DATA ON THE LIMANU CAVE MINERALOGY, SOUTH DOBROGEA

GABRIEL DIACONU[*], ŞTEFAN MARINCEA[**], DELI DUMITRAŞ[**]

Abstract. By means of diphractometric X-rays analyses on powders, we emphasize an association of minerals in the Limanu Cave from South Dobrogea, made up of *hydroxylapatite*, *brushite*, *calcite, gypsum* and *dolomite* as the main minerals and *quartz* and *illite* as secondary minerals.

Key words: cave minerals, Limanu Cave, Dobrogea de Sud.

1. INTRODUCTION

The E 95 highway, coming from Bulgaria and linking Vama Veche and Mangalia, crosses the Limanu commune situated close to the Mangalia Lake. A short distance away from the commune, in the right slope of the "La Peşteră" valley, is the entrance of the most important endokarstic void from the entire Dobrogea, namely the Peştera Limanu (Limanu Cave) (Fig. 1).

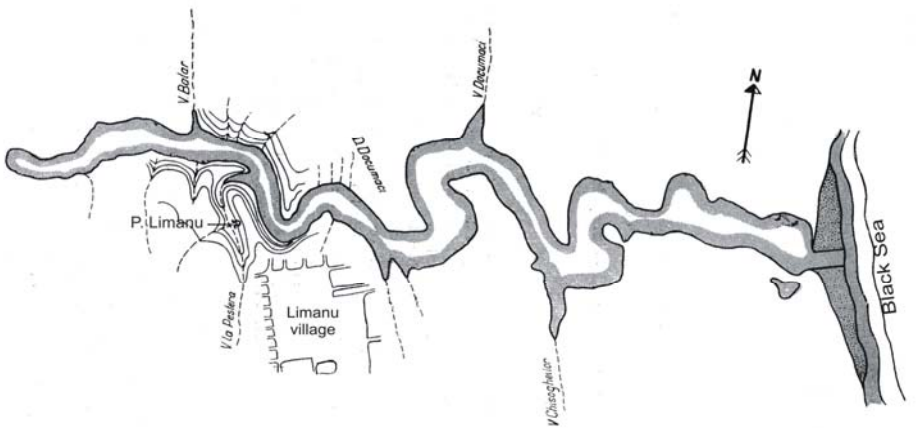

Fig. 1. – Geographic position of the Peştera Limanu (after DUMITRESCU *et al.,* 1965).

The labyrinthic cave, with a total length of 3,200 m, was initially shaped naturally as a karstic plateau void, subsequently the cave was influenced by its use in the past as a limestone quarry (the cave humid atmosphere facilitating the mining) as well as a shelter until a much more recent time.

The mineralogical samples were collected in places underneath bat colonies which produced the guano deposits on the floor (points 4, 22 and 25) (Fig. 2).

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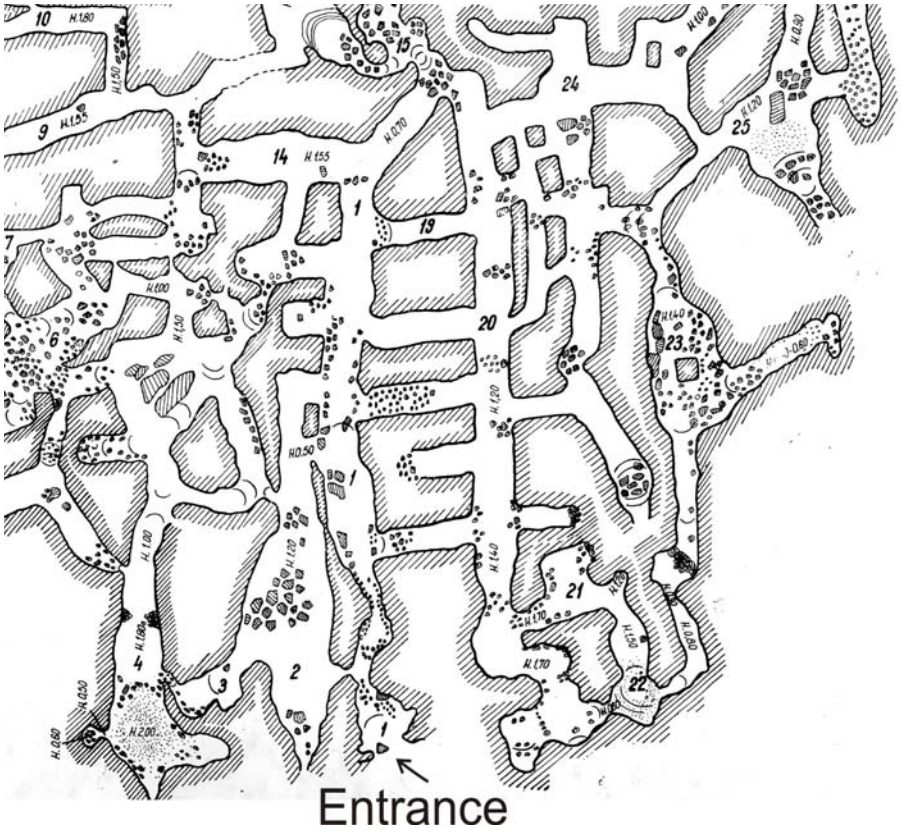

