

# MINERALOGICAL ANALYSES IN PEȘTERA\* POLOVRAGI (OLTEȚULUI GORGES) AND PEȘTERA MUIERII (GALBENULUI GORGES), GORJ COUNTY

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*Abstract.* Following a series of cave mineralogy researches in Peștera Polovragi and Peștera Muierii, Gorj County, we evidence an association made up of *hydroxylapatite*, *taranakite*, *calcite* and secondarily of *quartz* and *illite* and respectively, of *hydroxylapatite*, *brushite*, *calcite* and *aragonite*, and secondarily of  $\alpha$ -*quartz* and *illite*.

## 1. INTRODUCTION

The Olteț river represents the geographic limit between the Căpățâni Mountains, at the East, and the Parâng Mountains, at the west. Relatively parallel, the Galbenul river has its bed at approximately 2.5 km (in a straight line) west from the Olteț. Both rivers cut through the gorges with the same name, Oltețului Gorges, respectively, Galbenului Gorges, from north to south, the Malm-Neocomian limestone pile, conferred to the Danubian autochthonous (Fig. 1).

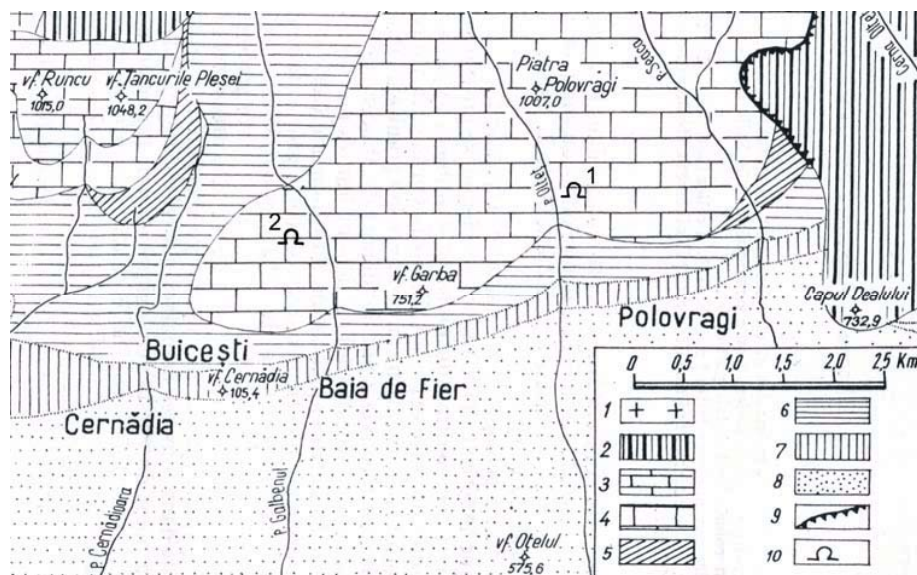


Fig. 1. – Geographic position of Peștera Polovragi, Oltețului Gorges, and Peștera Muierii, Galbenului Gorges.

\* Peștera = Cave

1 – Parang Granites; 2 – Crystalline schists; 3 – Lower Jurassic; 4 – Upper Jurassic; 5 – Upper Cretaceous; 6 – Lower Miocene; 7 – Middle Miocene; 8 – Upper Miocene; 9 – Getic Nappe; 10 – Cave (1 – Polovragi; 2 – Muierii).

In the left slope of the Oltețului Gorges, exactly at the western limit of the Căpățâni Mountains, is the entrance of Peștera Polovragi (peștera = cave), also known as Peștera lui Pahomie, the biggest cave in Gorj county, its galleries being more than 9,000 m long (9,171 m, GORAN, 1982).

The mineralogical samples were collected in “Bat Passage” and in some places with guano deposits from the first 200 m of the Main Gallery (Fig. 2).

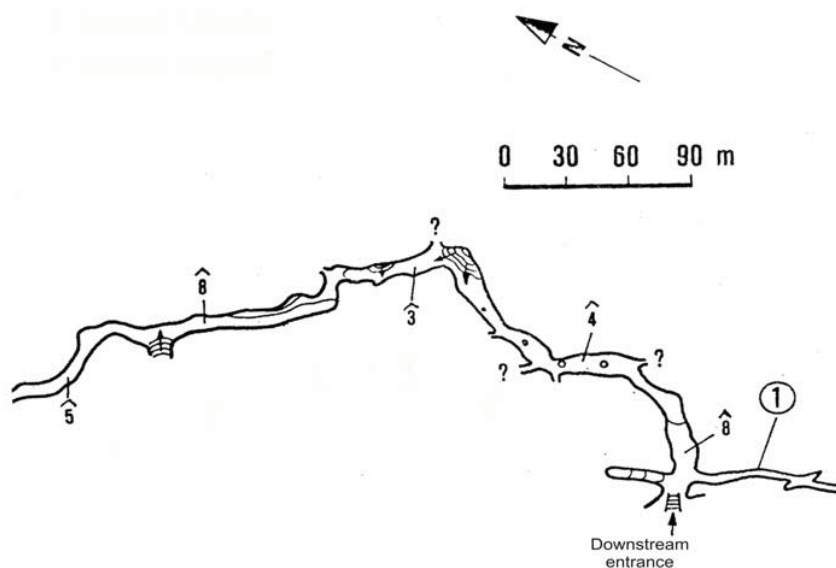


Fig. 2. – Peștera Polovragi (partial map; 1 – sampling place).

On the other side, in the right slope of Galbenului Gorges, is Peștera Muierii, one of the most representative caves from the Gorj County. The galleries total length, following a series of extensive exploratory campaigns made by the “Hades” Caving Club – Ploiești, is more than 7,000 m.

The analysed samples were collected from fossil guano deposits from the “Altar Hall” and the “Guano Hall” and from the new gallery (being recently discovered, it is not on the map yet), (Fig. 3).

## 2. ANALYTIC METHODS

The analytic method used was that of the X-rays diffractometry on powders.

