, carbonate-hydroxylapatite, gypse et α-quartz. Sont présentés des tableaux avec les données résultées des analyses diffractométriques, inclusivement les paramètres mesurés aux cellules élémentaires, séparément pour chaque espèce minérale, les résultats étant discutés comparativement avec les données existantes dans la littérature.

Mots-clé: minéralogie des grottes, carbonates, phosphates, sulfates, silicates, Monts Perşani.

1. INTRODUCTION

The endokarst of the Perşani Mountains, located in the southern group of the Eastern Carpathians, is 90% concentrated in the limestone bar of the Middle Jurassic–Lower Cretaceous (Tithonic-Neocomian) which is crossed by the Vârghiş River through the magnificent gorges bearing the same name. The rest of the caves are bored in olistolithic blocks of Triassic (Anisian) dolomite limestone built in the Barremian-Aptian wildflisch deposits from the northwestern area assigned to this physical geographic unit.

The two investigated spelean cavities from which the mineralogical sampling tests come from are Cave no. 9 from the Vârghiş Gorges known under the name of "The Cave with Lublinit" (Peştera cu Lublinit) and "The Cave from the Monastery Glade" (Peştera din Poiana Mânăstirii) named also "Comana Cave" (Peştera Comana) being located nearby the Comana de Sus village (Fig. 1).

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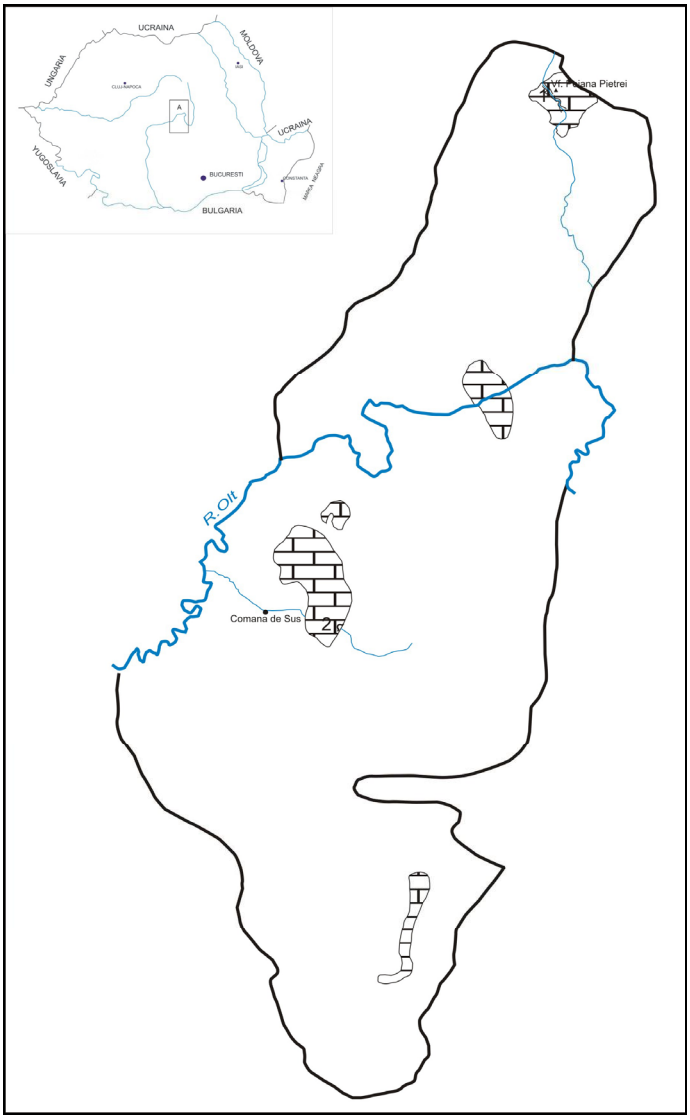

Fig. 1. – Geological map of the Perşani Mountains (simplified from CIOACĂ, 2002) with location of the Cave No. 9 from the Vârghiş Gorges (1) and the Cave from the Monastery Glade (2).
A – Location of the Perşani Mountains.

2. CAVE NO. 9 FROM VÂRGHIŞ GORGES (THE CAVE WITH LUBLINIT)

According to the *Romanian Cave Catalog* (GORAN, 1982), 110 caves have been explored and mapped in the Vârghiş Gorges. Among these, only 13 are considered important (DENES, 2002) among which "the Cave with Liublinit" (we

choose to use this word because we consider it more adequate, even though "liublinit" is nowadays out-of-date).

The cavity is placed on the right versant of the gorges, at 72 meters towards the thalweg (see Fig. 1).

As for the lithofacial aspect, the carbonatic rock pile in which the cave is dug is made of micritic algal limestone with calcarenitic levels of white through grey colours.

The main gallery, made upon a fracture orientated in the limestone body from east to west, is changing in its second part where some halls appear, which are positioned at the intersection of the fracture with a system of disjunctions relatively parallel to a northeastern–southwestern direction. The total length of the galleries from "The Cave with Liublinit" is of 300 m. (ORGHIDAN, DUMITRESCU, 1962–1963) (Fig. 2).