Fig. 2. – Peştera Limanu (partial map after DUMITRESCU *et al.,* 1965; points 4, 22 and 25, sampling sites).

The X-rays diphractometric analyses on powders evidenced an association of minerals made up of *hydroxylapatite*, *brushite*, *calcite, gypsum* and *dolomite* as the main minerals and *quartz* and *illite* as secondary minerals.

2. ANALYTIC METHODS

From the beginning, we have to point out the micronic-size of the crystals in the analyzed samples. The X-rays diphractometric analyses were made by the powders method.

The radiation (Cu, $K\alpha$, λ = 1.54056 Å) was monocromatized either by using a graphite monocromator or filtered with Ni. The scanning speed was 0.01º, respectively 0.02º (2θ) per second for 4, respectively 2.4 seconds per step.

The parameters of the elemental cells of the mineral species were computed using the refining program by the method of the smallest squares.

3. RESULTS AND DISCUSSIONS

Hydroxylapatite, $[Ca_5(PO_4)_3(OH)]$, appears as dirty-white, crème or brick-coloured, relatively massive crusts found on the floor covered by clay in a *terra rossa* facies or on the limestone surface of the walls.

Morphologically, the aggregates with a hexagonal habitus suggest an authigenic genesis resulting from precipitation processes.

The interreticular distances measured and computed for the main diphractometric reflexes for the two representative hydroxylapatite samples from Peştera Limanu, as well as the Miller indexes established for the hypothesis of the hexagonal symmetry, mineral spatial group $P6_3$, are given in Table 1. The average of the two sets of values leads to elemental cells with the size of a = 9.434 (2) Å; c = 6.881 (17) Å and V = 530.4 (11) Å^3, the values being very close to those given by BIGI *et al*. (1996), [a = 9.432 (3) Å; c = 6.881(16) Å].

Table 1

X-rays diphractometric data on powders from two representative samples of hydroxylapatite from Peştera Limanu*

Crt. no.	Sample PL 6 B			Sample PL 10 B			(hkl)
	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I / I_0	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I / I_0	
1	5.2666	5.2708	4	5.2581	5.2613	3	(101)
2	4.7231	4.7156	2	4.7503	4.7176	3	(110)
3	3.5094	3.5144	1	3.5241	3.5124	3	(201)
4	3.4394	3.4499	42	3.4399	3.4382	72	(002)
5	3.1744	3.1780	1	3.1763	3.1691	7	(102)
6	3.0740	3.0871	11	3.0810	3.0884	14	(210)
7	2.8153	2.8179	79	2.8258	2.8173	100	(211)
8	2.7959	2.7843	100	2.7717	2.7786	82	(112)
9	2.7194	2.7225	33	2.7317	2.7237	35	(300)
10	2.5434	2.5325	12	2.5347	2.5323	9	(301)
11	2.2315	2.2311	12	2.2346	2.2312	36	(221)
12	2.2076	2.2138	1	2.2144	2.2070	2	(103)
13	2.0664	2.0672	12	2.0630	2.0617	6	(113)
14	2.0054	2.0039	16	1.9975	1.9990	21	(203)
15	1.8906	1.8936	19	1.8899	1.8922	9	(132)
16	1.8695	1.8738	7	1.8739	1.8746	23	(230)
17	1.8456	1.8444	20	1.8361	1.8406	19	(213)
18	1.7841	1.7823	5	–	–	–	(410)
19	1.7519	1.7572	29	1.7565	1.7562	25	(402)
20	1.7237	1.7257	11	1.7300	1.7260	5	(141)