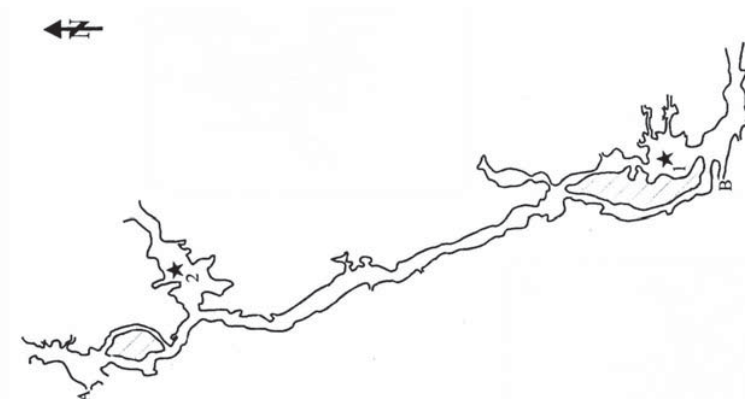


Fig. 3. – Peștera Muierii (partial map; ★ – sampling place).

The radiation (Cu,  $K\alpha$ ,  $\lambda = 1.54056 \text{ \AA}$ ) was monochromatized using a graphite bent monochromator. The scanning speed was 0.01, or 0.02° ( $2\theta$ ) per second for 4, respectively 2.4 seconds per step.

The elemental cell parameters were computed by the refining programme by the method of the smallest squares of APPELMAN & EVANS (1973), the version made by BENOIT (1987).

### 3. RESULTS AND DISCUSSIONS

The analyses made in the two caves pointed to the presence of the following mineral species: *hydroxylapatite* (*carbonate-hydroxylapatite*), *brushite*, *taranakite*, and secondarily, *calcite*, *quartz* and *illite* in Peștera Polovragi, respectively *hydroxylapatite*, *brushite*, *aragonite*, *calcite* and secondarily, *quartz* and *illite* in Peștera Muierii.

#### a. Peștera Polovragi, Oltețului Gorges

*Hydroxylapatite* (*carbonate-hydroxylapatite* ?),  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ , appears as a yellowish-orange crust at the periphery of the phosphatic deposit. Under the microscope, it appears either as compact, white granules with a slight orange hue, or as greenish-white granules or as powdery crusts on the detritic deposits forming the support of the phosphatic deposit. The occurrence pattern points to an authigenous genesis resulting from precipitation processes.

The X-rays diffractometric analysis (Table 1) and the parameters of the elemental cell of two representative samples of hydroxylapatite, given below the table, are relatively close to those given by WILSON *et al.* (1999), [ $a = 9.4172$  (1)  $\text{Å}$  and  $c = 6.8799$  (1)  $\text{Å}$ ].

The slightly lower value of the  $c$  parameter suggests slight substitutions of the carbonate-hydroxylapatite type which are characteristic for the cave apatite.

Table 1

X-rays diffractometric data from two representative samples of hydroxylapatite collected in Peștera Polovragi\*

Crt. no.	Sample PP 3 B			Sample PP 4 A			(hkl)
	$d_{\text{meas.}}(\text{Å})$	$d_{\text{calc.}}(\text{Å})$	$I / I_0$	$d_{\text{meas.}}(\text{Å})$	$d_{\text{calc.}}(\text{Å})$	$I / I_0$	
1	8.1683	8.1523	6	8.1784	8.1530	5	(100)
2	–	–	–	5.2757	5.2538	3	(101)
3	4.0754	4.0762	6	4.0802	4.0765	5	(200)
4	3.8856	3.8853	6	3.8863	3.8832	7	(111)
5	3.4441	3.4417	58	3.4331	3.4353	72	(002)
6	3.1714	3.1707	12	3.1608	3.1657	11	(102)
7	3.0817	3.0813	15	–	–	–	(210)
8	2.8137	2.8124	100	2.8052	2.8117	100	(211)
9	2.7811	2.7782	83	2.7731	2.7749	85	(112)
10	2.7219	2.7174	56	2.7100	2.7177	62	(300)
11	2.6285	2.6296	28	2.6292	2.6269	28	(202)
12	2.5231	2.5276	3	2.5260	2.5272	2	(301)
13	2.3555	2.3534	2	–	–	–	(220)
14	2.2583	2.2610	20	–	–	–	(130)
15	2.1454	2.1481	5	2.1447	2.1479	6	(131)
16	2.0632	2.0624	8	2.0571	2.0594	6	(113)
17	1.9998	1.9995	4	1.9971	1.9967	4	(203)
18	1.9448	1.9426	28	1.9393	1.9416	27	(222)
19	1.8895	1.8897	14	1.8882	1.8889	2	(132)
20	1.8403	1.8403	36	1.8406	1.8381	38	(213)
21	1.8064	1.8048	14	1.8058	1.8048	16	(321)
22	1.7802	1.7790	13	1.7807	1.7791	12	(410)
23	1.7526	1.7537	11	1.7552	1.7529	10	(402)
24	–	–	–	1.7512	1.7513	10	(303)
25	1.7212	1.7224	19	–	–	–	(141)
26	–	–	–	1.7186	1.7176	1	(004)
27	1.6472	1.6433	3	1.6449	1.6427	2	(322)
28	1.6108	1.6105	3	1.6075	1.6091	3	(313)

Crt. no.	Sample PP 3 B			Sample PP 4 A			(hkl)
	d <sub>meas.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>	d <sub>meas.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>	
29	1.5401	1.5406	4	1.5390	1.5408	5	(240)
30	1.5035	1.5034	6	1.5038	1.5034	6	(241)
31	1.4716	1.4735	6	1.4734	1.4731	7	(502)
32	–	–	–	1.4511	1.4520	12	(304)
33	1.4495	1.4497	10	–	–	–	(323)
34	1.4331	1.4322	6	1.4327	1.4322	6	(511)
35	1.4048	1.4059	2	1.4047	1.4050	1	(143)

$$a = 9.426(3) \text{ \AA}$$

$$c = 6.879(3) \text{ \AA}$$

$$V = 529.3(3) \text{ \AA}^3$$

$$n = 4$$

$$N = 38$$

$$a = 9.405(3) \text{ \AA}$$

$$c = 6.867(3) \text{ \AA}$$

$$V = 526.0(3) \text{ \AA}^3$$

$$n = 10$$

$$N = 41$$

\*Radiation Cu  $K\alpha$  filtered with Mn ( $\lambda = 1.93735 \text{ \AA}$ ,  $2\theta = 10\text{--}86^\circ$ . Number of refining cycles: 4; 3; 3.

