

# PEȘTERA LILIECILOR (LILIECILOR CAVE) FROM THE OLTEȚULUI GORGES. MINERALOGICAL DATA

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*Abstract.* By means of RX and IR analyses we emphasize an associations of minerals in Peștera Liliecilor (Liliecilor Cave) from the Oltețului Gorges made up by *hydroxylapatite*, *carbonate-hydroxylapatite*, *ardealite*, *brushite* and *gypsum* as the main minerals and *quartz* and *illite* as secondary minerals. In the final part of the paper, the authors present some opinions about the possible genesis of the mineral species.

*Key words:* cave minerals, hydroxylapatite, carbonate-hydroxylapatite, ardealite, brushite, gypse,

## 1. INTRODUCTION

Geographically, the Olteț River represents the conventional delineation within the Southern Carpathians between the Parâng Mountains in the West and the Căpățâni Mountains in the East.

From a geologic point of view, its upper streambed is shaped on rocks conferred to the eastern extremity of the Danubian Unit made up locally by a predominantly granitic basement sustaining both a Meozoic, carbonate for the most part (Malm–Neocomian) and, partially, the post-tectonic deposits of the Neogene (Aquitanian and Bessarabian) and the Quaternary (Pleistocene). The formations of the Danubian Unit are delineated, at their eastern edge, by the metamorphic rocks of the Getic Nappe (mezzo- and catazone crystalline schists) (Fig. 1).

Peștera Liliecilor (Liliecilor Cave) was shaped by waters in the limestone cliff from the right slope of the Oltețului Gorges (their downstream part). It is a small cave formed of one hall (22/10 m), the ceiling reaching heights of 10–12 m in the central zone.

The presence of a bat colony during the summer led, in time, to the accumulation on the floor of an important guano deposit.

The mineralogical samples were collected from the surface and from within the guano deposit or, from underneath it, at its contact with the lithic substratum (Fig. 2).

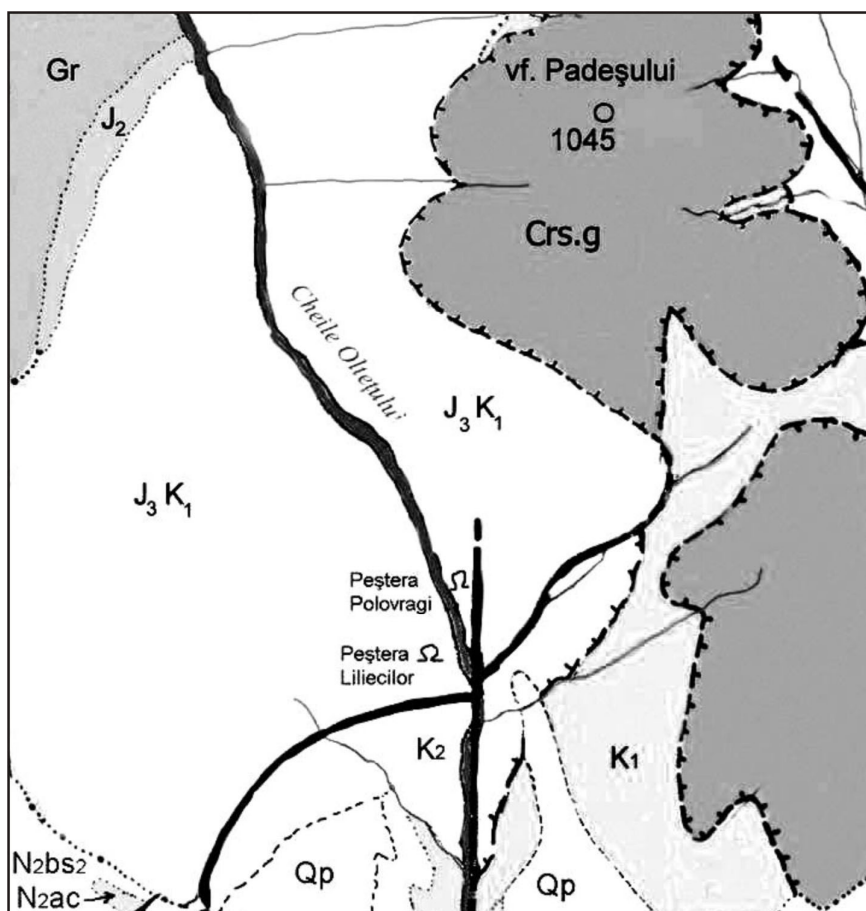


Fig. 1. – Location and a simplified geologic map of Liliəcilor Cave from the Olteului Gorges (after HUICA, 1967).