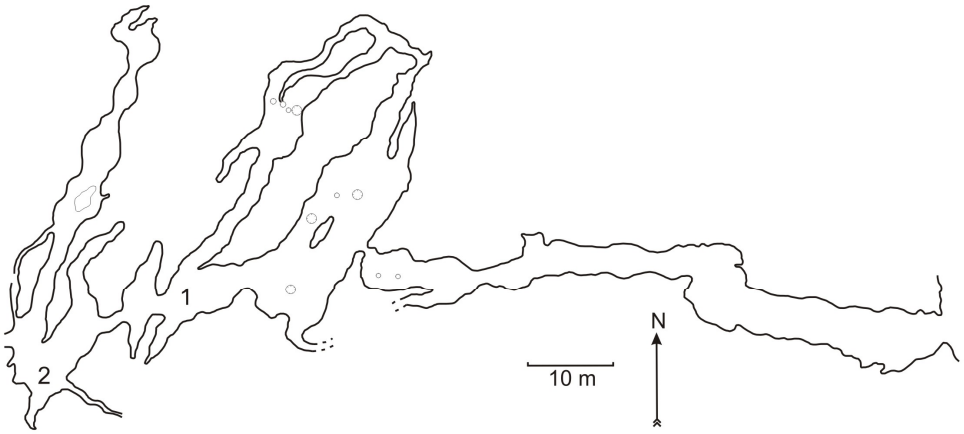

Fig. 2. – Map of the Cave No. 9 from the Vârghiş Gorges. (simplified from ORGHIDAN and DUMITRESCU, 1962-1963). 1 and 2 – Location of the sampling points.

The floor of the galleries is mostly covered with gravel, sand or stalagmitic crust and rimstone dams of small dimensions.

The samples we analyzed (noted with P9 symbol) are from the afferent halls of the terminal part of the cave: here, the floor presents some accumulations of guano from small colonies of bats and some bone fragments (probably from *Ursus spelaeus*) dispersed on the surface of the detritic bedding.

2.1. INTERPRETATION OF THE ANALYTICAL DATA

The mineral species identified – after exclusive investigations through X-rays diffractometry in powder – in the crusts underlying the guano deposits, interposed on red clay in facies of *terra rossa*, proved to be made of subordinated

hydroxylapatite, identifying calcite, α-quartz and a clay mineral assumed to be an illite-caolinite interbedding.

Hydroxylapatite: [$Ca_5(PO_4)_3(OH)$, hexagonal-bipyramidal] has a very low cristallinity. The cristallinity coefficient, computed by the SIMPSON (1964) method is for a representative sample (P9 – 1A sample) only of 0.19. The main reflexes, poorly acquired, have not permitted the calculus of the elementary cell parameters.

Calcite [CaCO3, trigonal-hexagonal scalenoedric] [a = 4.981(1) Å, c = 17.021(7) Å, V = 365.7(2) Å^3*]* and "low" or α-*quartz [α-*SiO_2*, trigonal] [*a = 4.908(2) Å, c = 5.397(5) Å, V = 112.6 (1) Å^3*]* are the only phases with good cristallinity.

While calcite is indubitable autigenic, quartz, because of some textural weak relations, cannot be pinpointed as such. Noteworthy, the elementary cell parameters determined after 3 cycles of refinement by the method of the smallest squares, beginning from 10 reflexes attributed to the try-out quartz, are relatively different from the ones determined by WILL *et al.* (1998) for stoichiometric α-quartz *[*a = 4.91239(4) Å, c = 5.40385(7) Å and V = 112.933 Å^3*]* probably because of the errors induced by the small number of reflexes.

In order to verify the theoretical possibility of other species of phosphates appearing in "the Cave with Liublinit", a number of three bone fragments presenting a white powdery layer on their surface, were sampled.

The diffractometric investigation of the powdery layer led to its identification as calcite. The elementary cells parameters computed by refinement by the smallest squares method of X-ray diffraction made on powders (*Fe Kα, λ = 1.93735* Å) are the following:

- sample P9 - 3A: a = 4.9813(8) Å, c = 17.047(4) Å, V = 366.3(1) Å^3;
- sample P9 - 3B: a = 4.9877(4) Å, c = 17.0635(19) Å, V = 367.62(6) Å^3;
- sample P9 - 4A: a = 4.979(1) Å, c = 17.034(5) Å, V = 365.8(2) Å^3.

In all three cases, the determined parameters are reasonably close to those given by EFFENBERGER *et al*. (1981) for synthetic calcite *[*a = 4.9896(2) Å, and c = 17.0610(11) Å*]*, indicating close stoichiometrical terms.

The diffractometric investigation of the bone fragments emphasized the presence of hydroxylapatite which, in this case, has the cristallisation indices relatively high compared with the one identified in subjacent drosses in the guano deposit.