The presence of the carbonate groups in the structure of the mineral was emphasized by the IR absorption spectrometry (DIACONU & MEDEȘAN, 1975) which points out the exact position of the absorption bands, their character and intensity [absorption bands at  $1460 \text{ cm}^{-1}$  and  $1425 \text{ cm}^{-1}$  which point to anti-symmetric  $\nu_3$  and respectively  $\nu$  stretching type vibrations of the carbonate and  $870 \text{ cm}^{-1}$  which points to non-planar deformation vibration of the O-C-O bond ( $\nu_2$  out-of-plane bending)].

**Brushite**,  $\text{CaH}(\text{PO}_4) \cdot 2 \text{H}_2\text{O}$ , was found as nodules and lens-like aggregates made of shining white, powder-like masses in the mass of the guano deposit. It is easily mistaken with the taranakite aggregates. The values of the interreticular distances, relative intensities and Miller indexes of the main diffractometric reflexes of a representative sample of brushite from Peștera Polovragi are given in Table 2.

Table 2

X-rays diffractometric data from one representative sample of brushite collected in Peștera Polovragi\*

Crt. no.	Sample PP 1 A			(hkl)	Crt. no.	Sample PP 1 A			(hkl)
	d <sub>meas.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>			d <sub>meas.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>	
1	7.4991	7.5819	100	(020)	36	1.6587	1.6562	4	(-3.2.3)
2	3.7841	3.7910	13	(040)	37	1.6258	1.6266	4	(181)
3	3.7241	3.7473	3	(031)	38	1.6021	1.5999	5	(-1.6.3)

Crt. no.	Sample PP 1 A			(hkl)	Crt. no.	Sample PP 1 A			(hkl)
	d <sub>meas.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>			d <sub>meas.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>	
4	3.0329	3.0407	51	(-1.4.1)	39	1.5869	1.5864	3	(053)
5	3.0329	3.0342	51	(-1.1.2)	40	1.5869	1.5843	3	(202)
6	2.9108	2.9235	32	(121)	41	1.5507	1.5484	4	(-2.0.4)
7	2.8375	2.8461	7	(-2.1.1)	42	1.5507	1.5508	4	(222)
8	2.8023	2.7919	4	(002)	43	1.5192	1.5169	2	(123)
9	2.6131	2.6195	26	(150)	44	1.5081	1.5085	3	(172)
10	2.6131	2.6199	26	(022)	45	1.5081	1.5044	3	(350)
11	2.5917	2.5988	20	(200)	46	1.4482	1.4522	3	(-4.0.2)
12	2.5480	2.5459	2	(-2.0.2)	47	1.4313	1.4333	2	(143)
13	2.4244	2.4312	9	(141)	48	1.4246	1.4265	2	(-3.7.2)
14	2.4244	2.4134	9	(-2.2.2)	49	1.4246	1.4230	2	(-4.2.2)
15	2.2573	2.2637	3	(-1.6.1)	50	1.4117	1.4118	3	(073)
16	2.1663	2.1668	12	(-1.5.2)	51	1.4117	1.4090	3	(-3.6.3)
17	2.1405	2.1435	12	(240)	52	1.4048	1.4049	2	(-4.1.1)
18	2.1158	2.1135	2	(-2.4.2)	53	1.3771	1.3784	4	(341)
19	2.0915	2.0951	4	(-2.5.1)	54	1.3687	1.3678	3	(1.10.1)
20	2.0783	2.0820	5	(112)	55	1.3422	1.3437	4	(-4.3.3)
21	1.9960	1.9995	7	(170)	56	1.3422	1.3423	4	(262)
22	1.9960	1.9940	7	(-1.2.3)	57	1.2999	1.2994	2	(400)
23	1.9659	1.9689	3	(-2.1.3)	58	1.2658	1.2665	3	(-4.5.3)
24	1.8939	1.8955	7	(080)	59	1.2658	1.2644	3	(-3.8.3)
25	1.8833	1.8808	4	(-3.1.2)	60	1.2658	1.2637	3	(0.12.0)
26	1.8719	1.8737	11	(062)	61	1.1838	1.1823	2	(-4.7.1)
27	1.8505	1.8536	5	(-3.2.1)	62	1.1671	1.1663	2	(381)
28	1.8505	1.8482	5	(-2.3.3)	63	1.1558	1.1572	3	(-3.4.5)
29	1.8505	1.8474	5	(013)	64	1.1558	1.1556	3	(460)
30	1.8123	1.8146	15	(-1.4.3)	65	1.1558	1.1527	3	(1.11.2)
31	1.8123	1.8118	15	(260)	66	1.1558	1.1512	3	(0.12.2)
32	1.7730	1.7764	4	(-1.8.1)	67	1.1317	1.1320	3	(-1.9.4)
33	1.7730	1.7751	4	(-1.7.2)	68	1.1317	1.1308	3	(-3.10.3)
34	1.7432	1.7466	4	(033)	69	1.1252	1.1265	3	(-4.1.5)
35	1.7061	1.7068	8	(-3.4.1)	70	1.1252	1.1240	3	(084)

\*Radiation Cu K $\alpha$  monochromatized ( $\lambda = 1.54056 \text{ \AA}$ ),  $2\theta = 5-90^\circ$ . Number of refining cycles: 7

The diphractogram indexation was made by comparison with JCPDS 72–0713, within the hypothesis of the monoclinic symmetry of the mineral and its belonging to the spatial group  $Ia$ , recorded by CURRY & JONES (1971).

The parameters of the elemental cell are:  $a = 5.797$  (2) Å,  $b = 15.163$  (7) Å,  $c = 6.228$  (3) Å and  $\beta = 116.28$  (2)°. They are slightly lower than those given by Curry & Jones:  $a = 5.812$  (2) Å,  $b = 15.180$  (3) Å,  $c = 6.239$  (2) Å and  $\beta = 116.42$  (2)° which seems to indicate a lesser degree of hydration of the analysed sample.

**Taranakite**,  $K_2Al_6(PO_4)_6(OH)_2 \cdot 18 H_2O$ , appears as white or whitish-crème nodules in the mass of the detritic-phosphatic levels with an illite dominance and *terra rossa* aspect given by the abundance of amorphous iron sesquioxides.