Gr – granite; J2 – Middle Jurassic (sandstones); J3K1 – Upper Jurassic – Lower Cretaceous (limestones); K1 – Lower Cretaceous (wildflysch); K2 – Middle Cretaceous (marls); N2 aq – Neogene – Aquitanian (detritic deposits); N2 bs – Neogene – Bessarabian (detritic deposits); Qp – Quaternary Pleistocene (detritic deposits), Crs. g. – crystalline schists, Getic Unit.

The RX and IR analyses of the samples emphasized a mineralogical association made up by *hydroxylapatite*, *carbonate-hydroxylapatite*, *ardealite*, *brushite* and *gypsum* as the main minerals and *quartz* and *illite* as secondary minerals.

## 2. MAIN MINERALS

*The hydroxylapatite,  $Ca_5(PO_4)_3(OH)$*  was collected from the periphery or from the base of the guano deposit where it appears as white aggregates made up of

crystalline nodules of variable sizes but less than 2 cm in diameter with a central-radial development.



Fig. 2. – Liliecilor Cave from the Oltețului Gorges, (after MIHAI and PONTA from PONTA and ALDICA, 1985). \* Location of the sampling points.

This suggests an authigenic genesis of this mineral resulting from precipitation processes.

Diffractometric analyses by RX on powders emphasize a large crystallized hydroxyl-apatite, the crystallinity indexes computed by the method proposed by SIMPSON (1964) vary between 0.06 and 0.04 (Table I) in agreement with the I.C. interval placed between 0.07 and 0.03 mentioned by Marincea *et al.* (2003).

Table I

Parameters of two elementary cells of two representative hydroxylapatite samples from the Liliecilor Cave, Oltețului Gorges\*

Occurrence	Sample	$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	$n$ <sup>(1)</sup>	$N$ <sup>(2)</sup>	I.C. <sup>(3)</sup>
Liliecilor Cave (Oltet)	LCO 2	9.428(3)	6.871 (3)	528.9(3)	6	45	0.060
Liliecilor Cave (Oltet)	LCO 3 B	9.431(3)	6.866(3)	528.9(4)	5	43	0.053
Liliecilor Cave (Oltet)	LCO 6 B	9.424(2)	6.885(3)	529.5(2)	4	56	0.042

\*Monochromatized Cu  $K\alpha$  radiation, filtered with Ni ( $\lambda = 1.54056$  Å),  $2\theta = 10-90^\circ$ ; (1) number of refinement cycles; (2) number of reflections used for refinement ( $2\theta = 10-90^\circ$ ); (3) indicele de cristalinitate calculat prin metoda Simpson (1964).

The interreticular distances, the Miller indexes (hkl) and the relative intensities of the main diffractometric reflexes obtained for the two representative hydroxylapatite samples from the Liliecilor Cave (Olteţului Gorges) are given in Table II.

Table II

X-rays diffractometric data obtained from powders on two representative hydroxylapatite samples from the Liliecilor Cave, Olteţului Gorges\*

No.	Sample LCO 2			Sample LCO 3 B			(hkl)
	d <sub>mess.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>	d <sub>mess.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>	
1	4.6930	4.7139	17	4.6964	4.7159	6	(110)
2	3.8675	3.8894	11	3.8594	3.8871	24	(111)
3	3.4275	3.4353	61	3.4189	3.4328	47	(002)
4	3.1856	3.1665	72	-	-	-	(102)
5	-	-	-	3.0673	3.0873	60	(210)
6	2.8096	2.8150	100	2.8050	2.8157	100	(211)
7	2.7757	2.7763	89	2.7730	2.7754	92	(112)
8	2.3900	2.3569	22	2.3626	2.3579	6	(220)
9	2.2775	2.2645	33	2.2664	2.2654	19	(130)
10	2.2329	2.2294	11	-	-	-	(221)
11	2.1498	2.1507	17	2.1690	2.1513	16	(131)
12	2.1229	2.1332	28	2.1417	2.1332	12	(302)
13	1.9910	1.9974	22	1.9984	1.9965	9	(203)
14	1.8960	1.8907	22	1.8956	1.8908	15	(132)
15	1.8379	1.8391	33	-	-	-	(213)
16	1.8168	1.8072	89	1.8096	1.8078	29	(321)
17	-	-	-	1.7808	1.7824	13	(410)
18	1.7517	1.7548	11	1.7636	1.7550	20	(402)
19	1.7517	1.7523	11	-	-	-	(303)
20	1.6484	1.6445	17	1.6764	1.6448	16	(322)
21	1.6110	1.6103	11	1.6172	1.6100	12	(313)
22	1.5007	1.5008	17	1.4978	1.5001	9	(124)
23	1.4774	1.4748	11	1.4701	1.4751	9	(502)
24	1.4231	1.4526	17	1.4533	1.4520	12	(304)
25	-	-	-	1.4322	1.4347	14	(511)
26	-	-	-	1.4086	1.4062	11	(143)
27	1.3804	1.3882	44	1.3884	1.3877	5	(224)
28	1.3557	1.3551	6	1.3513	1.3541	16	(105)
29	1.3483	1.3487	6	1.3450	1.3490	13	(152)
30	1.3483	1.3423	6	1.3450	1.3428	13	(430)
31	1.3323	1.3349	22	-	-	-	(601)
32	-	-	-	1.3267	1.3296	11	(503)
33	-	-	-	1.3122	1.3139	13	(404)
34	1.3014	1.3023	11	-	-	-	(205)