These, computed by the algorithm proposed by SIMPSON (1962), as a report of the peak breadth (211) + (112) (measured in 2θ degrees at half of the peak amplitude), vary between 0.06 (in sample P9-2A) and 0.08 (in sample P9-4B). The interreticular distances of the principal diffractometric reflexes registered for the representative hydroxylapatite bone samples, aside from the values of the interreticular computed distances and the Miller indices established in the hexagonal symmetry hypothesis, the spatial group of the mineral P63/m, are shown in Table I. The elementary cells parameters of the samples, stated at the footnote of

the table, are relatively far from those given by different authors for the hydroxylapatite stoichiometry, but they have values relatively similar with carbonate-hydroxylapatite *[$Ca_5(PO_4,CO_3)_3(OH)$, hexagonal-bipyramidal]*, an aspect justified by the presence in the spelean medium of carbonated solutions that facilitate, by a metasomatose of low temperature, the substitution from hydroxylapatite, preexisting probably in the bone tissue, of groups PO_4^{2-} with those of CO_3^{2-}.

Table I

Diffractometric data obtained by the powder method for two samples of bone tissue come from the bone fragments (P9 - 2A and P9 - 4B)*

Crt. no.	Sample P9 - 2A			Sample P9 - 4B			(hkl)
	$d_{meas.}$(Å)	$d_{calc.}$(Å)	I / I_0	$d_{meas.}$(Å)	$d_{comp.}$(Å)	I / I_0	
1	–	–	–	8.1721	8.1788	9	(100)
2	3.8821	3.8852	8	3.8807	3.8889	7	(111)
3	3.330	3.4423	60	3.4177	3.4280	42	(002)
4	–	–	–	3.1666	3.1615	10	(102)
5	3.0846	3.0810	31	3.0940	3.0913	82	(210)
6	2.8130	2.8122	100	2.8160	2.8181	100	(211)
7	2.7685	2.7712	75	2.7777	2.7786	80	(112)
8	–	–	–	2.6252	2.6271	23	(202)
9	–	–	–	2.2723	2.2684	28	(130)
10	2.1492	2.1480	5	2.1576	2.1536	5	(131)
11	–	–	–	2.0539	2.0571	6	(113)
12	1.9408	1.9426	31	1.9443	1.9444	26	(222)
13	–	–	–	1.8969	1.8917	24	(132)
14	1.8403	1.8404	16	1.8375	1.8377	16	(213)
15	–	–	–	–	–	–	(321)
16	–	–	–	–	–	–	(402)
17	1.7216	1.7223	14	–	–	–	(141)
18	1.7216	1.7211	14	1.7161	1.7140	9	(004)
19	1.6130	1.6105	4	–	–	–	(313)
20	–	–	–	–	–	–	(241)
21	1.4535	1.4540	8	–	–	–	(304)
22	1.4488	1.4497	4	1.4539	1.4502	4	(323)
23	–	–	–	1.4359	1.4364	4	(511)
	a = 9.413(7) Å			a = 9.444(6) Å			
	c = *6.885(4)* Å			c = 6.856(5) Å			
	V = 528.2(7) Å^3			V = 529.6(7) Å^3			

* *Fe K α* filtrated radiation with Ni, λ = 193735 Å, 2θ = 10^0–86^0. The numbers of refinement cycles: 3; 3; 3.

3. THE CAVE FROM THE MONASTERY GLADE

The Cave from the Monastery Glade, is located in the central zone of the Perşani Mountains, very close to the Comana Monastery from Comana de Sus

village, the cavity being dug by waters in the body of a Triassic dolomitic limestone olistolith, included in the deposit group of Cretaceous wildflysch (see Fig. 1).

The endokarstic cavity represented by a receptor cave was known initially only by a large hall (15 / 8 / 3.5 m) carved in the vestibular area of the present day cave by the waters of a creek infiltrating at the southeastern extremity of the hall. Today, that river flows into a sinkhole located at the base of the exterior wall (Fig. 3). (In 1987, the speleologists from the "Silex" Club in Braşov, in a favorable hydrological moment in the sinkhole, mapped another 1,000 m of galleries).

The samples [marked with the PC symbol meaning the Peştera Comana (Comana Cave)] were collected from the cave floor at the entrance (the only cave sector presented in Fig. 3) with a guano deposit and from the Lower Level Gallery where the aragonite speleothems had been identified.