The values of the interreticular distances, the relative intensities and the corresponding are given in Table 3. The reflexes indexation was made by comparison with ICDD 89–0894, computed from the structural refining made by DICK *et al.* (1998).

The parameters of the elemental cell, computed after 3 cycles of refining by the method of the smallest squares are:  $a = 8.690$  (3) Å,  $c = 94.90$  (5) Å. They are close to the values given by Dick *et al.* based on neutronic diffraction [ $a = 8.6882$  (3) Å,  $c = 94.98$  (2) Å].

Table 3

X-rays diphractometric data for a representative sample of taranakite from Peștera Polovragi\*

Crt. no.	Sample PP 1 B			(hkl)	Crt. no.	Sample PP 1 B			(hkl)
	d <sub>meas.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>			d <sub>meas.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>	
1	15.4389	15.8169	100	(006)	45	1.8719	1.8713	3	(2.0.44)
2	7.8098	7.9085	16	(0.0.12)	46	1.8505	1.8480	5	(2.2.27)
3	7.4391	7.4331	21	(012)	47	1.8505	1.8456	5	(4.0.10)
4	5.8918	5.8968	4	(1.0.10)	48	1.8123	1.8173	1	(0.3.36)
5	4.6941	4.6985	2	(1.0.16)	49	1.8123	1.8130	1	(0.4.14)
6	4.2071	4.1899	2	(116)	50	1.8123	1.8120	1	(3.1.26)
7	3.9912	4.0174	2	(119)	51	1.8123	1.8090	1	(0.2.46)
8	3.9912	4.0139	2	(0.1.20)	52	1.7939	1.7954	6	(1.2.412)
9	3.7841	3.8082	13	(1.1.12)	53	1.7939	1.7934	6	(4.0.16)
10	3.7241	3.7512	3	(202)	54	1.7939	1.7908	6	(2.2.30)
11	3.7241	3.7425	3	(1.0.22)	55	1.7730	1.7773	4	(1.3.28)
12	3.5680	3.5869	5	(208)	56	1.7730	1.7736	4	(1.0.52)
13	3.5680	3.5818	5	(1.1.15)	57	1.7432	1.7437	4	(2.1.43)
14	3.2866	3.2901	4	(2.0.14)	58	1.7061	1.7059	8	(238)

Crt. no.	Sample PP 1 B			(hkl)	Crt. no.	Sample PP 1 B			(hkl)
	d <sub>meas.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>			d <sub>meas.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>	
15	3.2866	3.2842	4	(0.1.26)	59	1.7061	1.7069	8	(3.1.32)
16	3.1731	3.1774	3	(0.2.16)	60	1.6681	1.6732	3	(2.3.14)
17	3.1731	3.1634	3	(0.0.30)	61	1.6681	1.6716	3	(1.3.34)
18	3.1226	3.1322	6	(1.1.21)	62	1.6681	1.6701	3	(2.1.46)
19	2.9108	2.9245	4	(1.1.24)	63	1.6587	1.6540	4	(3.1.35)
20	2.8375	2.8394	7	(122)	64	1.6587	1.6532	4	(0.1.56)
21	2.8375	2.8357	7	(0.2.22)	65	1.6470	1.6495	3	(2.3.17)
22	2.8023	2.8131	5	(125)	66	1.6470	1.6423	3	(410)
23	2.6131	2.6200	6	(2.0.26)	67	1.6258	1.6292	4	(1.1.54)
24	2.6131	2.6170	6	(1.0.34)	68	1.6258	1.6227	4	(149)
25	2.5480	2.5574	2	(1.1.30)	69	1.6258	1.6225	4	(2.3.20)
26	2.3407	2.3420	2	(1.2.23)	70	1.6021	1.6030	5	(3.2.22)
27	2.2573	2.2628	3	(1.0.40)	71	1.6021	1.6016	5	(3.1.38)
28	2.2573	2.2596	3	(0.0.42)	72	1.5869	1.5896	3	(4.1.15)
29	2.2573	2.2538	3	(1.1.36)	73	1.5869	1.5887	3	(0.4.32)
30	2.1663	2.1726	1	(220)	74	1.5507	1.5547	4	(1.1.57)
31	2.1663	2.1675	1	(223)	75	1.5507	1.5501	4	(3.1.41)
32	2.1405	2.1469	2	(1.2.29)	76	1.5274	1.5271	2	(2.3.29)
33	2.0915	2.0868	4	(131)	77	1.5192	1.5167	2	(1.4.24)
34	2.0915	2.0838	4	(2.1.31)	78	1.5192	1.5165	2	(1.3.43)
35	2.0783	2.0808	5	(2.0.38)	79	1.5081	1.5039	3	(3.2.31)
36	2.0783	2.0793	5	(134)	80	1.5014	1.5000	2	(0.1.62)
37	2.0783	2.0783	5	(315)	81	1.5014	1.4999	2	(3.1.44)
38	2.0783	2.0734	5	(0.1.44)	82	1.4482	1.4484	3	(330)
39	1.9960	1.9923	7	(2.1.34)	83	1.4482	1.4469	3	(333)
40	1.9960	1.9897	7	(1.0.46)	84	1.4313	1.4349	2	(339)
41	1.9659	1.9581	3	(2.2.21)	85	1.4313	1.4347	2	(5.0.20)
42	1.8939	1.8973	7	(1.1.45)	86	1.4313	1.4323	2	(3.2.37)
43	1.8833	1.8800	4	(042)	87	1.4246	1.4233	2	(1.1.63)
44	1.8833	1.8789	4	(1.3.22)	88	1.4246	1.4221	2	(241)

\*Radiation Cu K $\alpha$  monochromatized ( $\lambda = 1.54056 \text{ \AA}$ ),  $2\theta = 20\text{--}90^\circ$ . Number of refining cycles: 3.

**Calcite**, CaCO<sub>3</sub>, appears as microcrystalline crusts forming the supporting element of the association of phosphatic minerals. (Our note does not treat the classic

calcite speleothemes which are frequent in this cave. We analyse only calcite samples associated with phosphatic sediments. This is also the case for quartz and illite).

Table 4 presents the results of the diffractometric analysis of two representative calcite samples from Peștera Polovragi. Under the table, the parameters of the elemental cells of the two samples are presented.

