MINERALOGICAL ANALYSES IN VARIOUS CAVES FROM THE BĂILE HERCULANE AREA, THE CERNA PASSAGE

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Abstract. In this paper we present the results from the mineralogical analyses performed on samples from three caves in the Băile Herculane area. All minerals are recorded for the first time in the investigated caves.

Key words: endokarst, spelean mineralogy.

The Băile Herculane caves from where samples were drawn in order to perform mineralogical analyses through X-ray diffractometry are Peştera lui Adam, Gaura Ungurului Cave and the Grota Haiducilor Cave, (Fig. 1).

1. PEŞTERA LUI ADAM

This cavity, lays at the base of the first morphological level of the Malm-Neocomian limestone, developed in the mount of the Ciorici Peak, on the right slope of the Cerna Passage (under the Elisabeta Peak) which is lined with the Roman Hotel from the Băile Herculane balneal spa.

What makes this natural hole, consisting of two relatively parallel spaces (the Guano Gallery and the Aburi (Steam) Gallery summing to 169 m in length), so particular is the fact that, being a thermal cavity [with temperatures up to 36–38°C in the Guano Gallery and more than 45°C in the Aburi (Steam) Gallery] provides – during the hot season – an excellent shelter for one of the largest chiropters colony in the country, (Fig. 2).

A direct consequence for the presence of this colony is the accumulation (on the floor of the southern gallery) of a large quantity of guano. A probe drilled by POVARĂ *et al.* (1972) at a depth of 25 m failed to reach the lythic floor.

The samples we have drawn, therefore, come from the upper layer of the guano deposit, and should be rightfully considered to be more recent compared to those dated by CARBONNEL *et al.* (1999) (using C^{14} methods) as being 7600 y.o. at 2.5 m deep, and 2740 y.o. at 1.2 m deep. The mineral association evidenced heretofore is made of hydroxylapatite, brushite, ardealite, gypsum and quartz.