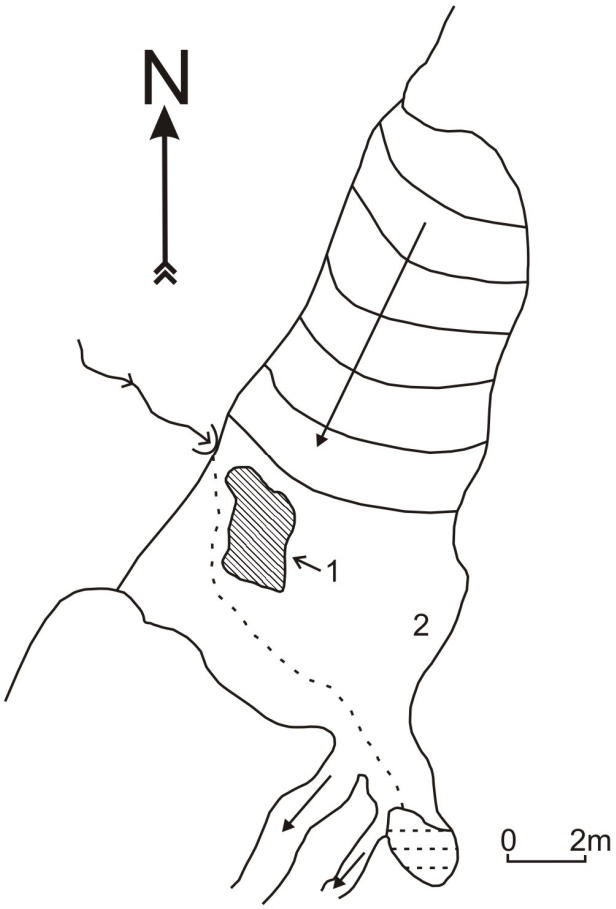

Fig. 3. – Map of the Cave from the Monastery Glade (after C.S. "Silex" Braşov, 1987).
1 and 2 – Location of the sampling points.

3.1. INTERPRETATION OF THE ANALYTICAL DATA

The samples collected at the entrance, from the floor, analyzed in X-ray diffractometry by powders, presented an interesting mineralogical association comprising *gypsum* (that proved to be omnipresent in all samples), *hydroxylapatite* (*carbonate-hydroxylapatite* ?) *brushite*, *dolomite*, *calcite*, *aragonite, α–quartz*, clay minerals and iron oxy-hydroxides gels (difficult to identify).

Gypsum [$CaSO_4$. $2H_2O$, monoclinic-prismatic] appears under the form of crusts and eflorescences found both on the phosphate deposit surface, but also on the surface of *terra rossa* – type clay or the carbonate parietal crusts and on the floor.

The gypsum crusts are formed of microscopic crystallites and have a sparkling white color.

The identification of gypsum was made on the interreticular distances measured and computed, the relative intensity and the Miller indices (hkl) of the main diffractometric reflexes registered on the two representative Samples (Table II).

Table II

Diffractometric data obtained from two gypsum samples (PC 1 A, and PC 2 B) from the Cave from the Monastery Glade*

Crt. no.	Sample PC 1 A			SamplePC 2 B			(hkl)
	$d_{meas.}$(Å)	$d_{calc.}$(Å)	I / I_0	$d_{meas.}$(Å)	$d_{calc.}$(Å)		
1	7.5714	7.6020	41	7.6037	7.6039	53	(020)
2	4.7276	4.7456	4	4.7551	4.7495	2	(110)
3	4.2649	4.2732	85	4.2806	4.2783	100	(–121)
4	3.7923	3.8010	13	3.8029	3.8019	11	(040)
5	3.7923	3.7932	13	3.8029	3.7968	11	(031)
6	3.1584	3.1575	3	3.1605	3.1639	4	(–112)
7	3.0585	3.0617	60	3.0646	3.0640	70	(–141)
8	2.8692	2.8732	100	2.8740	2.8762	60	(121)
9	2.7844	2.7860	13	2.7898	2.7890	12	(–211)
10	2.6729	2.6767	42	2.6776	2.6812	33	(022)
11	2.5960	2.5974	4	2.6006	2.5985	4	(150)
12	2.4956	2.4976	30	2.4986	2.4998	12	(200)
13	2.4711	2.4735	2	2.4765	2.4757	2	(–231)
14	2.4449	2.4460	5	2.4490	2.4496	7	(–222)
15	2.4039	2.4039	4	2.4051	2.4059	5	(141)
16	2.2840	2.2853	1	2.2875	2.2882	1	(042)
17	2.2130	2.2133	9	2.2163	2.2158	10	(–152)
18	2.1361	2.1366	2	2.1388	2.1392	1	(–242)
19	2.0858	2.0873	20	2.0904	2.0887	15	(240)
20	2.0708	2.0720	20	2.0733	2.0761	14	(–123)
21	2.0708	2.0715	20	2.0733	2.0744	14	(112)
22	2.0708	2.0732	20	2.0733	2.0747	14	(–251)
23	2.0362	2.0386	3	2.0415	2.0426	3	(–213)

24	1.9903	1.9919	3	1.9941	1.9925	3	(170)
25	1.8964	1.8966	11	1.8985	1.8984	10	(062)
26	1.8738	1.8737	6	1.8753	1.8768	8	(–143)
27	1.8095	1.8090	8	1.8122	1.8110	9	(–262)
28	1.7986	1.7989	6	1.7997	1.8006	3	(–321)
29	1.7799	1.7788	9	1.7785	1.7798	6	(260)
30	1.6799	1.6797	1	1.6824	1.6823	2	(–323)
31	1.6648	1.6645	5	1.6663	1.6659	4	(–314)
32	1.6419	1.6410	2	1.6434	1.6432	2	(–163)
33	1.6216	1.6207	3	1.6225	1.6216	3	(181)
34	1.5830	1.5829	2	1.5845	1.5840	2	(082)
35	1.5830	1.5819	2	1.5845	1.5832	2	(330)
36	1.5532	1.5517	1	1.5511	1.5535	1	(202)
37	1.5316	1.5309	1	1.5319	1.5320	1	(–282)
38	1.4585	1.4586	1	–	–	–	(–1.10.1)
39	1.4585	1.4599	1	1.4606	1.4608	1	(271)
40	1.4382	1.4375	4	1.4388	1.4355	3	(143)
41	1.4022	1.4029	4	1.4039	1.4059	2	(321)
	a = 5.673(1) Å			a = 5.679(1) Å			
	b = 15.204(4) Å			b = 15.208(3) Å			
	c = 6.496(2) Å			c = 6.510(2) Å			
	$\beta = 118.30(1)^0$			$\beta = 118.33(1)^0$			

[*] *Fe K α* filtrated radiation with Ni (λ = 193735 Å), 2θ = 10–90^0. The numbers of refinement cycles: 8; 6; 7. Total number of reflexes used for the calculus of elementary cell parameters: 54; 38; 46.