35	1.2808	1.2797	22	–	–	–	(243)
36	1.2643	1.2660	17	1.2672	1.2657	16	(234)
37	1.2643	1.2651	17	1.2672	1.2655	16	(602)
38	1.2565	1.2553	22	1.2554	1.2546	19	(215)
39	1.2346	1.2366	17	1.2398	1.2364	9	(414)
40	1.2346	1.2350	17	1.2330	1.2351	12	(513)
41	1.1898	1.1871	11	1.1863	1.1866	11	(225)
42	1.1833	1.1835	22	1.1811	1.1833	11	(504)
43	1.1651	1.1664	11	1.1624	1.1669	8	(350)
44	1.1651	1.1615	11	1.1624	1.1620	8	(441)
45	1.1482	1.1479	22	1.1441	1.1477	8	(244)
46	1.1186	1.1153	11	–	–	–	(514)

\*Monochromatized Cu  $K\alpha$  filtered with Ni ( $\lambda = 1.54056 \text{ \AA}$ ).  $2\theta = 18 - 90^\circ$ .  
Number of refinement cycles: 6; 5; 4.

**Carbonate-hydroxylapatite,  $Ca_5(PO_4)_3(OH)$** , appears as yellow-orange crusts on the surface of the guano deposit.

The interreticular distances, the Miller indexes (hkl) and the relative intensities of the main diffractometric reflexes obtained for the two representative carbonate-hydroxyl-apatite samples from Liliecilor Cave (Oltetului Gorges) are given in Table III.

Table III

X-rays diffractometric data obtained from powders on a representative carbonate-hydroxylapatite sample from the Liliecilor Cave, Oltetului Gorges\*

No.	Sample LCO 6 B			(hkl)
	$d_{\text{mess. \AA}}$	$d_{\text{calc. \AA}}$	$I / I_0$	
1	3.8761	3.8885	8	(111)
2	3.4382	3.4424	43	(002)
3	3.1709	3.1718	8	(102)
4	3.0843	3.0848	16	(210)
5	2.8145	2.8151	100	(211)
6	2.7797	2.7796	51	(112)
7	2.3588	2.3560	5	(220)
8	2.2641	2.2636	27	(130)
9	2.2364	2.2291	9	(221)
10	2.1481	2.1504	7	(131)
11	2.1294	2.1344	7	(302)
12	2.0593	2.0003	6	(203)
13	1.8935	1.8913	5	(132)
14	1.8411	1.8413	27	(213)
15	1.8077	1.8068	17	(321)

16	1.7804	1.7810	19	(410)
17	1.7584	1.7552	14	(402)
18	1.7584	1.7541	14	(303)
19	1.6446	1.6448	8	(322)
20	1.6228	1.6116	5	(313)
21	1.5051	1.5030	6	(124)
22	1.4764	1.4749	7	(502)
23	1.4541	1.4545	12	(304)
24	1.4345	1.4337	7	(511)
25	1.4047	1.4070	6	(143)
26	1.3917	1.3898	4	(224)
27	1.3525	1.3578	5	(105)
28	1.3465	1.3487	9	(152)
29	1.3411	1.3417	9	(430)
30	1.3344	1.3345	5	(601)
31	1.3287	1.3302	5	(503)
32	1.3175	1.3156	7	(404)
33	1.3040	1.3047	5	(205)
34	1.2820	1.2801	8	(243)
35	1.2665	1.2671	7	(234)
36	1.2665	1.2651	7	(602)
37	1.2586	1.2574	8	(215)
38	1.2389	1.2377	5	(414)
39	1.2337	1.2354	5	(513)
40	1.1884	1.1888	5	(225)
41	1.1806	1.1844	8	(504)
42	1.1649	1.1659	8	(350)
43	1.1608	1.1611	5	(441)
44	1.1491	1.1487	8	(244)
45	1.1163	1.1160	8	(541)