Table 4

X-rays diffractometric data for two representative samples of calcite from Peștera Polovragi\*

Crt. no.	Sample PP 1 C			Sample PP 4 A			(hkl)
	d <sub>meas.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>	d <sub>meas.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>	
1	3.8424	3.8526	9	3.8443	3.8504	7	(012)
2	3.0286	3.0334	100	3.0297	3.0317	100	(104)
3	2.8374	2.8407	3	2.8391	2.8395	15	(006)
4	2.4904	2.4937	14	2.4905	2.4922	16	(110)
5	2.2820	2.2834	19	2.2807	2.2821	27	(1.1.-3)
6	2.0924	2.0934	18	2.0910	2.0922	22	(202)
7	1.9258	1.9263	6	1.9229	1.9252	7	(024)
8	1.9103	1.9107	17	1.9085	1.9081	19	(018)
9	1.8726	1.8740	18	1.8728	1.8730	20	(1.1.-6)
10	1.6251	1.6251	4	1.6230	1.6241	4	(1.2.-1)
11	1.6033	1.6033	7	1.6016	1.6024	8	(122)
12	–	–	–	1.5839	1.5847	5	(1.0.10)
13	1.5247	1.5244	7	1.5236	1.5236	12	(1.2.-4)
14	1.5169	1.5167	5	1.5155	1.5159	7	(208)
15	1.5090	1.5081	2	1.5068	1.5074	8	(1.1.-9)
16	1.4736	1.4724	1	1.4711	1.4715	1	(2.1.-5)
17	1.4404	1.4397	5	–	–	–	(300)
18	1.4218	1.4204	2	–	–	–	(0.0.12)
19	1.3550	1.3559	2	1.3518	1.3552	5	(1.2.-7)
20	–	–	–	1.3384	1.3373	5	(0.2.10)
21	1.2946	1.2958	2	1.2951	1.2951	4	(2.1.-8)
22	–	–	–	–	–	–	(036)
23	1.2491	1.2468	1	1.2471	1.2461	9	(220)
24	1.2367	1.2341	3	1.2342	1.2336	9	(1.1.-12)
25	1.1864	1.1863	1	1.1859	1.1855	4	(1.3.-2)
26	–	–	–	1.1812	1.1783	4	(1.2.-10)

Crt. no.	Sample PP 1 C			Sample PP 4 A			(hkl)
	$d_{\text{meas.}}(\text{Å})$	$d_{\text{calc.}}(\text{Å})$	$I / I_0$	$d_{\text{meas.}}(\text{Å})$	$d_{\text{calc.}}(\text{Å})$	$I / I_0$	
27	–	–	–	–	–	–	(0.1.14)
28	1.1537	1.1532	4	1.1523	1.1520	2	(134)
29	1.1419	1.1417	2	1.1443	1.1410	6	(2.2.–6)
30	1.1252	1.1238	1	1.1218	1.1233	4	(2.1.–11)

$$a = 4.9873(9) \text{ Å}$$

$$c = 17.044(6) \text{ Å}$$

$$V = 367.2(2) \text{ Å}^3$$

$$n = 4$$

$$N = 25$$

$$a = 4.9843(9) \text{ Å}$$

$$c = 17.037(6) \text{ Å}$$

$$V = 366.5(2) \text{ Å}^3$$

$$n = 4$$

$$N = 26$$

\*Radiation Cu  $K\alpha$  filtered with Ni ( $\lambda = 1.54056 \text{ Å}$ ),  $2\theta = 20\text{--}90^\circ$ . Number of refining cycles: 4; 4; 3.

**Quartz**,  $\alpha\text{-SiO}_2$ , appears as milky-white granules included in the hydroxylapatite mass.

The parameters of the elemental cells of two representative quartz samples coming from the inside and the immediate vicinity of the hydroxylapatite crusts, established after “n” refining cycles by the smallest squares method, starting from “N” diffractometric reflexes from  $2\theta = 5\text{--}90^\circ$  (Cu  $K\alpha$ , ( $\lambda = 1.54056 \text{ Å}$ ), conferred to the quartz, are the following:

- Sample PP 1 A:  $a = 4.909(1) \text{ Å}$ ,  $c = 5.401(3) \text{ Å}$ ,  $V = 112.72(7) \text{ Å}^3$  ( $n = 3$ ,  $N = 16$ );
- Sample PP 2 A:  $a = 4.909(1) \text{ Å}$ ,  $c = 5.398(2) \text{ Å}$ ,  $V = 112.64(6) \text{ Å}^3$  ( $n = 4$ ,  $N = 20$ ).

In both cases, the computed parameters are relatively close to those given by WILL *et al.* (1988) for the stoichiometric  $\alpha$ -quartz [ $a = 4.91239(4) \text{ Å}$ ,  $c = 5.40385(7) \text{ Å}$  and  $V = 112.933(7) \text{ Å}^3$ ].

**Illite**,  $[(K, H_3O)(Al, Mg, Fe)_2(Si, Al)_4O_{10}(OH)_2 \cdot H_2O]$ , beside the quartz and the amorphous iron sesquioxides, is the dominant mineral in the mass of *terra rossa* detritic deposits. The recorded diffractograms, without a treatment with glycol, allowed us to identify the monoclinic polytype (2M1) of the mineral. The identification was made by the *fitting* method, after the indexation in two monoclinic polytypes (1 M and 2 M1) and the comparison between the measured and the computed interreticular distances of the main diffractometric reflexes.

The parameters of the elemental cells of two representative illite samples established after “n” refining cycles by the smallest squares method, based on “N” diffractometric reflexes from  $2\theta = 5\text{--}90^\circ$  (Cu  $K\alpha$ , ( $\lambda = 1.54056 \text{ Å}$ ), conferred to the quartz, are the following:

- Sample PP 1 B:  $a = 5.215(8) \text{ \AA}$ ,  $b = 8.974(6) \text{ \AA}$ ,  $c = 19.98(2) \text{ \AA}$ ,  $\beta = 94.27(9)^\circ$ ,  $V = 932.3(15) \text{ \AA}^3$ , ( $n = 6$ ,  $N = 20$ );
- Sample PP 2 B:  $a = 5.210(8) \text{ \AA}$ ,  $b = 9.03(1) \text{ \AA}$ ,  $c = 19.93(3) \text{ \AA}$ ,  $\beta = 94.50(12)^\circ$ ,  $V = 934.9(17) \text{ \AA}^3$ , ( $n = 4$ ,  $N = 18$ ).