The elementary cells parameters of the three samples, given in the footnote of Table II, are relatively similar to those computed for the quasi-stoichiometric gypsum from Hampshire, Great Britain by PENDERSEN and SEMMINGSEN (1992) [a = 5.679(5) Å; b = 15.202(14) Å; c = 6.522(6) Å; $\beta = 118.43(4)^0$].

This fact lets us assume that the gypsum from the Cave from the Monastery Glade has a chemical composition very close to the stoichiometric one.

Genetically, the presence of gypsum in various forms of deposition, is in our opinion due to the chemistry of organic deposits of guano, conditioned by the diet of the bats, rather than on the eventuality of oxidation of some sedimentary pyrites that could be disseminated in the dolomite limestone mass (in which the cave was molded) or, eventually, deposited, also disseminated, in the mass of the crystalline schists subjacent to the carbonate rocks.

Hydroxylapatite [$Ca_5(PO_4)_3(OH)$, *hexagonal-bipyramidal*], appears under the form of some dirty white color or cream-colored crusts with a massive aspect, laid-down both on the surface of the floor (partially covered by red clay) and foliated, on the parietal eastern surface of the hall.

The pattern of occurrence (the relations with the other associated minerals) and the textural aspects indicate the fact that we are dealing with the presence of hydroxylapatite resulted from chemical precipitation.

The measured and computed interreticular distances of the main diffractometric reflexes recorded on representative samples of hydroxylapatite from the Cave from the Monastery Glade using Fe anticathode (λ = 1.93735 Å), besides the Miller indices, established in the hexagonal symmetry hypothesis of the mineral (spatial group $P6_3/m$), are given in the Table III in comparison with a carbonate-hydroxylapatite sample from the Muierilor Cave (Parâng Mountains, Baia de Fier, Gorj county) (MARINCEA *et al.,* 2003).

Table III

Diffractometric data obtained by the powder method for a representative sample of hydroxylapatite from the Cave from the Monastery Glade (PC 1B), in comparison with a sample of carbonate-hydroxylapatite from the Muierii Cave (PM 13)*

Crt. no.	Sample PC 1 B			Sample PM 13			(hkl)
	$d_{meas.}$(Å)	$d_{calc.}$(Å)	I / I_0	$d_{meas.}$(Å)	$d_{calc.}$(Å)	I / I_0	
1	–	–	–	5.2667	5.2628	4	(101)
2	3.8856	3.8813	43	3.8842	3.8879	8	(111)
3	3.4245	3.4307	42	3.4373	3.4438	55	(002)
4	3.1491	3.1622	21	3.1791	3.1727	10	(102)
5	3.0816	3.0812	13	–	–	–	(210)
6	2.8089	2.8108	100	2.8187	2.8143	95	(211)
7	2.7779	2.7724	100	2.7832	2.7800	100	(112)
8	2.7189	2.7174	80	2.7175	2.7194	55	(300)
9	–	–	–	2.6385	2.6314	27	(202)
10	2.2606	2.2610	20	2.2605	2.2626	21	(230)
11	–	–	–	2.1503	2.1496	10	(131)
12	2.0583	2.0571	9	–	–	–	(113)
13	1.9387	1.9406	27	1.9461	1.9440	16	(222)
14	–	–	–	1.8740	1.8716	19	(230)
15	1.8345	1.8365	23	1.8426	1.8415	27	(213)
16	1.8089	1.8044	18	1.8055	1.8061	13	(321)
17	1.7786	1.7790	20	–	–	–	(410)
18	–	–	–	1.7524	1.7549	7	(402)
19	–	–	–	1.7524	1.7543	7	(303)
20	–	–	–	1.7227	1.7236	13	(141)
21	1.7187	1.7154	25	1.7227	1.7219	13	(004)
22	1.6411	1.6421	6	–	–	–	(322)
23	1.5400	1.5406	13	1.5417	1.5417	3	(240)
24	–	–	–	1.5046	1.5045	5	(241)
25	1.4945	1.4988	12	–	–	–	(124)
26	1.4490	1.4505	10	1.4537	1.4546	6	(304)
27	1.4490	1.4478	10	1.4537	1.4507	6	(323)
28	–	–	–	1.4367	1.4332	4	(511)
	a = 9.413(5) Å			a = 9.420(3) Å			
	c = 6.861(5) Å			c = 6.888(3) Å			
	V = 526.5(5) Å^3			V = 529.3(4) Å^3			

**Fe K α* filtrated radiation with Ni (λ = 193735 Å). The numbers of refinement cycles: 3; 3; 3.

They allowed the detailed calculus by the smallest squares method of the next elementary cells parameters: a = 9.413(5) Å; c = 6.861(5) Å and V=526.5(5) $Å^3$. These differ in value in comparison with the parameters of the elementary cells of stoichiometric hydroxylapatite, suggesting the presence of carbonate-hydroxylapatite in the Cave from the Monastery Glade, a very plausible possibility because of the cave environment where it originated, the pluvial solutions from this area being exclusively carbonated.