\*Monochromatized Cu K  $\alpha$  filtered with Ni ( $\lambda = 1.54056 \text{ \AA}$ ),  $2\theta = 18-90^\circ$ .  
Number of refinement cycles: 6; 5; 4.

The IR analysis (Fig. 3) confirms the presence of carbonate-hydroxylapatite. By studying the reticular parameters, the presence of the carbonate groups in the minerals structure is indicated by the absorption bands at  $1452 \text{ cm}^{-1}$ ,  $1420 \text{ cm}^{-1}$  (which point out the  $\nu_3$  asymmetric stretching and, respectively, the  $\nu_3$  vibrations of the carbonate group) and at  $872 \text{ cm}^{-1}$  pointing to the non-planar deformation vibration of the O-C-O bond ( $\nu_2$  out-of-plane bending).

*Ardealite*,  $\text{Ca}_2(\text{SO}_4)(\text{HPO}_4)\cdot 4\text{H}_2\text{O}$  is a current presence within the powdery phosphatic deposits from the Liliecilor Cave, Olteţului Gorges, where it appears in earthy aggregates beside brushite and gypsum, differing from it by its white-cream colour and a less obvious shine.



The interreticular distances measured computed, the Miller indexes and the relative intensities of the main diffractometric reflexes recorded for two representative ardealite samples are given in Table IV.

Table IV

X-rays diffraction data on powders from two representative ardealite samples from the Liliecilor Cave, Olteţului Gorges\*

No.	Sample LCO 3 A			Sample LCO 5 A			(hkl)
	d <sub>mess.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>	d <sub>mess.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>	
1	7.6913	7.7600	49	7.6871	7.7489	96	(040)
2	4.3386	–	6	4.3243	–	6	–
3	4.1287	–	6	4.1315	–	17	–
4	3.8706	3.8800	8	3.8676	3.8775	26	(080)
5	3.7970	3.7864	15	3.7808	3.7808	6	(061)
6	3.3397	3.3434	9	3.3404	3.3405	69	(-171)
7	2.9918	2.9810	6	2.9683	2.9763	16	(131)
8	2.8122	2.8112	100	2.8051	2.8165	100	(-221)
9	2.7848	2.7785	14	–	–	–	(002)
10	–	–	–	2.7353	2.7307	4	(022)
11	–	–	–	2.6934	2.7059	8	(0.10.1)
12	2.5436	2.5449	5	2.5398	2.5456	12	(-202)
13	2.5436	2.5389	5	2.5398	2.5444	12	(200)
14	2.4980	2.5114	21	2.5003	2.5109	10	(220)
15	2.4051	2.4131	5	2.4199	2.4184	12	(-242)
16	2.2828	2.2792	5	2.2716	2.4175	7	(-262)
17	–	–	–	2.1268	2.1275	8	(-282)
18	–	–	–	2.1268	2.1268	8	(280)
19	2.0722	2.0691	9	2.0683	2.0652	9	(112)
20	1.9342	1.9400	3	1.9373	1.9372	11	(0.16.0)
21	1.9194	1.9169	3	–	–	–	(-1.15.1)
22	1.9194	1.9163	3	–	–	–	(1.15.0)
23	1.8969	1.8946	20	1.8929	1.8918	4	(1.13.1)
24	1.8969	1.8932	20	1.8929	1.8904	4	(0.12.2)
25	1.8718	1.8785	11	1.8739	1.8750	12	(172)
26	1.8100	1.8119	18	1.8153	1.8127	25	(2.12.0)
27	–	–	–	1.7948	1.8007	17	(-352)
28	1.7786	1.7747	16	1.7779	1.7736	7	(-193)
29	1.6660	1.6710	3	1.6654	1.6702	7	(-2.14.2)
30	1.6660	1.6700	3	1.6654	1.6681	7	(1.11.2)
31	1.6426	1.6470	7	1.6404	1.6446	7	(0.18.1)
32	1.5839	1.5846	5	1.5834	1.5841	7	(370)
33	–	–	–	1.5708	1.5725	10	(1.17.1)
34	1.5521	1.5555	3	1.5502	1.5536	8	(1.19.0)
35	1.5433	1.5428	2	1.5418	1.5416	13	(2.16.0)