Crt. no.	Sample PL 6 B			Sample PL 10 B			(hkl)
	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I / I_0	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I / I_0	
21	1.7237	1.7250	11	1.7153	1.7191	22	(004)
22	1.6888	1.6877	4	1.6849	1.6823	10	(104)
23	1.6454	1.6466	20	1.6407	1.6459	30	(322)
24	1.6454	1.6464	20	1.6407	1.6439	30	(223)
25	–	–	–	1.6132	1.6116	32	(313)
26	1.5792	1.5835	2	1.5799	1.5829	6	(412)
27	1.5046	1.5058	11	–	–	–	(124)
28	1.4669	1.4670	1	1.4705	1.4676	7	(510)
29	1.4527	1.4527	2	1.4527	1.4511	5	(323)
30	1.4354	1.4349	20	1.4321	1.4353	7	(511)
31	1.4104	1.4088	16	1.4064	1.4074	7	(143)
32	1.3645	1.3613	13	1.3615	1.3619	24	(600)
33	1.3222	1.3180	21	1.3185	1.3184	18	(431)
34	1.3154	1.3177	26	–	–	–	(404)
35	1.2819	1.2850	22	1.2859	1.2854	24	(521)
36	1.2705	1.2691	9	–	–	–	(234)
37	1.2551	1.2598	16	1.2567	1.2563	26	(215)
38	1.2551	1.2513	16	1.2512	1.2512	9	(342)
39	1.2478	1.2456	9	1.2460	1.2460	27	(610)
40	1.2352	1.2368	21	1.2344	1.2360	36	(513)
41	1.2240	1.2229	20	–	–	–	(252)
42	1.1871	1.1910	7	1.1889	1.1881	21	(225)
43	1.1871	1.1861	7	1.1840	1.1845	8	(504)
44	1.1803	1.1789	7	1.1773	1.1794	5	(440)
45	1.1666	1.1668	6	–	–	–	(350)
46	1.1614	1.1621	12	1.1639	1.1624	3	(441)
47	1.1469	1.1508	32	1.1526	1.1508	28	(351)
48	1.1354	1.1326	16	1.1338	1.1331	8	(260)
49	1.1182	1.1175	10	1.1181	1.1162	14	(514)
50	1.1182	1.1172	10	1.1130	1.1137	15	(116)
51	1.1108	1.1112	20	1.1083	1.1089	3	(235)
52	1.0940	1.0953	14	1.0941	1.0948	16	(613)

*Radiation Cu *Kα* filtered with Ni (λ = 1.54056 Å) 2 θ = 22–89º. Number of refining cycles: 4, 5, 3.

***Brushite*,** $CaH(PO_4) \cdot 2\ H_2O$, appears sporadically as local, powdery deposits on the surface or in the fissures of the hydroxylapatite crusts. The shining white micro-nodules were collected with difficulty but in a sufficient quantity for the diphractometric analysis: the computed and measured interreticular distances and the recorded relative intensities, with the corresponding Miller indexes, are given in Table 2.

Table 2

X-rays diphractometric data from a representative sample of brushite from Peştera Limanu*