To confirm these suppositions, a third diffractometric analysis of another sample of hydroxylapatite, PC 4 A, was made using a Cu anticathode (λ=1.54056).

The 50 diffractometric reflexes exclusively ascribed to the mineral, allowed the calculation of the following elementary cells parameters: a = 9.425(3) A; c = 6.867(3) and V = 528.8(3)A^3, close to those given in literature for the carbonate-hydroxylapatite.

The crystallinity indices computed for other 4 representative samples, according to the proposed Simpson method (1964) are: IC = 0.15 for the PC6A sample, IC = 0.05 for the PC4A sample, IC = 0.21 for the PC4C sample and respectively IC = 0.08 for the PC1B sample, showing a large variability of the crystallinity degree.

Brushite [$CaHPO_4 \cdot 2H_2O$, *monoclinic-prismatic*] was identified under the form of powdery sparkling white deposits found on the surface and on the crust of the PC1B sample. The interreticular measured distances, the relative intensities and the Miller indices of the diffractometric reflects exclusively of brushite are: 7.5621 Å, 100, (020); 4.9570 Å, 5, (110); 4.2609 Å, 68, (–121); 3.7889 Å, 15, (040); 3.0576 Å, 51, (–141) and (–211); 2.8089 Å, 66, (002); 2.6697 Å, 20, (051); 2.4488 Å, 6, (141); 1.7786 Å, 9, (–172) and (–181); 1.7187 Å, 10, (–341); 1.6162 Å, 2, (091) and (–352), respectively, 1.5400 Å, 6, (280).

On the basis of this reflex from the 2θ angular values interval between 5^0 and 90^0, after four cycles of refinement by the smallest squares method, the following parameters of the elementary cell could be computed: a = 5.847(4) Å, b = 15.184(8) Å, c = 6.265(8) Å, β = 116.09(7)^0. These differ from those given by BEEVERS (1958) or CURRY and JONES (1971) for stoichiometric brushite [a = 5.812(2) Å, b = 15.180(3) Å, c = 6.239(2) Å, β = 116.43 (3)^0], a phenomenon based mainly on the small number of lines used in the calculus and, subsidiarily, on the interference with the lines from the apatite sample.

In the case of the analyzed sample, the association of brushite with gypsum seems surprising, at a first glance. Taking into account the experiments to synthesize brushite from the calcium-sulfate saturated solutions (RINAUD *et al*., 1994), the association gypsum-brushite cannot be a syncrystallization. Consequently, the brushite nucleation took place in a precedent phase of a significant decrease of the solutions pH, which permitted the precipitate of the two minerals phase, their presence within the same sample resulting from a simple spatial superposition.

Anyway, the significant decrease of the pH of the cave depositional environment may explain the rarity of brushite.

Calcium carbonate $CaCO_3$ appears in the Cave from the Monastery Glade in two of its allotropical phases: the calcite identified in the samples from the halls entrance floor and aragonite as a constitutive mineral of the numerous speleothems from the galleries at the lower level of the cavity.

Calcite [$CaCO_3$, *trigonal-hexagonal scalenohedric*] in the samples collected from the entrance hall floor appears as crust levels mixed in *terra rossa*-type clay or also as crust substrate of hydroxylapatite or gypsum deposits.

The elementary cells parameters of some calcite samples calculated by refinement by the smallest squares method of the X-ray diffraction data obtained using a diffractometer equipped with Fe anticathode (λ = 1.93735 Å), on the basis of 18 main reflexes from the 2θ interval between 25^0 and 90^0, are the following:

(1) PC 6 A sample: a = 4.978(1) Å, c = 17.000(4) Å, V = 364.9(1) Å^3 (n = 5);
(2) PC 7 B sample: a = 4.941(5) Å, c = 16.994(4) Å, V = 359.3(7) Å^3 (n = 3).

They are relatively similar to those determined using a Cu anticathode (λ = 1.54056 Å):

(3) PC 5 A sample: a = 4.979(1) Å, c = 17.019(1) Å, V = 365.43(4) Å^3 (n = 3; N = 26);
(4) PC 6 B sample: a = 4.981(1) Å, c = 17.028(2) Å, V = 365.82(5) Å^3 (n = 3; N = 28);
(5) PC 7 A sample: a = 4.981(1) Å, c = 17.034(2) Å, V = 366.01(5) Å^3 (n = 5; N = 25).