36	1.5109	1.5122	5	1.5106	1.5111	4	(-134)
37	1.4823	1.4843	4	1.4837	1.4832	7	(-154)
38	–	–	–	1.4473	1.4443	8	(-1.19.2)
39	–	–	–	1.4473	1.4444	8	(1.19.1)
40	1.4362	1.4348	7	1.4389	1.4338	8	(331)
41	–	–	–	1.4085	1.4099	7	(351)
42	–	–	–	1.4085	1.4089	7	(0.22.0)
43	1.3961	1.3992	3	1.3940	1.3964	7	(193)
44	1.3898	1.3892	3	1.3871	1.3872	9	(004)
45	1.3367	1.3380	4	1.3383	1.3391	8	(-461)
46	1.3148	1.3120	4	1.3128	1.3111	4	(3.15.0)
47	1.3075	1.3095	4	1.3066	1.3095	4	(-3.17.1)
48	1.3075	1.3079	4	1.3066	1.3058	4	(084)
49	1.2890	1.2889	2	1.2883	1.2878	5	(3.11.1)
50	–	–	–	1.2692	1.2680	7	(420)
51	–	–	–	1.2616	1.2642	5	(-2.22.1)
52	1.2571	1.2580	4	1.2574	1.2562	7	(0.22.2)
53	–	–	–	1.2574	1.2554	7	(-444)

\*Monochromatized Cu  $K \alpha$  filtered with Ni ( $\lambda = 1.54056 \text{ \AA}$ ),  $2\theta = 6\text{--}78^\circ$ .  
Number of refinement cycles: 10; 9; 9.

The computed parameters of the elemental cells [ $a = 5.7289(2) \text{ \AA}$ ,  $b = 30.996(11) \text{ \AA}$ ,  $c = 6.243(3) \text{ \AA}$ ,  $\beta = 117.28(2)^\circ$ ] are relatively close to those of the ardealite from Cioclovina Cave, Sebeș Mountains, recorded by DUMITRAȘ & MARINCEA (2000), [ $a = 5.722(3) \text{ \AA}$ ,  $b = 6.245(8) \text{ \AA}$  and  $\beta = 117.26(19)^\circ$ ].

Additionally, an IR analysis was made for ardealite. The spectre from Fig. 4 presents, in the region of the O–H fundamental stretching, a wide absorption band delineated by two inflexions whose frequencies and character point to the presence of some O–H bindings featuring hydrogen bonds belonging to molecular water. The stretching band of the water from the ardealite is placed at  $3400 \text{ cm}^{-1}$  while the “shearing” bending H–O–H of the molecular water is emphasized by a wide complex of absorption bands, centred at  $1644 \text{ cm}^{-1}$  and with an inflexion at  $1718 \text{ cm}^{-1}$ . Out-of-plane bending vibrations H–O–H are emphasized by the bands from  $672$ , respectively  $660 \text{ cm}^{-1}$ .

The absorption band emphasized as an inflexion centred at  $2960 \text{ cm}^{-1}$  corresponds to a hydrogen bond between the OH groups belonging to the protonated phosphate. Another valence vibration of the P–OH bond from the protonated phosphate groups is emphasized by the wide centred band at  $2248 \text{ cm}^{-1}$ . Out-of-plane bending vibrations of the P–OH bond are emphasized by the  $1207 \text{ cm}^{-1}$  band.

The bands from the median area of the spectrum belong to the molecular vibrations of the sulphate anions and protonated phosphate. They belong to the asymmetrical valence vibrations O–P(S)–O (bands from  $1145$ ,  $1108$  and  $1005 \text{ cm}^{-1}$ ),



symmetrical valence vibrations P–O (H) (band from  $866\text{ cm}^{-1}$ ), out-of-plane bending vibrations O–P (S)–O (bands from  $600$ ,  $568$  and  $528\text{ cm}^{-1}$ ) and, respectively, out-of-plane bending vibrations O–P (S)–O (band from  $420\text{ cm}^{-1}$ ). The band from  $630\text{ cm}^{-1}$  may be attributed to a composed mode ( $\nu_2'$  H–O–H +  $\nu_2'$  O–S–O).

**Brushite,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$** , was found as shiny-white powdery crusts directly at the base of the guano deposit.