Crt. no.	Sample PL 6 B			(hkl)	Crt. no.	Sample PL 6 B			(hkl)
	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I / I_0			$d_{meas.}$(Å)	$d_{calc.}$(Å)	I / I_0	
1	7.5461	7.5986	100	(020)	38	1.3720	1.3707	16	(1.10.1)
2	4.9710	4.9265	95	(110)	39	1.3645	1.3674	13	(–1.5.4)
3	4.2388	4.2362	49	(–1.2.1)	40	1.3487	1.3489	24	(–3.8.1)
4	3.8073	3.7993	14	(040)	41	1.3487	1.3466	24	(–4.3.3)
5	3.0271	3.0401	29	(–1.1.2)	42	1.3342	1.3353	20	(0.10.2)
6	2.8453	2.8522	78	(–2.1.1)	43	1.3342	1.3354	20	(1.11.0)
7	2.7959	2.7967	95	(002)	44	1.3203	1.3230	21	(–2.6.4)
8	2.6548	2.6460	18	(–1.3.2)	45	1.3154	1.3173	26	(192)
9	2.5434	2.5329	12	(060)	46	1.3005	1.3019	11	(400)
10	2.5434	2.5514	12	(–2.0.2)	47	1.2819	1.2832	22	(420)
11	2.4735	2.4633	1	(220)	48	1.2819	1.2820	22	(–4.5.1)
12	2.1127	2.1181	6	(–2.4.2)	49	1.2705	1.2693	9	(–4.5.3)
13	1.9682	1.9729	33	(–2.1.3)	50	1.2541	1.2516	16	(093)
14	1.8502	1.8520	18	(–2.3.3)	51	1.2478	1.2476	9	(–2.11.1)
15	1.8021	1.7975	18	(–2.6.2)	52	1.2352	1.2340	21	(233)
16	1.7841	1.7903	5	(–181)	53	1.2298	1.2316	27	(440)
17	1.7841	1.7788	5	(–1.7.2)	54	1.2240	1.2251	20	(–1.10.3)
18	1.7337	1.7388	11	(–2.7.1)	55	1.2240	1.2242	20	(064)
19	1.7337	1.7308	11	(152)	56	1.2173	1.2179	32	(282)
20	1.7142	1.7105	21	(–341)	57	1.2173	1.2178	32	(114)
21	1.6888	1.6938	4	(251)	58	1.2112	1.2116	24	(332)
22	1.6667	1.6648	7	(–2.5.3)	59	1.2112	1.2104	24	(390)
23	1.6454	1.6421	20	(330)	60	1.1728	1.1747	8	(–4.7.3)
24	1.6256	1.6300	23	(181)	61	1.1666	1.1686	6	(381)
25	1.5496	1.5535	16	(222)	62	1.1614	1.1595	12	(–3.4.5)
26	1.5496	1.5514	16	(–2.0.4)	63	1.1441	1.1443	19	(0.13.1)
27	1.5396	1.5347	14	(280)	64	1.1441	1.1439	19	(2.11.1)
28	1.5046	1.5074	11	(350)	65	1.1403	1.1406	16	(1.13.0)
29	1.4669	1.4643	1	(242)	66	1.1403	1.1394	16	(–4.6.4)
30	1.4587	1.4549	2	(321)	67	1.1354	1.1343	16	(–1.9.4)
31	1.4587	1.4597	2	(–2.9.1)	68	1.1287	1.1288	18	(–4.1.5)

Crt. no.	Sample PL 6 B			(hkl)	Crt. no.	Sample PL 6 B			(hkl)
	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I / I_0			$d_{meas.}$(Å)	$d_{calc.}$(Å)	I / I_0	
32	1.4354	1.4358	20	(143)	69	1.1182	1.1173	10	(–3.11.2)
33	1.4267	1.4296	10	(–3.7.2)	70	1.1182	1.1157	10	(015)
34	1.4267	1.4261	10	(–4.2.2)	71	1.0988	1.0977	14	(273)
35	1.4104	1.4079	16	(–4.1.1)	72	1.0988	1.0976	14	(2.10.2)
36	1.3937	1.3910	1	(–4.1.3)	73	1.0988	1.0974	14	(–3.6.5)
37	1.3804	1.3809	8	(341)	74	1.0940	1.0940	14	(–1.13.2)

*Monocromatic radiation Cu $K\alpha$ (λ = 1.54056 Å) 2 θ = 5–90º. Number of refining cycles: 10.

The average of the set of values leads to a elemental cells with the size of a = 5. 811(3) Å; b = 15.196(6) Å; c = 6.241 (3) Å and β = 116.33(2)º, the values being very close to those given by CURRY & JONES (1971), [a = 5.812(2) Å; b = 15.180(3) Å; c = 6.239(2) Å, β = 116.43(3)º].

Calcite, $CaCO_3$, is the most widespread mineral in the cave environments and, according to HILL & FORTI (1997) it is the main component of the speleothems resulting from the speleogenesis (we excluded from our study the calcite that forms the mineralogical basis of the carbonate rocks).

In Peştera Limanu, the speleothems have characteristic features: they are shaped as relatively thin, bothrioidal crusts on the spaces between the stratification levels of the lumachellic limestones.

The diphratometric data of two representative samples of calcite are given in Table 3.