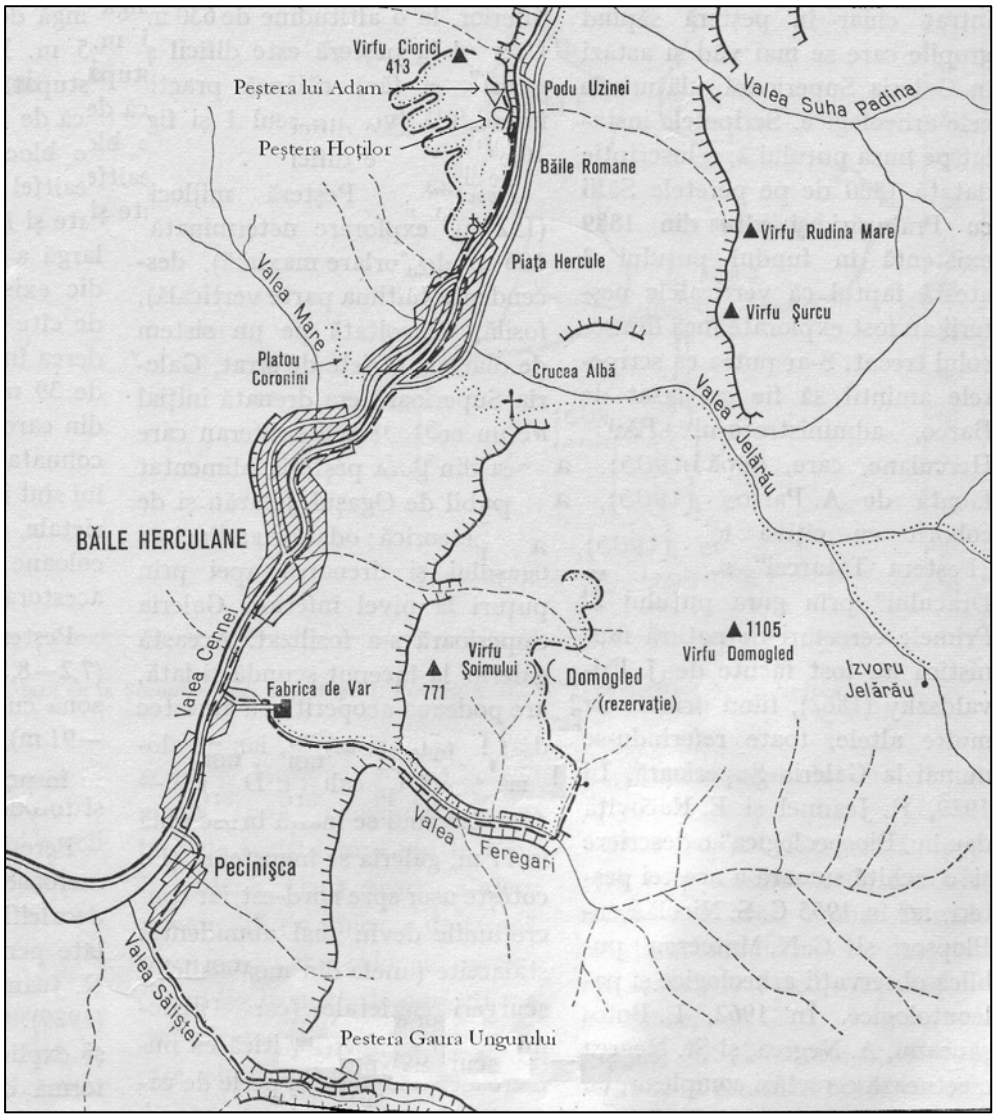

Fig. 1 – Site area Herculane Spa. Location of the caves.
(After Bleahu *et al*., 1976).

1.1. Hydroxylapatite, $Ca_5(PO4)_3(OH)$ is the most abundant mineral, represented by crusts of creamy white consistence, less frequently ochre, and which often coats the limestone debris in the guano layer, while nodular formations or bony, digested fragments are rarer.

The diffractometry assay evidenced a high degree of crystallinity; the reticular distances, both measured and calculated, the relative intensities and the

Miller indices (hkl) for the reflexes attributed univocally to hydroxylapatite in two representative samples from the Peştera lui Adam (Cave) are shown in Table 1.

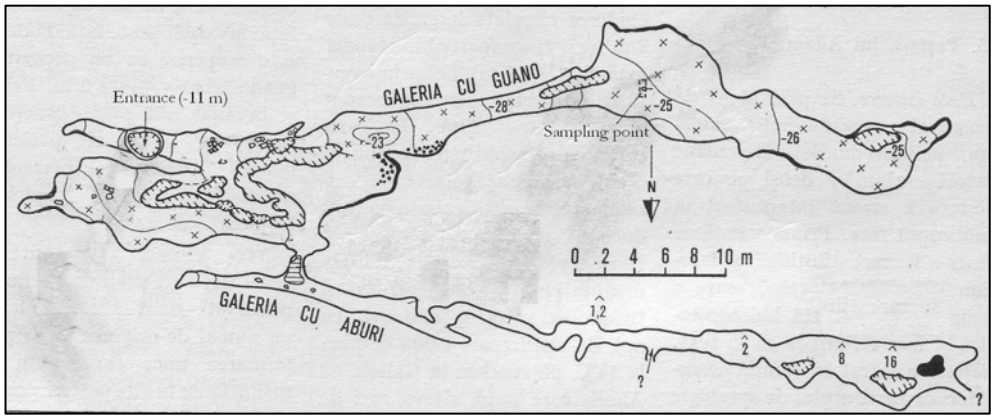

Fig. 2 – Peştera lui Adam. Sketch; location of the sampling point.

(Map modified after Povară *et al*., 1972).

Table 1

X-ray diffractometric data obtained from hydroxylapatite powders from the Peştera lui Adam