### b. Peștera Muierii, Galbenului Gorges

**Hydroxylapatite**,  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ , was identified as dirty-white, crème or pinkish-orange crusts on the floor covered with *terra rosa* clay in some sectors of the “Altar Hall” and the “Guano Hall”. (In 1975, DIACONU & MEDEȘAN evidenced in the northern lower level of Peștera Muierii, under the name of *dahllite*, MC CONNELL, 1960, a carbonate-hydroxylapatite represented by splendid speleothemes with a range of various colours: from light yellow and orange to dark brown with greenish hues. The hydroxylapatite presented here was identified only in samples collected only from the floor in areas with guano deposits).

The measured and computed interreticular distances of the main diffractometric reflexes recorded for two representative samples of hydroxylapatite, beside the Miller indexes established under the hypothesis of the hexagonal symmetry,  $\text{P6}_3/\text{m}$  spatial group of the mineral, are given in Table 5. They allowed us to compute by refining, by the smallest squares method, the parameters of the elemental cells given under the table.

Table 5

X-rays diffractometric data for two representative samples of hydroxylapatite from Peștera Muierii\*

Crt. no.	Sample PM 12			Sample PM 13			(hkl)
	$d_{\text{meas.}}(\text{Å})$	$d_{\text{calc.}}(\text{Å})$	$I / I_0$	$d_{\text{meas.}}(\text{Å})$	$d_{\text{calc.}}(\text{Å})$	$I / I_0$	
1	–	–	–	5.2667	5.2628	4	(101)
2	3.8840	3.8817	7	3.8842	3.8879	8	(111)
3	3.4365	3.4378	60	3.4373	3.4438	55	(002)
4	3.1642	3.1673	22	3.1791	3.1727	10	(102)
5	2.8054	2.8099	100	2.8187	2.8143	95	(211)
6	2.7702	2.7754	95	2.7832	2.7800	100	(112)
7	2.7107	2.7152	50	2.7175	2.7194	55	(300)
8	–	–	–	2.6385	2.6314	27	(202)
9	2.2551	2.2592	20	2.2605	2.2626	21	(130)
10	2.1441	2.1463	5	2.1503	2.1496	10	(131)
11	2.0577	2.0603	5	–	–	–	–
12	1.9407	1.9409	21	1.9461	1.9440	16	(222)
13	1.8732	1.8687	11	1.8740	1.8716	19	(230)
14	1.8401	1.8384	15	1.8426	1.8415	27	(213)

Crt. no.	Sample PM 12			Sample PM 13			(hkl)
	d <sub>meas.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>	d <sub>meas.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>	
15	–	–	–	1.8055	1.8061	13	(321)
16	1.7512	1.7521	6	1.7524	1.7549	7	(402)
17	1.7512	1.7514	6	1.7524	1.7543	7	(303)
18	1.7227	1.7210	12	1.7227	1.7236	13	(141)
19	–	–	–	1.7227	1.7219	13	(004)
20	1.6405	1.6419	4	–	–	–	(322)
21	–	–	–	1.5417	1.5417	3	(240)
22	1.5029	1.5022	5	1.5046	1.5045	5	(241)
23	1.4538	1.4523	7	1.4537	1.4546	6	(304)
24	1.4538	1.4483	7	1.4537	1.4507	6	(323)
25	–	–	–	1.4367	1.4332	4	(511)

$$a = 9.406(4) \text{ \AA}$$

$$c = 6.876(5) \text{ \AA}$$

$$V = 526.7(5) \text{ \AA}^3$$

$$a = 9.420(3) \text{ \AA}$$

$$c = 6.888(3) \text{ \AA}$$

$$V = 529.3(4) \text{ \AA}^3$$

\*Radiation Cu K $\alpha$  filtered with Ni ( $\lambda = 1.93735 \text{ \AA}$ ),  $2\theta = 10\text{--}86^\circ$ . Number of refining cycles: 3; 3; 3.

**Brushite**, CaH(PO<sub>4</sub>) · 2 H<sub>2</sub>O, is the dominant mineral in the phosphatic deposits from Peștera Muierii. It appears as shining white, powdery deposits, up to 1 cm thick, coating the hydroxylapatite crusts.

The diffractometric analyses of two representative samples of brushite are given in Table 6 and the parameters of the elemental cells are presented in Table 7.

Table 6

X-rays diffractometric data for two representative samples of brushite from Peștera Muierii\*

Crt. no.	Sample PM 6 A			Sample PM 6 B			(hkl)
	d <sub>meas.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>	d <sub>meas.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>	
1	7.5246	7.5858	100	7.5673	7.5923	100	(020)
2	4.2248	4.2370	44	4.2300	4.2368	30	(–121)
3	3.7804	3.7929	10	–	–	–	(040)
4	3.6168	3.6260	1	–	–	–	(130)
5	–	–	–	3.0429	3.0464	34	(–141)
6	–	–	–	3.0429	3.0403	34	(–112)
7	2.9171	2.9232	25	2.9220	2.9242	14	(121)
8	2.6616	2.6665	3	2.6676	2.6682	2	(051)
9	–	–	–	2.6206	2.6228	15	(150)
10	–	–	–	2.6206	2.6217	15	(022)
11	2.2635	2.2662	3	2.2667	2.2675	3	(–161)