Table 3

X-rays diphractometric data from two representative samples of calcite from Peştera Limanu*

Crt. no.	Sample PL 5 A			Sample PL 8 B			(hkl)
	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I / I_0	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I / I_0	
1	3.8455	3.8486	7	3.8455	3.8519	10	(012)
2	3.0283	3.0300	100	3.0281	3.0348	100	(104)
3	2.8410	2.8373	3	–	–	–	(006)
4	2.4895	2.4911	11	2.4884	2.4921	10	(110)
5	2.2798	2.2810	19	2.2788	2.2828	31	(1.1.–3)
6	2.0903	2.0913	15	2.0907	2.0924	19	(202)
7	1.9241	1.9243	6	1.9243	1.9259	6	(024)
8	1.9085	1.9085	17	1.9107	1.9129	12	(018)

Crt. no.	Sample PL 5 A			Sample PL 8 B			(hkl)
	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I / I_0	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I / I_0	
9	1.8711	1.8720	19	1.8723	1.8747	13	(1.1.–6)
10	1.6228	1.6234	5	1.6218	1.6241	4	(1.2.–1)
11	1.6022	1.6017	8	1.6029	1.6024	6	(122)
12	1.5821	1.5836	1	1.5843	1.5875	5	(1.0.10)
13	1.5236	1.5229	5	1.5264	1.5239	9	(1.2.–4)
14	–	–	–	1.5192	1.5174	6	(208)
15	1.5066	1.5065	2	1.5103	1.5093	5	(1.1.–9)
16	1.4708	1.4708	2	1.4724	1.4720	5	(2.1.–5)
17	1.4388	1.4383	5	1.4385	1.4388	13	(300)
18	1.4196	1.4186	3	–	–	–	(0.0.12)
19	1.3554	1.3545	1	1.3548	1.3560	5	(1.2.–7)
20	1.3405	1.3364	1	1.3393	1.3389	10	(0.2.10)
21	1.2943	1.2944	3	1.2938	1.2961	2	(2.1.–8)
22	1.2825	1.2829	1	1.2875	1.2840	5	(036)
23	1.2457	1.2456	2	1.2483	1.2460	5	(220)
24	1.2322	1.2328	2	1.2348	1.2355	10	(1.1.–12)
25	1.1866	1.1851	1	1.1860	1.1856	1	(1.3.–2)
26	1.1796	1.1777	1	1.1800	1.1795	11	(1.2.–10)
27	–	–	–	1.1752	1.1735	8	(0.1.14)
28	1.1515	1.1520	2	1.1528	1.1527	21	(134)
29	1.1410	1.1405	2	–	–	–	(2.2.–6)
30	1.1227	1.1226	1	1.1211	1.1244	2	(2.1.–11)

*Radiation Cu *Kα* filtered with Ni (λ = 1.54056 Å), 2 θ = 20–90º. Number of refining cycles: 3; 4; 3.

The parameters of the elemental cells, computed by the method of the smallest squares, are: $a = 4.9823(7)$ Å; $c = 17.024(4)$ Å and $V = 365.97(9)$ Å^3, n = 4, N = 28, respectively, $a = 4.984(2)$ Å; $c = 17.071(9)$ Å and $V = 367.3(3)$ Å^3, n = 3. They are close to those given by MARKGRAF & REEDER (1985) for low magnesium calcite [$a = 4.988(1)$ Å, $c = 17.061(1)$ Å].

***Dolomite*,** $CaMg(CO_3)_2$, appears as porcelain-like, white powders on some places close to the low magnesium calcite crusts.

The diphractometric data obtained from two representative samples from Limanu Cave, are given in Table 4.

Table 4

X-rays diphractometric data from two representative samples of dolomite from Peştera Limanu*

Crt. no.	Sample PL 3 B			Sample PL 7 A			(hkl)
	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I / I_0	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I / I_0	
1	4.0276	4.0409	1	4.0169	4.0355	1	(101)
2	3.7042	3.7035	7	3.6929	3.6987	6	(012)
3	2.8976	2.8919	100	2.8885	2.8884	100	(104)
4	2.6828	2.6727	3	2.6763	2.6698	4	(006)
5	2.5468	2.5435	2	2.5410	2.5406	4	(015)
6	2.4082	2.4108	3	2.4049	2.4076	9	(110)
7	2.1991	2.1977	11	2.1932	2.1947	30	(1.1.–3)
8	2.0722	2.0703	12	2.0663	2.0676	3	(021)
9	2.0198	2.0205	7	2.0162	2.0178	13	(202)
10	1.8548	1.8518	3	1.8506	1.8494	2	(024)
11	1.8035	1.8070	4	1.8012	1.8051	9	(018)
12	1.7932	1.7901	7	1.7905	1.7880	15	(1.1.–6)
13	–	–	–	1.7492	1.7475	1	(205)
14	1.5696	1.5707	2	1.5691	1.5685	5	(1.2.–1)
15	1.5452	1.5485	3	1.5462	1.5465	7	(122)
16	1.5452	1.5431	3	1.5462	1.5412	7	(027)
17	1.4973	1.4970	2	1.4939	1.4954	1	(1.0.10)
18	1.4707	1.4686	3	1.4674	1.4666	5	(1.2.–4)
19	–	–	–	1.4434	1.4442	1	(208)
20	1.4343	1.4329	2	1.4298	1.4312	2	(1.1.–9)
21	1.4210	1.4161	6	1.4148	1.4142	2	(2.1.–5)
22	1.3912	1.3918	3	1.3890	1.3900	6	(300)
23	1.3751	1.3763	1	–	–	–	(0.1.11)
24	–	–	–	1.3413	1.3452	1	(303)
25	1.3028	1.2997	1	1.2978	1.2980	3	(1.2.–7)
26	1.2758	1.2718	1	–	–	–	(0.2.10)
27	–	–	–	1.2363	1.2385	1	(2.1.–8)
28	1.2343	1.2345	3	–	–	–	(036)
29	–	–	–	1.2013	1.2038	1	(220)
30	1.1944	1.1953	2	–	–	–	(2.0.11)
31	1.1772	1.1759	2	1.1739	1.1743	3	(2.2.–3)