In all five cases, the determined parameters are lower than those given by EFFENBERGER (1981) for synthetic calcite [a = 4.9896(2) Å and c = 17.0610(11) Å] indicating the presence in the Cave from the Monastery Glade of some magnesium calcite, a situation in perfect concordance with the co-existence of dolomite. If we accept the presence of Mg as a unique substitute for Ca in the sample, on the basis of the elementary cells volumes obtained, and using the data concerning the analyzed magnesium calcite, published by MCKENZIE *et al*. (1983), we can estimate that they have up to 1.7-8 moli % magnesite contained in solid solution.

Aragonite, [*$CaCO_3$, orthorhombic-bipyramidal*] was identified by one author of this paper (Diaconu 1979, unpublished material), based on the morphological crystallization pattern in orthorhombic geometry of this mineral species: acicular prismatic individuals associated in typical central-radiar aggregates. The diagnosis made in 1979 was confirmed after X-ray diffractometry (Table IV), on a significant sample collected from the Lower Level Gallery (not on the map in Fig. 3).

Table IV

X-ray powder diffraction data for sample of aragonite (PC 1B), from the Cave from the Monastery Glade*

Crt. No.	Sample PC 1B			(hkl)
	$d_{meas.}$ (Å)	$d_{calc.}$ (Å)	I / I_0	
1	4.1883	4.2085	4	(110)
2	3.3847	3.3933	100	(111)
3	3.2632	3.2703	25	(021)
4	2.8622	2.8683	3	(002)
5	2.7227	2.7299	4	(121)
6	2.6937	2.6985	39	(012)
7	2.4784	2.4828	46	(102)
8	2.4784	2.4790	46	(200)
9	2.4057	2.4084	6	(031)
10	2.3670	2.3702	30	(112)
11	2.3366	2.3395	37	(130)
12	2.1856	2.1880	13	(211)
13	2.1018	2.1066	51	(122)
14	2.1018	2.1042	51	(220)
15	1.9739	1.9755	47	(221)
16	1.8783	1.8756	44	(202)
17	1.8119	1.8130	16	(132)
18	1.7573	1.7581	3	(141)
19	1.7403	1.7410	72	(113)
20	1.6991	1.6966	3	(222)
21	1.5311	1.5316	3	(232)
22	1.4738	1.4799	4	(321)
23	1.4652	1.4656	5	(151)
24	1.4028	1.4028	5	(330)
25	1.3571	1.3575	14	(114)
26	1.3404	1.3402	3	(152)
27	1.3275	1.3268	3	(060)
28	1.2922	1.2927	3	(061)
29	1.2606	1.2602	6	(332)
30	1.2356	1.2352	6	(313)
31	1.2233	1.2236	3	(053)
32	1.2233	1.2227	3	(134)
33	1.2051	1.2051	11	(243)
34	1.2051	1.2042	11	(062)
35	1.1881	1.1879	5	(153)
36	1.1701	1.1702	9	(162)
37	1.1701	1.1698	9	(260)
38	1.1246	1.1246	3	(351)
39	1.1246	1.1244	3	(234)
40	1.1075	1.1068	3	(115)
41	1.0945	1.0940	4	(422)

	a = 4.958(2) Å	
	b = 7.961(2) Å	
	c = 5.737(2) Å	
	V = 226.42(8) Å^3	

*Monochromatized Cu $K\alpha$ radiation, λ = 1.54056 Å, 2θ = 20^0–90^0. Number of refining cycles: 5.

Dolomite [*$CaMg(CO_3)_2$, trigonal-romboedric*] was rarely found in earthy phosphate aggregates, as deposits on the secondary discontinuities within their mass, which is probably diagenetical. Its presence may be correlated with the magnesium character of the calcite from the mineral association, probably linked to a local magnesium excess in the solutions from which it precipitated.

Dolomite is present under the form of white, porcelain-like, microcrystalline powder. The elementary cell parameters computed for a representative sample (PC-4B sample) by the smallest squares refinement method (n = 5), beginning at 21 diffractometric reflexes recorded for a mineral in the 2θ interval between 25^0 and 90^0 (Fe $K\alpha$, λ = 1.93735 Å), are: a = 4.798(2) Å, c = 16.001(9) Å, and V = 319.0(3) Å^3 . The elementary cell parameters computed for a second sample (PC-4C sample) using a diffractometer equipped with Cu anticathode (λ = 1.54056 Å), for the same 2θ interval, are: a = 4.8016(6) Å, c = 16.026(3) Å and V = 321.17(7) Å^3 (n = 4, N = 26).

The parameters from both sets are slightly lower than those given for a low-calcium dolomite (with 50.5 moli % $CaCO_3$ in solid solution) taken from Lake Arthur, New Mexico, by REEDER (1983): a = 4.8069(2) Å, c = 16.0034(6) Å, therefore we conclude that the dolomite from "the Cave from the Monastery Glade", although very similar to the stoichiometry, can be defined as calcium dolomite.

Quartz [*α SiO_2, trigonal-trapezoidal*] appears under the shape of milky-white microgranules, deposited on the surface of *terra rossa*-type red clays near the hydroxylapatite crusts. It is difficult to establish if those granules are autigenic results of the final deposition from the solutions generating the phosphate and gypsum deposits, or allogenic, levigated from the outside by the mixing waters.

A representative quartz sample taken at the hydroxylapatite/clay limit (PC-3B sample) was separated and analyzed by X-ray difractometry on powders.