The interreticular distances measured and computed, the Miller indexes and the relative intensities of the main diffractometric reflexes recorded for two representative brushite samples are given in Table V.

Table V

Diffractometric data obtained by the powder method on two representative samples of brushite from the Liliecilor Cave, Oltețului Gorges

No.	Sample LCO 4 A			Sample LCO 4 B			(hkl)
	d <sub>mess.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>	d <sub>mess.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>	
1	7.5411	7.5928	76	7.6871	7.5881	96	(020)
2	4.2294	4.2331	100	4.2337	4.2357	100	(1.2.–1)
3	3.0397	3.0451	34	–	–	–	(1.4.–1)
4	3.0397	3.0395	34	3.0447	3.0435	41	(1.1.–2)
5	2.6656	2.6703	23	2.6663	2.6688	8	(051)
6	2.6233	2.6254	52	2.6207	2.6227	24	(150)
7	2.6233	2.6293	52	2.6207	2.6281	24	(022)
8	2.5445	2.5495	26	2.5398	2.5526	12	(2.0.–2)
9	2.4140	2.4169	27	2.4199	2.4193	12	(2.2.–2)
10	2.2664	2.2670	19	2.2716	2.2664	7	(1.6.–1)
11	2.1690	2.1702	16	2.1713	2.1710	3	(1.5.–2)
12	2.1690	2.1513	16	2.1434	2.1477	9	(240)
13	2.0364	2.0290	12	–	–	–	(211)
14	1.9984	1.9986	9	1.9702	2.0002	3	(1.2.–3)
15	–	–	–	1.9495	1.9464	2	(132)
16	1.8956	1.8982	15	1.8929	1.8970	4	(080)
17	1.7944	1.7962	15	1.7958	1.7967	17	(2.6.–2)
18	1.7490	1.7529	16	–	–	–	(033)
19	1.6997	1.6976	15	1.6992	1.6942	6	(251)
20	1.6277	1.6307	12	1.6282	1.6289	4	(181)
21	1.6172	1.6157	12	1.6145	1.6147	8	(091)
22	1.6070	1.6031	15	–	–	–	(1.6.–3)
23	–	–	–	1.5221	1.5226	5	(2.8.–2)
24	1.4591	1.4597	20	1.4587	1.4583	6	(2.9.–1)
25	1.4591	1.4591	12	1.4587	1.4560	6	(321)
26	1.4086	1.4103	11	1.4085	1.4082	8	(4.1.–1)
27	–	–	–	1.3583	1.3555	7	(370)
28	1.3450	1.3462	13	1.3449	1.3468	6	(4.3.–3)

29	1.3201	1.3225	11	1.3249	1.3236	9	(2.6.–4)
30	1.3122	1.3125	13	1.3187	1.3113	4	(2.10.0)
31	1.2672	1.2662	12	1.2692	1.2667	7	(3.8.–3)
32	1.2554	1.2572	19	–	–	–	(4.2.–4)
33	–	–	–	1.2451	1.2462	7	(2.11.–1)
34	1.2398	1.2381	9	1.2329	1.2356	10	(233)
35	1.2330	1.2346	12	1.2329	1.2320	10	(440)
36	1.1863	1.1860	11	–	–	–	(4.7.–1)
37	1.1762	1.1743	16	1.1740	1.1745	7	(4.7.–3)
38	1.1441	1.1436	8	1.1428	1.1432	7	(2.11.1)
39	1.1389	1.1384	12	–	–	–	(2.12.0)
40	1.1340	1.1324	12	1.1334	1.1326	5	(3.10.–3)
41	1.1291	1.1279	11	1.1290	1.1296	3	(4.1.–5)
42	–	–	–	1.1249	1.1268	2	(084)
43	1.1080	1.1072	12	1.1047	1.1053	5	(5.2.–1)
44	–	–	–	1.0992	1.0985	8	(273)
45	1.0938	1.0932	9	1.0936	1.0928	7	(1.13.–2)

\*Monochromatized Cu  $K\alpha$  filtered with Ni ( $\lambda = 1.54056 \text{ \AA}$ ),  $2\theta = 10\text{--}90^\circ$ .  
Number of refinement cycles: 4; 10.