Crt. no.	Sample PL 3 B			Sample PL 7 A			(hkl)
	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I / I_0	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I / I_0	
32	1.1536	1.1551	3	–	–	–	(3.1.–1)
33	1.1262	1.1248	1	1.1214	1.1235	3	(1.2.–10)
34	1.1084	1.1126	2	1.1114	1.1111	3	(3.1.–4)
35	1.1036	1.1046	1	1.0983	1.1034	2	(0.1.14)
36	1.0993	1.0988	1	1.0983	1.0974	2	(2.2.–6)

*Radiation Cu *Kα* filtered with Ni (λ = 1.54056 Å) 2 θ = 20–90^0. Number of refining cycles: 3; 3; 3.

The parameters for the two samples, computed by the method of the smallest squares, are: a = 4. 815 (1) Å, c = 16.019 (9) Å, V = 321. 6 (2) Å^3, n = 3, respectively, a = 4. 821 (2) Å; c = 16.010 (9) Å and V = 322. 2 (9) Å, n = 4, being close to those obtained by REEDER & WENK (1983), [a = 4.8054 (5) Å, c = 16.006 (2) Å].

Gypsum appears as shining-white, microcrystalline powders, situated in the immediate vicinity of the guano deposits or even on their surface or inside them.

The diphractometric data obtained from one representative sample of gypsum from Peştera Limanu, are presented in Table 5.

Table 5

X-rays diphractometric data from one representative sample of gypsum from Peştera Limanu*

Crt. no.	Sample PL 6 B			(hkl)	Crt. no.	Sample PL 6 B			(hkl)
	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I / I_0			$d_{meas.}$(Å)	$d_{calc.}$(Å)	I / I_0	
1	7.5644	7.5932	23	(020)	44	1.5192	1.5188	2	(–134)
2	4.7417	4.7438	2	(110)	45	1.5192	1.5186	2	(0.10.0)
3	4.2736	4.2745	48	(–121)	46	1.5104	1.5112	1	(280)
4	3.7938	3.7966	9	(040)	47	1.5104	1.5065	1	(172)
5	3.7938	3.7942	9	(031)	48	1.4587	1.4593	3	(271)
6	3.5526	3.5550	1	(130)	49	1.4587	1.4571	3	(–1.10.1)
7	3.1591	3.1641	2	(–112)	50	1.4511	1.4498	2	(–291)
8	3.0538	3.0605	40	(–141)	51	1.4368	1.4391	8	(143)
9	2.8650	2.8743	100	(121)	52	1.4368	1.4338	8	(073)
10	2.8650	2.8659	100	(002)	53	1.4250	1.4255	3	(–183)
11	2.7796	2.7856	9	(–211)	54	1.4250	1.4248	3	(–363)
12	2.7250	2.7259	2	(–132)	55	1.4173	1.4169	3	(–402)