No.	Sample PAA 4 A			Sample PAA 5 B			(hkl)
	$d_{meas.}$ (Å)	$d_{calc.}$ (Å)	I / I_0	$d_{meas.}$ (Å)	$d_{calc.}$ (Å)	I / I_0	
1	4,0515	4,0776	7	4,0917	4,0807	7	(200)
2	–	–	–	3,8668	3,8868	7	(111)
3	3,4355	3,4391	61	3,4325	3,4377	57	(002)
4	3,1649	3,1689	9	3,1558	3,1681	12	(102)
5	3,0709	3,0823	14	3,0863	3,0847	13	(210)
6	2,8018	2,8128	100	2,8112	2,8144	100	(211)
7	2,7759	2,7772	76	2,7807	2,7772	85	(112)
8	2,7069	2,7184	53	2,7182	2,7204	63	(300)
9	2,2905	2,2954	11	2,2825	2,2959	15	(212)
10	2,2601	2,2619	15	2,2592	2,2635	27	(130)
11	2,0569	2,0613	10	2,0508	2,0610	8	(113)
12	2,0008	1,9985	15	1,9992	1,9983	8	(203)
13	1,9385	1,9426	38	1,9430	1,9434	33	(222)
14	1,8881	1,8898	18	1,8921	1,8905	23	(132)
15	1,8392	1,8396	33	1,8400	1,8396	36	(213)
16	1,8153	1,8053	12	–	–	–	(321)
17	1,7972	1,7796	15	1,7821	1,7809	10	(410)
18	1,7534	1,7538	15	1,7504	1,7546	13	(402)
19	1,7206	1,7229	21	1,7196	1,7240	25	(141)

20	1,7019	1,7196	3	1,7196	1,7189	25	(004)
21	1,6713	1,6826	5	1,6797	1,6820	6	(104)
22	1,5837	1,5870	4	–	–	–	(501)
23	1,5837	1,5805	4	–	–	–	(412)
24	1,5765	1,5695	6	1,5728	1,5706	7	(330)
25	1,5410	1,5410	32	1,5487	1,5423	4	(240)
26	1,4707	1,4737	12	1,4737	1,4745	7	(502)
27	1,4525	1,4532	7	1,4511	1,4531	21	(304)
28	1,3540	1,3564	4	1,3579	1,3560	2	(105)
29	–	–	–	1,3488	1,3484	5	(105)
30	1,3282	1,3290	6	1,3271	1,3295	4	(503)
31	1,3150	1,3145	9	1,3160	1,3146	10	(404)
32	1,3014	1,3035	7	1,3013	1,3031	6	(205)
33	1,2325	1,2343	12	1,2343	1,2348	4	(513)
34	1,2221	1,2208	5	1,2221	1,2216	9	(252)
35	1,1753	1,1752	6	1,1764	1,1752	5	(135)
36	1,1432	1,1464	9	–	–	–	(006)
37	1,1156	1,1150	10	1,1162	1,1153	5	(514)
38	1,1156	1,1149	10	1,1162	1,1153	10	(116)
39	–	–	–	1,1040	1,1041	6	(352)

Parameters for the elemental cells calculated by refinement using the least-square method on the two samples (Cu *Kα* radiation filtered through *Ni* = 1.54056 Å, $2\theta = 10 - 88^0$, number of refinement cycles: 3, 6, 4) are:

– α (Å) = 9.417(3), *c* (Å) = 6.878 (3), *V* (Å³) = 582.2 (3), n $^{(1)}$ = 4, N $^{(2)}$ = 31, I.C. $^{(3)}$ = 0.053 (for the PAA 4A sample) and,

– α (Å) = 9.424 (2), *c* (Å) = 6.875 (3), *V* (Å³) = 528.8 (3), n $^{(1)}$ = 3, N $^{(2)}$ = 62, I.C. $^{(3)}$ = 0.047 (for the PAA 5B sample).

These are close to those determined by BRUNET *et al.* (1999) for the stoechiometric hydroxylapatite: α = 9.421 (2) Å, *c* = 6.882 (3) Å

1.2. The Ardealite, $Ca_2(PO_3OH)$ SO4 . $4H_2O$, appears frequently in powder-like state together with gypsum from which it is nevertheless distinct due to its creamy-white color and a less evident shine, on the hydroxylapatite crusts.

The identification of the mineral was performed exclusively by diffractometric techniques, after obtaining relatively pure separates. The measured and calculated inter-reticular distances, the Miller indices and the relative intensities for the main diffractometric reflexes are given in the Table 2 for two representative ardealite samples.