The elementary cell parameters determined after 3 cycles of refinement by the smallest squares methods, starting with a number of 16 reflexes attributed exclusively to the quartz sample from the 2θ interval between 25^0 and 90^0, are: a = 4.901(2) Å, c = 5.396(3) Å, V = 112.23(8) Å^3. They are somehow lower than those determined by WILL *et al.* (1988) for stoichiometric α-quartz [a = 4.91239(4) Å, c = 5.396(3) Å, V = 112.933 Å^3], but the minor difference can be due to the relative inaccuracy of the calculus method we used, starting with a small number of diffractometric reflexes.

4. DISCUSSIONS ON THE MINERAL GENESIS AND CONCLUSIONS

The carbonate rocks lithofacies in which the two caves were developed, the micritic limestone for the Lublinite Cave and, respectively, the dolomite limestone for the Cave from the Monastery Glade, also controlled without a doubt the chemistry of the mixing waters, dampening the floor of the galleries with guano deposits, conditioning the differentiated rush of mineral species: carbonates, phosphates, sulfates and silicates.

The presence of *calcite*, considered as the most common carbonate deposited in the cave environment from a solution saturated in calcium carbonate, can not be considered special, even though it is a magnesium calcite, like the one identified in the Cave from the Monastery Glade, where its presence is, without a doubt, a consequence of the dolomite limestone, washed by the mixing waters from the gallery.

Aragonite, identified only in the lower level galleries of the same cave, could be considered as a particular case. The aragonite genesis, argued in the literature in an extremely diverse manner, is based on the existence of a Sr/Ca molar ratio between 0.002 and 0.003% (KITANO and KAWASAKI, 1958) or on the critical molar concentration of Mg^{2+} in a solution of 0.01% (LIPPMANN, 1960), or on a temperature range of the solutions between 30 c and 80 c (GIROU, 1970).

On the basis of some direct observations made in many caves from the Romanian karst regarding the frequent gypsum-aragonite paragenesis, DIACONU (1983 and 1990) concludes that the cations listed above must be interpreted more as a consequence of their origin due to reactions between the water in which they are dissociated and the chemical compounds in which they are uptaken. If these reactions release a great amount of free hydrogen (H^+), we think it will very quickly combine with water molecules forming hydronium H_3O^+. According to ONICIU (1974), these H_3O^+ ions are associated in a tetrahedral coordination with other 3 water molecules, the fourth binding electrostatically at the triangular pyramid at a relatively greater distance. A notable presence of the hydronium ions capable to "structure" the generating solution has as consequence a partial blocking of the dissociation possibilities of the carbonic acid, excessively maintaining the HCO_3^- radical. Thus is favoured the monohydrocalcite nucleation or, for that account, the vaterite mineral species with a very unstable net symmetry in the physical conditions of the underground environment, considered by BOSCHOFF (1968) and GIROU (1970) as turning rapidly to the orthorhombic symmetry of aragonite crystallization.

The identified phosphates from the two caves have, without any doubt, the guano deposit as the main source of the PO_4^{2-} ion. According to the chemical formula of the identified mineral species, a successive genesis in the manner of brushite-hydroxylapatite (except the hydroxylapatite from the bone fragments that can be considered preexisting and then transformed, by a metasomatic process of

low temperature of partial replacement of PO_4^{2-} with CO_3^{2-} in hydroxylapatite carbonate) is presumable.

In the case of the Cave from the Monastery Glade we can appreciate that, after the fixing of Ca in the three species of phosphates, the solutions have become locally enriched in Mg, favoring the deposition of dolomite, an aspect sustained by its identification in the microfractures on the walls of the preformed hydroxylapatite crusts.

It is difficult to conclude if the sampled α-quartz is autigenic or allogenic; nevertheless, its microgranular aspects and its disposal at the limit of the hydroxylapatite crusts and the *terra rossa*-type red clays would argue for the first hypothesis. In this case, its genesis can be attributed to the mobilization of a part of silica from the clay mass. But we can not exclude its allogenic origin, transported by the mixing waters, by levigation, from the surface.

We have willingly left for the end the comment on the gypsum genesis, a mineral species permanently present where the galleries of the caves have guano deposits. This association of hydrated guano-calcium sulfate leads undoubtedly to the conclusion that the ion source of SO_4^{2-} could be the organic deposit. The European chiroptera, including the Romanian ones, being exclusively insectivorous, it is hard to assume that only by meat digestion we could get (directly in the guano deposits as a mélange of dejections and urine) at parity with the phosphates or nitrates, groups of sulfates which, uptaken in solution, can generate gypsum. Rather than that, we consider that it is more plausible that by organic fermentation processes, the sulfured hydrogen appears which, by oxidation in the cave environment, will be converted to sulfates. This presumption does not exclude the question: from where is coming the sulfur necessary for the H_2S accumulated in the guano, in a quantity matching phosphor or ammonium?

We will try to answer this question by a direct chemical analysis of the guano deposits, correlated with the trophic parameters of the bat species from the generating colony.

As a conclusion of the present paper, we can state that our analytical data complete the mineralogical inventory of the endokarst from the Perşani Mountains.

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