Crt. no.	Sample PL 6 B			(hkl)	Crt. no.	Sample PL 6 B			(hkl)
	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I / I_0			$d_{meas.}$(Å)	$d_{calc.}$(Å)	I / I_0	
13	2.6797	2.6837	41	(051)	56	1.4023	1.4029	4	(321)
14	2.6797	2.6812	41	(022)	57	1.3648	1.3643	4	(1.10.1)
15	2.4925	2.4969	23	(200)	58	1.3648	1.3630	4	(–264)
16	2.4691	2.4727	3	(–231)	59	1.3369	1.3361	5	(341)
17	2.4002	2.4037	6	(141)	60	1.3316	1.3307	2	(1.11.0)
18	2.2110	2.2143	9	(–152)	61	1.3235	1.3252	4	(–381)
19	2.0846	2.0862	19	(240)	62	1.3235	1.3250	4	(163)
20	2.0688	2.0765	26	(–123)	63	1.3235	1.3235	4	(262)
21	2.0688	2.0739	26	(112)	64	1.3187	1.3206	1	(370)
22	2.0688	2.0720	26	(–251)	65	1.3187	1.3148	1	(–431)
23	2.0393	2.0423	2	(–213)	66	1.2925	1.2930	2	(–404)
24	1.9894	1.9898	3	(170)	67	1.2601	1.2610	1	(–235)
25	1.8949	1.8971	13	(062)	68	1.2523	1.2550	1	(–392)
26	1.8949	1.8957	13	(013)	69	1.2499	1.2484	1	(400)
27	1.8722	1.8766	11	(–143)	70	1.2446	1.2433	2	(361)
28	1.8387	1.8375	1	(231)	71	1.2446	1.2421	2	(–1.10.3)
29	1.8081	1.8088	8	(–262)	72	1.2268	1.2293	2	(–1.12.1)
30	1.7986	1.7983	5	(–321)	73	1.2268	1.2286	2	(–374)
31	1.7787	1.7821	9	(–181)	74	1.2020	1.2019	6	(282)
32	1.7787	1.7775	9	(260)	75	1.2020	1.2004	6	(–345)
33	1.7613	1.7602	1	(–332)	76	1.1972	1.1963	1	(134)
34	1.6645	1.6638	7	(–341)	77	1.1855	1.1860	2	(440)
35	1.6195	1.6187	6	(091)	78	1.1855	1.1850	2	(390)
36	1.6195	1.6176	6	(–240)	79	1.1580	1.1580	2	(–194)
37	1.6002	1.5986	2	(190)	80	1.1580	1.1578	2	(0.12.2)
38	1.6002	1.5969	2	(–352)	81	1.1524	1.1525	2	(1.11.2)
39	1.5821	1.5826	5	(082)	82	1.1524	1.1514	2	(–464)
40	1.5821	1.5821	5	(–224)	83	1.1408	1.1409	4	(381)
41	1.5821	1.5813	5	(330)	84	1.1408	1.1396	4	(–3.10.3)
42	1.5509	1.5527	3	(202)	85	1.1376	1.1375	2	(1.13.0)
43	1.5305	1.5303	3	(–282)	86	1.1376	1.1367	2	(–2.12.2)

*Radiation Cu *Kα* filtered with Ni (λ = 1.54056 Å), 2 θ = 10–84º. Number of refining cycles: 10.

The computed parameters of the elemental cell are: a = 5.674 (2) Å, b = 15.188 (5) Å, c = 6. 510 (3) Å, β = 118. 34^0 (2), V = 493. 8 (2) Å^3, (n = 10). They are very close to those given by INNORTA *et al.* (1980), [a = 5.677 (7) Å, b = 15.187 (40) Å, c = 6.527 (7) Å, β = 118.39º (5)].

Quartz was found as transparent granules, up to 30 μm in size, often grouped in skeleton-like aggregates, inside the carbonates or, more frequently, on the surface of the illite mass of the *terra rossa* clay. X-rays diphractometric analyses on a concentrated quartz sample, emphasized the α-quartz**,** low-temperature polytype (see Table 6).

Table 6

X-rays diphractometric data obtained on two representative samples of quartz from Peştera Limanu*