The parameters for the elemental cells computed after "n" refinement cycles using the least squares method, on the basis of "N" diffractometric reflexes from the value interval 2θ ranging from 10^0 and 90^0 and univocally attributed to ardealite (Cu *Kα,* filtered by Ni, λ = 1.54056 Å, where the number of cycles was respectively 3, 4, 7) are:

– *a* (Å) = 5.716 (2), *b* (Å) = 40.985 (10), *c* (Å) = 6.261 (3), $\beta^{(0)}$ = 117.16 (2) *V* (Å³) = 986.8 (5), n $^{(1)}$ = 4, N $^{(2)}$ = 88,

– *a* (Å) = 5.719 (2), *b* (Å) = 30.967 (9), *c* (Å) = 6.250 (2), $\beta^{(0)}$ = 117.12 (2) *V* (Å³) = 984.7 (4), n $^{(1)}$ = 7, N $^{(2)}$ = 93

These values are comparable to those calculated by SAKAE *et al.* (1978) for synthetic ardealite (*a* = 5.721 (5) Å, *b* = 30.992 (5) Å, *c* = 6.250 (4) Å and *β* = 117.26 (6)^0

Table 2

X-ray diffractometric data obtained from ardealite powders from the Peştera lui Adam (Cave)

No.	Sample PAA 6 A			Sample PAA 6 B			(hkl)
	$d_{meas.}$ (Å)	$d_{calc.}$ (Å)	I / I_0	$d_{meas.}$ (Å)	$d_{calc.}$ (Å)	I / I_0	
1	7,6868	7,7464	100	7,6765	7,7418	100	(040)
2	4,2507	–	40	4,2509	–	60	–
3	4,1292	–	7	4,1311	–	6	–
4	3,9164	3,9314	4	3,9391	3,9319	4	(–151)
5	3,9164	3,9313	4	3,9391	3,9294	4	(150)
6	3,8610	3,8732	24	3,8633	3,8709	28	(080)
7	3,7941	3,7874	4	3,7919	3,7829	10	(061)
8	3,3270	3,3390	6	3,3355	3,3383	75	(–171)
9	3,3270	3,3389	6	3,3355	3,3372	75	(170)
10	–	–	–	3,1704	3,1769	13	(081)
11	2,9732	2,9819	6	2,9936	2,9796	11	(131)
12	–	–	–	2,8009	2,8117	34	(–221)
13	2,5378	2,5429	17	–	–	–	(200)
14	2,4419	2,4518	19	2,4452	2,4478	15	(062)
15	2,1567	2,1582	3	2,1538	2,1573	4	(–1.13.1)
16	2,1567	2,1581	3	2,1538	2,1570	4	(1.13.0)
17	–	–	–	2,0685	2,0690	20	(0.10.2)
18	–	–	–	1,9767	1,9779	1	(–223)
19	1,9657	1,9784	4	1,9767	1,9761	1	(221)
20	1,9308	1,9366	11	1,9370	1,9355	15	(0.16.0)
21	1,8917	1,8937	4	1,8959	1,8916	10	(1.13.1)
22	1,8917	1,8928	4	1,8959	1,8914	10	(0.12.2)
23	1,8729	1,8798	5	1,8728	1,8776	9	(172)

24	1,8617	1,8608	5	1,8568	1,8587	9	(261)
25	1,6953	1,6928	5	1,6881	1,6920	10	(–313)
26	1,6953	1,6927	5	–	–	–	(310)
27	1,6668	1,6695	5	1,6692	1,6696	14	(–2.14.2)
28	1,5847	1,5832	3	1,5845	1,5835	8	(–373)
29	1,5692	1,5656	3	1,5643	1,5640	8	(–1.13.3)
30	1,5417	1,5407	9	1,5409	1,5403	13	(–2.16.2)
31	1,5417	1,5406	9	1,5409	1,5399	13	(2.16.0)
32	1,4953	1,4926	2	1,4904	1,4916	13	(0.20.1)
33	1,4191	1,4171	2	1,4160	1,4163	4	(–1.21.0)
34	–	–	–	1,4064	1,4059	9	(–442)
35	–	–	–	1,3691	1,3685	9	(–1.17.3)
36	1,3490	1,3469	3	1,3496	1,3450	6	(–1.11.4)
37	1,3490	1,3468	3	1,3496	1,3446	6	(1.11.3)
38	1,3392	1,3370	2	–	–	–	(–463)
39	1,3392	1,3369	2	–	–	–	(–461)
40	1,3331	1,3334	2	1,3338	1,3326	10	(1.21.1)
41	1,3242	1,3231	3	1,3216	1,3223	10	(–2.20.2)
42	–	–	–	1,2974	1,2903	4	(–4.10.2)
43	1,2884	1,2880	3	1,2869	1,2877	9	(–3.11.4)
44	1,2818	1,2826	2	1,2801	1,2814	8	(–1.19.3)
45	1,2723	1,2714	8	1,2742	1,2719	10	(400)
46	–	–	–	1,2554	1,2558	10	(0.22.2)
47	–	–	–	1,2554	1,2541	10	(–444)
48	1,2513	1,2503	5	1,2554	1,2506	10	(–4.12.2)