The computed parameters of the elemental cells [ $a = 5.810 (2) \text{ \AA}$ ,  $b = 15.176 (5) \text{ \AA}$ ,  $c = 6.247 (3) \text{ \AA}$  and  $\beta = 116.30 (2)^\circ$ ] are relatively close to those given by DUMITRAŞ *et al.* for Nadru Cave (Sebeş Mts.), [ $a = 5.808 (2) \text{ \AA}$ ,  $b = 15.174 (7) \text{ \AA}$ ,  $c = 6.237 (4) \text{ \AA}$  and  $\beta = 116.38 (3)^\circ$ ].

**Gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$** , was found inside the guano deposit as efflorescences associated with ardealite, but differing from it by its shining-white coloration.

The interreticular distances measured and computed, the Miller indexes and the relative intensities of the main diffractometric reflexes recorded for two representative gypsum samples are given in Table VI.

Table VI

Diffractometric data obtained by the powder method on a representative samples of gypsum from the Liliecilor Cave, Olteţului Gorges

No.	Sample LCO 3 C			(hkl)	No.	Sample LCO 3 C			(hkl)
	$d_{\text{mess. \AA}}$	$d_{\text{calc. \AA}}$	$I/I_0$			$d_{\text{mess. \AA}}$	$d_{\text{calc. \AA}}$	$I/I_0$	
1	7.5768	7.6007	49	(020)	45	1.4883	1.4883	2	(–244)
2	5.3934	5.3593	2	(011)	46	1.4823	1.4844	4	(–314)
3	4.2725	4.2789	100	(–121)	47	1.4362	1.4384	7	(143)
4	3.7970	3.8004	15	(040)	48	1.4362	1.4338	7	(073)
5	3.7970	3.7950	15	(031)	49	1.4312	1.4318	5	(004)
6	3.1517	3.1642	7	(–112)	50	1.4295	1.4261	5	(–183)
7	3.0627	3.0636	92	(–141)	51	1.4197	1.4187	3	(–402)
8	2.8718	2.8741	76	(121)	52	1.3961	1.3946	3	(–422)

9	2.7848	2.7893	14	(-211)	53	1.3819	1.3858	4	(-413)
10	2.6772	2.6854	48	(051)	54	1.3652	1.3634	5	(-264)
11	2.6772	2.6797	48	(022)	55	1.3652	1.3653	5	(1.10.1)
12	2.5956	2.5974	7	(150)	56	1.3367	1.3366	4	(341)
13	2.4980	2.4988	21	(200)	57	1.3148	1.3142	4	(192)
14	2.4464	2.4504	12	(-222)	58	1.3075	1.3066	4	(-293)
15	2.4051	2.4043	5	(141)	59	1.2958	1.2943	4	(-404)
16	2.3719	2.3738	3	(220)	60	1.2958	1.2970	4	(-215)
17	2.2828	2.2870	5	(042)	61	1.2755	1.2775	5	(-383)
18	2.2127	2.2155	17	(-152)	62	1.2755	1.2759	5	(-424)
19	2.0859	2.0879	26	(-240)	63	1.2690	1.2708	4	(-1.11.2)
20	2.0722	2.0758	23	(-123)	64	1.2571	1.2564	4	(-392)
21	2.0722	2.0727	23	(112)	65	1.2471	1.2484	7	(-325)
22	2.0722	2.0744	23	(-251)	66	1.2471	1.2465	7	(064)
23	2.0403	2.0431	6	(-213)	67	1.2376	1.2378	5	(-462)
24	1.9951	1.9917	5	(170)	68	1.2332	1.2328	5	(420)
25	1.9573	1.9558	4	(211)	69	1.2332	1.2317	5	(-284)
26	1.9342	1.9339	3	(132)	70	1.2245	1.2252	3	(-444)
27	1.8969	1.8975	20	(062)	71	1.2176	1.2191	4	(233)
28	1.8969	1.8941	20	(013)	72	1.2035	1.2029	9	(183)
29	1.8718	1.8764	11	(-143)	73	1.1911	1.1907	4	(-145)
30	1.8630	1.8656	4	(-312)	74	1.1769	1.1780	6	(332)
31	1.7786	1.7791	16	(260)	75	1.1769	1.1753	6	(-3.10.1)
32	1.7634	1.7624	3	(-332)	76	1.1719	1.1729	5	(1.12.1)
33	1.7089	1.7064	3	(-253)	77	1.1719	1.1717	5	(-473)
34	1.6816	1.6829	4	(-323)	78	1.1588	1.1585	3	(0.12.2)
35	1.6660	1.6657	12	(-341)	79	1.1532	1.1544	6	(-471)
36	1.6426	1.6427	7	(-163)	80	1.1532	1.1526	6	(-464)
37	1.6188	1.6175	10	(-204)	81	1.1532	1.1531	6	(1.11.2)
38	1.6188	1.6207	10	(181)	82	1.1414	1.1407	7	(-3.10.3)
39	1.5839	1.5833	5	(082)	83	1.1220	1.1219	4	(-523)
40	1.5839	1.5825	5	(330)	84	1.1220	1.1214	4	(-512)
41	1.5661	1.5713	3	(-343)	85	1.1179	1.1180	3	(-394)
42	1.5521	1.5523	3	(202)	86	1.1179	1.1165	3	(-275)
43	1.5172	1.5201	5	(0.10.0)	87	1.0980	1.0985	3	(-514)
44	1.5122	1.5125	4	(280)	88	1.0926	1.0924	2	(-1.12.3)