Crt. no.	Sample PL 5 B			Sample PL 7 B			(hkl)
	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I / I_0	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I / I_0	
1	4.2533	4.2576	15	4.2426	4.2538	14	(100)
2	3.3430	3.3454	100	3.3344	3.3417	100	(101)
3	2.4562	2.4581	6	2.4523	2.4559	5	(110)
4	2.2821	2.2828	12	2.2770	2.2798	7	(012)
5	2.2361	2.2378	3	2.2352	2.2356	2	(1.1.–1)
6	2.1286	2.1288	5	2.1247	2.1269	5	(200)
7	–	–	–	1.9772	1.9790	3	(021)
8	1.8193	1.8190	13	1.8159	1.8169	11	(1.1.–2)
9	1.8073	1.8029	2	1.7975	1.8002	1	(003)
10	1.6733	1.6727	4	1.6702	1.6709	3	(202)
11	1.6592	1.6601	1	1.6543	1.6579	1	(103)
12	1.6064	1.6092	2	–	–	–	(120)
13	1.5418	1.5424	6	1.5404	1.5410	6	(2.1.–1)
14	1.4540	1.4538	2	1.4525	1.4519	2	(1.1.–3)
15	1.4169	1.4192	1	1.4149	1.4179	1	(300)
16	1.3823	1.3820	5	1.3822	1.3815	3	(1.2.–2)
17	1.3757	1.3758	8	1.3739	1.3741	6	(023)
18	1.3738	1.3727	7	1.3739	1.3714	6	(301)
19	1.2896	1.2887	2	1,2873	1.2869	2	(014)
20	1.2570	1.2566	3	1.2563	1.2554	2	(032)
21	1.2283	1.2291	2	1.2287	1.2280	1	(220)
22	–	–	–	1.1991	1.1992	2	(2.1.–3)

Crt. no.	Sample PL 5 B			Sample PL 7 B			(hkl)
	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I / I_0	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I / I_0	
23	1.2001	1.1985	3	–	–	–	(2.2.–1)
24	1.1840	1.1847	3	1.1838	1.1832	1	(1.1.–4)
25	1.1813	1.1808	3	1.1803	1.1798	2	(310)
26	1.1539	1.1537	2	1.1520	1.1526	1	(311)

*Radiation Cu *Kα* filtered with Ni (λ = 1.54056 Å) 2 θ = 20–90º. Number of refining cycles: 4; 3; 3.

The parameters of the elemental cell, computed by "n" refining cycles by the method of the smallest squares, are the following: a = 4.911 (1) Å, c = 5. 402 (3) Å, V = 112. 81 (7) Å^3 (n = 4). They are relatively close to those determined by WILL *et al.* (1988) for the stoechiometric α-quartz [a = 4.91239 (4) Å, c = 5.40385 (7) Å, V = 112.933 Å^3].

Illite represents the dominant mineral in the *terra rossa* clay from the cave. It was also found as inclusions in the crust-like deposits of hydroxylapatite and calcite from the cave; here, it is a support for the crystallization of some phosphatic and carbonate gels.

The recorded diphractograms, without a treatment with glycol, allowed us to identify the monoclinic polytype (2*M*1) of the mineral. The identification was made by the *fitting* method, after the indexation in two hypotheses of monoclinic polytype (1 *M* and respectively 2 *M*1) and a triclinic one (1*A*) and a comparison of the measured and computed interreticular distances of the main diphractometric reflexes.

The parameters of the elemental cells, computed for three representative samples of illite associated with phosphates and carbonates, after "n" refining cycles by the smallest squares method and based on "N" diphractometric reflexes from the interval 2 θ = 5–80º (Cu *Kα*, λ = 1.54056 Å) conferred to the illite are the following:

1. Sample PL 5 B: a = 5.197 (8) Å, b = 9.015 (9) Å, c = 20.13 (4) Å, β = 95.10 (12)º, V = 939.5 (18) Å^3, (n = 4, N = 22);
2. Sample PL 6 C: a = 5.206 (8) Å, b = 9.008 (9) Å, c = 20.10 (4) Å, β = 95.37 (11)º, V = 938.5 (21) Å^3, (n = 5, N = 23);
3. Sample PL 8 A: a = 5.197 (9) Å, b = 9.006 (9) Å, c = 20.06 (3) Å, β = 94.53 (13)º, V = 936.1 (15) Å^3, (n = 5, N = 23).

They are reasonably close to the similar values given for 2*M*1 illite from the ICDD (JCPDS) 9–334 record [a = 5.20 Å, b = 9.00 Å, c = 20.00 Å, β = 95.50º], respectively the ICDD 26–911 record [a = 5.19 Å, b = 9.00 Å, c = 20.16 Å, β = 95.18º].

4. CONCLUSIONS

Our paper presents the first complete mineralogical analysis made in the Limanu Cave from South Dobrogea, one of the most significant caves of the entire Dobrogea. The data obtained are relevant and give an image about the cave mineralogenetical possibilities from an area with a low-precipitation regime.

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[*] *"Emil Racovitza" Speleological Institute,*
Calea 13 Septembrie nr. 13, Sector 5,
050711 Bucureşti, Romania
[**] *Dept. of Mineralogy, Geological Institute of Romania,*
str. Caransebeş nr. 1, 012271 Bucureşti, Romania