Crt. no.	Sample PM 6 A			Sample PM 6 B			(hkl)
	d <sub>meas.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>	d <sub>meas.</sub> (Å)	d <sub>calc.</sub> (Å)	I / I <sub>0</sub>	
12	2.1423	2.1450	9	2.1441	2.1459	8	(240)
13	2.0951	2.0982	3	2.0956	2.0989	3	(-251)
14	2.0805	2.0818	3	2.0816	2.0822	4	(112)
15	2.0167	2.0182	2	2.0174	2.0188	3	(211)
16	1.9990	1.9975	8	–	–	–	(-123)
17	1.9417	1.9408	1	–	–	–	(132)
18	1.8948	1.8965	2	1.8972	1.8981	3	(080)
19	1.8741	1.8748	10	1.8754	1.8756	5	(062)
20	1.8545	1.8568	3	1.8557	1.8569	2	(-321)
21	1.8131	1.8130	14	1.8135	1.8140	9	(260)
22	1.7957	1.7969	5	1.7977	1.7973	3	(-262)
23	1.7777	1.7779	2	1.7796	1.7791	2	(-181)
24	1.7777	1.7772	2	1.7796	1.7779	2	(-172)
25	1.6272	1.6272	2	–	–	–	(181)
26	1.6131	1.6139	2	–	–	–	(091)
27	1.6026	1.6020	2	1.6012	1.6022	1	(-163)
28	1.5517	1.5523	3	1.5515	1.5516	2	(-204)
29	1.5170	1.5505	3	1.5515	1.5509	2	(222)
30	1.5319	1.5524	3	1.5394	1.5333	1	(280)
31	–	–	–	1.5224	1.5232	1	(-282)
32	–	–	–	1.5224	1.5226	1	(-114)
33	1.4634	1.4651	1	1.4657	1.4648	1	(-134)
34	1.4525	1.4525	3	1.4528	1.4529	3	(321)
35	1.4525	1.4523	3	1.4528	1.4520	3	(-402)
36	1.4332	1.4334	2	1.4343	1.4337	1	(143)
37	1.3962	1.3969	1	–	–	–	(004)
38	1.3777	1.3786	1	–	–	–	(341)
39	1.3688	1.3683	6	1.3699	1.3694	4	(1.10.1)
40	1.3324	1.3333	2	1.3351	1.3343	1	(1.11.0)
41	1.3009	1.3004	1	1.3012	1.3007	2	(400)
42	1.2236	1.2238	3	1.2245	1.2243	3	(-1.10.3)
43	1.2099	1.2093	1	1.2097	1.2097	1	(332)
44	1.2099	1.2087	1	1.2097	1.2093	1	(390)

\*Radiation Cu K $\alpha$  monocromatized,  $\lambda = 1.54056 \text{ \AA}$ ,  $2\theta = 10\text{--}90^\circ$ . Number of refining cycles: 7; 9.

Table 7

Parameters of the elemental cells from the analysed samples

Proba	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta^{(0)}$	<i>V</i> (Å <sup>3</sup> )	<i>n</i> <sup>(1)</sup>	<i>N</i> <sup>(2)</sup>
PM 6 A	5.810(1)	15.172(2)	6.241(1)	116,46(1)	492,6(1)	7	72
PM 6 B	5.810(1)	15.184(1)	6.239(1)	116,42(1)	492,9(9)	9	53

(1) number of refining cycles; (2) number of reflexes used in the computations ( $2\theta = 10\text{--}90^\circ$ ).

**Calcite**, CaCO<sub>3</sub> (trigonal), is omnipresent as the support of the hydroxylapatite crusts. It appears as white or crème-white, porous masses. Table 8 presents the diffractometric data of two representative calcite samples from Peștera Muierii; under the table are given the parameters of the elemental cells of the samples.

Table 8

X-rays diffractometric data on powders of two representative calcite samples from Peștera Muierii\*

Crt. no.	Sample PM 12 A			Sample PM 13			(hkl)
	<i>d</i> <sub>meas.</sub> (Å)	<i>d</i> <sub>calc.</sub> (Å)	<i>I</i> / <i>I</i> <sub>0</sub>	<i>d</i> <sub>meas.</sub> (Å)	<i>d</i> <sub>calc.</sub> (Å)	<i>I</i> / <i>I</i> <sub>0</sub>	
1	3.8569	3.8456	8	3.8482	3.8491	7	(012)
2	3.0285	3.0284	100	3.0317	3.0303	100	(104)
3	2.8405	2.8369	3	2.8387	2.8375	2	(006)
4	2.4841	2.4888	11	2.4921	2.4916	11	(110)
5	2.2763	2.2792	15	2.2805	2.2814	21	(1.1.-3)
6	2.0882	2.0894	12	2.0903	2.0916	10	(202)
7	1.9215	1.9228	4	1.9246	1.9260	2	(024)
8	1.9074	1.9080	16	1.9076	1.9086	13	(018)
9	1.8698	1.8709	14	1.8740	1.8722	15	(1.1.-6)
10	1.6215	1.6219	2	1.6255	1.6237	1	(1.2.-1)
11	1.6002	1.6003	5	1.6020	1.6020	4	(122)
12	1.5835	1.5832	1	1.5839	1.5837	1	(1.0.10)
13	1.5220	1.5216	3	1.5231	1.5231	1	(1.2.-4)
14	1.5120	1.5142	2	1.5160	1.5152	1	(208)
15	1.5056	1.5059	2	1.5075	1.5066	1	(1.1.-9)
16	1.4708	1.4699	1	1.4719	1.4710	1	(2.1.-5)
17	1.4367	1.4369	4	1.4367	1.4385	3	(300)
18	1.4183	1.4184	3	1.4189	1.4187	1	(0.0.12)

*a* = 4.978(1) Å  
*c* = 17.022(6) Å  
*V* = 365.3(2) Å<sup>3</sup>  
*n* = 3  
*N* = 18

*a* = 4.983(2) Å  
*c* = 17.025(1) Å  
*V* = 366.1(2) Å<sup>3</sup>  
*n* = 3  
*N* = 18

\*Radiation Cu *K*α filtered with Mn ( $\lambda = 1.93735$  Å),  $2\theta = 20\text{--}90^\circ$ . Number of refining cycles: 3; 3; 3; 3.

**Aragonite**,  $\text{CaCO}_3$  (orthorhombic) recorded for the first time in 1974 by DIACONU & HANN on the channel of some conical stalactites from Peștera Muierii, was recently re-discovered by Diaconu as splendid feathers in the lower southern sector explored by the cavers of the “Hades” Caving Club – Ploiești.

A X-rays diffractometric analysis of a representative sample collected in the lower southern sector of Peștera Muierii is presented in Table 9 along with the parameters of the elemental cell.