1.3. Brushite, $CaH(PO_4) \cdot 2H_2O$ was identified as being totally isolated in the phosphate sediment included in this analysis, where it is present in the form of micro-crystalline powdery aggregates, of bright white texture with a *specific* shine.

Because of the mixing with ardealite we could not obtain pure enough separates which would have allowed the recording of reproducible diffractograms. However, the reflex doubling around the 7.7 Å mark confirms a mixture of ardealite, brushite and quartz, with a possible indexing of brushite using diffractometric lines. The elemental cells values, obtained through refinement using the least squares method for the 2θ interval, between 5^0 and 90^0, (Cu *Kα,* λ = 1.5406 Å) attributed to brushite are a = 5.803 (2) Å, b = 15.179 (7) Å, c = 6.261 (4) Å, $\beta = 116.12\ (3)^0$.

The main contrast with numbers given by BEEVERS (1958) or CURRY and JONES (1971) for the stoechiometric brushite [a = 5.812 (2) Å, b = 15.180 (3) Å, c = 6.239 (2) Å, $\beta = 116.43\ (3)^0$] is mainly due the interference with ardealite lines included in the sample used for analysis.

1.4. Gypsum, $CaSO_4 \cdot 2H_20$ appears in the shape of efflorescent layers associated with crust-like ardealite sediments, from which it's distinct because of its shiny white color. Table 3 contains both measured and calculated inter-reticular distances, the relative intensities and Miller indices (hkl) for the main diffractometric reflexes recorded on a representative sample of gypsum from Peştera lui Adam (Cave).

Table 3

X-ray diffractometric data obtained for gypsum powder from the Peştera lui Adam (Cave)

No.	Sample PAA 6 B			(hkl)	Nr. crt.	Sample PAA 6 B			(hkl)
	$d_{meas.}$ (Å)	$d_{calc.}$ (Å)	I / I_0	(hkl)		$d_{meas.}$ (Å)	$d_{calc.}$ (Å)	I / I_0	(hkl)
1	7,6765	7,5868	79	(020)	47	1,4975	1,4947	10	(–361)
2	4,7901	4,7492	3	(110)	48	1,4842	1,4857	6	(–314)
3	4,2539	4,2771	100	(–121)	49	1,4379	1,4417	5	(143)
4	3,7919	3,7934	8	(040)	50	1,4379	1,4352	5	(073)
5	3,7919	3,7963	8	(031)	51	1,4379	1,4363	5	(004)
6	3,1704	3,1698	10	(–112)	52	1,4297	1,4262	5	(–183)
7	3,0578	3,0602	73	(–141)	53	1,4160	1,4183	4	(–402)
8	2,8722	2,8788	41	(121)	54	1,4064	1,4050	7	(321)
9	2,8722	2,8726	41	(002)	55	1,3943	1,3942	4	(–422)
10	2,7164	2,7290	15	(–132)	56	1,3862	1,3855	6	(–413)
11	2,5986	2,5943	3	(150)	57	1,3561	1,3576	8	(–411)
12	2,5323	2,5289	7	(060)	58	1,3265	1,3254	8	(–381)
13	2,4973	2,5002	18	(200)	59	1,3265	1,3269	8	(163)
14	2,4452	2,4504	12	(–222)	60	1,3265	1,3251	8	(262)
15	2,4027	2,4058	9	(141)	61	1,3216	1,3213	10	(370)
16	2,3700	2,3746	6	(220)	62	1,3115	1,3142	7	(192)
17	2,2991	2,2901	4	(042)	63	1,2974	1,3000	3	(–215)
18	2,2089	2,2153	7	(–152)	64	1,2974	1,2946	3	(–404)
19	2,0862	2,0876	13	(240)	65	1,2869	1,2851	7	(–174)
20	2,0685	2,0783	16	(–251)	66	1,2801	1,2824	6	(291)
21	2,0319	2,0281	4	(071)	67	1,2742	1,2766	8	(–383)
22	1,9370	1,9380	12	(132)	68	1,2742	1,2761	8	(–424)
23	1,8959	1,8982	8	(062)	69	1,2554	1,2550	8	(–392)
24	1,8959	1,9000	8	(013)	70	1,2489	1,2502	6	(–325)
25	1,8728	1,8793	7	(–143)	71	1,2489	1,2501	6	(400)
26	1,8353	1,8400	7	(231)	72	1,2489	1,2489	6	(064)
27	1,7844	1,7810	9	(–181)	73	1,2334	1,2335	8	(420)
28	1,7760	1,7780	8	(260)	74	1,2334	1,2321	8	(–284)
29	1,7647	1,7616	3	(–332)	75	1,2290	1,2295	5	(–374)
30	1,7282	1,7258	5	(152)	76	1,2290	1,2284	5	(–1.12.1)
31	1,7282	1,7224	5	(–271)	77	1,2235	1,2252	6	(–444)
32	1,7084	1,7069	8	(–253)	78	1,2208	1,2220	5	(233)
33	1,6881	1,6831	5	(–323)	79	1,2095	1,2096	6	(312)
34	1,6692	1,6649	11	(–341)	80	1,2041	1,2042	7	(183)
35	1,6444	1,6439	5	(–163)	81	1,2041	1,2029	7	(282)