\*Monochromatized Cu  $K\alpha$  filtered with Ni ( $\lambda = 1.54056 \text{ \AA}$ ),  $2\theta = 10 - 84^\circ$ . Number of refinement cycles: 8.

The computed parameters of the elemental cells,  $a = 5.681 (1) \text{ \AA}$ ,  $b = 15.201 (4) \text{ \AA}$ ,  $c = 6.510 (2) \text{ \AA}$  and  $\beta = 118.39 (1)^\circ$  are close to those given by PEDERSEN

and SEMMINGSEN (1982), [ $a = 5.679$  (5) Å,  $b = 15.202$  (14) Å,  $c = 6.522$  (6) Å and  $\beta = 118.43$  (4)<sup>0</sup>].

### 3. SECONDARY MINERALS

**Quartz**,  $\alpha$   $\text{SiO}_2$ , represents a common presence associated with the hydroxyl-apatite crusts and especially the nodules, appearing as milky-white granules.

The computed parameters of the elemental cells,  $a = 4.911$  (1) Å,  $c = 5.402$  (1),  $V = 112.82$  (4) Å<sup>3</sup>, are relatively close to those computed by WILL *et al.* (1988) for the stoichiometric  $\alpha$ -quartz:  $a = 4.91239$  (4) Å,  $c = 5.40385$  (7),  $V = 112.933$  Å<sup>3</sup>.

**Illite**,  $K_{1-1.5}Al_4 [(Al_{1-1.5}Si_{7-6.5})O_{20}](OH)_4$ , is the dominant mineral in the mass of the terra rossa-like detrital deposits, placed inside or in some places, at the base of the guano deposit.

The computed parameters of the elemental cells are the following:  $a = 5.17$  (1) Å,  $b = 9.01$  (2) Å,  $c = 20.07$  (5) Å,  $\beta = 95.32$  (9)<sup>0</sup> and  $V = 930.9$  (21) Å<sup>3</sup> (the ICDD 26 – 0911 file was used to establish the Miller indexes of the reflexes used in the computations).

### 4. DISCUSSIONS ON THE GENESIS OF THE IDENTIFIED MINERALS

Incontestably, the presence of the guano deposits is the main cause of the mineral association recorded in the Lilecilor Cave, Olteţului Gorges. Covering the floor in a thick layer, wet by the percolation water dripping from the ceiling, they have led, in time, to fermentation reactions with chemical results on the solutions locally dampening the floor and the walls, being in this way a convincing explanation for the presence of the mineral species.

Undoubtedly, the first precipitate is brushite, hydrated acidic calcium phosphate, frequently found at the edge of the guano deposit with the lithic substratum. At a higher level, when the guano deposit is important, hydroxyl-apatite appears. If the guano deposit has a lower thickness, the percolated solutions, rich in carbonate ions, facilitate the deposition of carbonate-hydroxyl-apatite carbonate.

The genesis of ardealite and gypsum (minerals including  $\text{SO}_4$  in their chemical composition) in the Lilecilor Cave, needs a supplementary explanation.

In 1989, following some observations made on fresh guano deposits from some Japanese caves, YOSHIMURA *et al.* recorded the presence of sulphuric acid in a 0,4–0,6% ratio and suggested it was the result of the bacterial oxidations.

So, we can appreciate that in any other cave with bacterial activity, the genesis of ardealite and then that of gypsum may be confirmed.

The presence of some bacteria that facilitate the formation of sulphuric acid, supposes the existence of sulphur (or hydrogen sulphate) in the guano substratum.

The oxidative reactions need a long period of time while the bat species should eat insect species providing sulphur by digestion.

In this case, the first precipitate would be ardealite but if sulphate is in excess, gypsum will precipitate in the end.

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