Table 9

X-rays diffractometric data on powders of a representative sample of aragonite from Peștera Muierii\*

Crt. no.	Sample PM 19			(hkl)	Crt. no.	Sample PM 19			(hkl)
	$d_{\text{meas.}}(\text{Å})$	$d_{\text{calc.}}(\text{Å})$	$I / I_0$			$d_{\text{meas.}}(\text{Å})$	$d_{\text{calc.}}(\text{Å})$	$I / I_0$	
1	4.1836	4.2058	3	(110)	27	1.4735	1.4740	5	(321)
2	3.3881	3.3908	100	(111)	28	1.4644	1.4649	6	(151)
3	3.2567	3.2685	26	(021)	29	1.4118	1.4102	4	(014)
4	2.8600	2.8658	5	(002)	30	1.3787	1.3765	3	(104)
5	2.7216	2.7282	6	(121)	31	1.3634	1.3641	4	(242)
6	2.6893	2.6963	90	(012)	32	1.3634	1.3618	4	(331)
7	2.4735	2.4807	40	(102)	33	1.3212	1.3263	3	(060)
8	2.4735	2.4771	40	(200)	34	1.3000	1.3008	2	(124)
9	2.4022	2.4073	7	(031)	35	1.2604	1.2593	3	(332)
10	2.3640	2.3683	29	(112)	36	1.2476	1.2406	2	(341)
11	2.3322	2.3385	24	(130)	37	1.2476	1.2403	2	(204)
12	2.3322	2.3254	24	(022)	38	1.2384	1.2343	8	(313)
13	2.1819	2.1863	11	(211)	39	1.2229	1.2228	5	(053)
14	1.9865	1.9897	7	(040)	40	1.2229	1.2218	5	(134)
15	1.9717	1.9742	7	(221)	41	1.2159	1.2131	3	(252)
16	1.8729	1.8741	19	(202)	42	1.2052	1.2042	6	(243)
17	1.8581	1.8577	2	(013)	43	1.1955	1.1920	3	(323)
18	1.8113	1.8118	15	(132)	44	1.1878	1.1872	13	(153)
19	1.7544	1.7572	4	(141)	45	1.1878	1.1841	13	(224)
20	1.7386	1.7395	51	(113)	46	1.1760	1.1696	2	(162)
21	1.7217	1.7264	24	(231)	47	1.1702	1.1692	2	(260)
22	1.6954	1.6954	3	(222)	48	1.1242	1.1237	5	(351)
23	1.6346	1.6342	2	(042)	49	1.1242	1.1236	5	(234)
24	1.6168	1.6170	4	(310)	50	1.1050	1.1060	5	(115)
25	1.5550	1.5562	6	(311)	51	1.0939	1.0932	3	(422)
26	1.5550	1.5511	6	(240)					

$$a = 4.954(2) \text{ Å}; b = 7.958(4) \text{ Å}; c = 5.732(2)$$

\*Radiation Cu  $K\alpha$  filtered with Ni ( $\lambda = 1.54056 \text{ Å}$ ),  $2\theta = 20\text{--}90^\circ$ . Number of refining cycles: 3.

**Quartz**,  $\alpha$ -SiO<sub>2</sub> represents a constant presence, appearing as milky-white granules on the surface of the *terra rossa* clay in the immediate vicinity of the hydroxylapatite crusts. A quartz sample, collected and isolated from the limit between hydroxylapatite and *terra rossa*, was analysed by diffractometry (Table 10), while the computed parameters of the elemental cell, [ $a = 4.908$  (3) Å,  $c = 5.401$  (5) Å,  $V = 112.66$  (12) Å<sup>3</sup>], are only slightly lower than those computed by WILL *et al.* (1988) for the stoichiometric  $\alpha$ -quartz [ $a = 4.91239$  (4) Å,  $c = 5.40385$  (7) Å,  $V = 112.933$  Å<sup>3</sup>].

Table 10

X-rays diffractometric data of a representative quartz sample from Peștera Muierii\*

Crt. no.	Sample PM 11 B			(hkl)
	$d_{\text{meas.}}$ (Å)	$d_{\text{calc.}}$ (Å)	$I / I_0$	
1	4.2480	4.2562	19	(100)
2	3.3388	3.3434	100	(101)
3	2.4567	2.4573	7	(110)
4	2.1264	2.1281	5	(200)
5	1.8171	1.8178	14	(1.1.-2)
6	1.6709	1.6717	3	(202)
7	1.6564	1.6586	7	(103)
8	1.6082	1.6087	4	(120)
9	1.5412	1.5418	12	(2.1.-1)
10	1.4536	1.4526	5	(1.1.-3)
11	1.3820	1.3822	5	(1.2.-2)
12	1.3740	1.3748	10	(023)
13	1.3740	1.3722	10	(301)
14	1.2890	1.2875	5	(014)
15	1.2299	1.2287	3	(220)
16	1.1999	1.1998	4	(2.1.-3)
17	1.1840	1.1837	7	(114)
18	1.1132	1.1184	4	(2.2.-2)
19	1.1132	1.1145	4	(033)

$$a = 4.915(2) \text{ \AA}$$

$$c = 5.402(2) \text{ \AA}$$

\*Radiation Cu  $K\alpha$  monochromatized, ( $\lambda = 1.54056$  Å),  $2\theta = 20$ – $87^\circ$ . Number of refining cycles: 3; 3; 3.

*Illite*,  $[(K, H_3O)(Al, Mg, Fe)_2(Si, Al)_4O_{10}(OH)_2 \cdot H_2O]$  represents the dominant mineral in Peștera Muierii in the *terra rossa* clay situated at the base of the phosphatic deposit. The recorded diphractogram, without a treatment with glycol, allowed us to identify the monoclinic polytype (2M1) of the mineral. The computed parameters of the elemental cell are:  $a = 5.202 (5) \text{ \AA}$ ,  $c = 19.84 (5) \text{ \AA}$ ,  $\beta = 94.96 (10) \text{ \AA}^\circ$ .

#### 4. CONCLUSIONS

The data on the cave mineralogy presented in our paper bring new facts about two of the biggest and the most interesting caves from the Gorj County: Peștera Polovragi from Oltețului Gorges and Peștera Muierii from Galbenului Gorges. Added to the data on cave morphology and of biospeleology, they provide an ensemble image of the subterranean natural domain found at the western limit of the Căpățâni Mountains, respectively at the eastern limit of the Parâng Mountains.

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