36	1,5942	1,5977	10	(–352)		82	1,2041	1,2022	7	(–345)
37	1,5942	1,5976	10	(190)		83	1,1981	1,1988	4	(134)
38	1,5845	1,5828	7	(082)		84	1,1941	1,1936	6	(–145)
39	1,5845	1,5831	7	(330)		85	1,1889	1,1873	7	(440)
40	1,5746	1,5711	12	(–343)		86	1,1707	1,1714	3	(1.12.1)
41	1,5321	1,5301	6	(–282)		87	1,1707	1,1709	3	(–473)
42	1,5235	1,5267	8	(123)		88	1,1629	1,1631	5	(253)
43	1,5235	1,5218	8	(–134)		89	1,1629	1,1612	5	(–415)
44	1,5145	1,5174	8	(0.10.0)		90	1,1571	1,1573	6	(0.12.2)
45	1,5145	1,5111	8	(280)		91	1,1514	1,1526	5	(–464)
46	1,4975	1,4949	10	(–273)		92	1,1514	1,1526	5	(1.11.2)

The elemental cells parameters obtained after 8 refinement cycles using the least-squares method, on the basis of 103 diffractometric reflexes from the values interval 2θ ranging from 5^0 to 90^0 (Cu *Kα*, λ = 1.54056 Å) are α = 5.679 (2) Å, b = 15.174 (5) Å, c = 6.525 (2) Å and β = 118.29 (2) ^{0}. Values are close to those calculated for the Hampshire gypsum, in the UK, by PEDERSEN and SEMMINGSEN (1982), [α = 5.679 (5) Å, b = 15.202 (14) Å, c = 6.522 (6) Å, β = 118.43(4) ^{0}].

1.5. Quartz, *αSiO₂* is a common occurrence, in association with hydroxylapatite, where it appears in the shape of milky-white granules or pellets.

The elemental cells parameters for two representative samples of α-quartz taken from Peştera lui Adam, established after "n" refinement cycles using the least-squares method, starting from "N" diffractometric reflexes from the values interval 2θ ranging from 5 to 90° (Cu *Kα*, λ = 1.54056 Å), attributed univocally to quartz, are as following:

– Sample PAA 5A: α = 4.914 (18) Å, c = 5.499 (34) Å, V = 113.0(6) Å^3, (n = 3, N = 19)

– Sample PAA 5B: α = 4.912 (2) Å, c = 5.405 (5) Å, V = 113.0(1) Å^3, (n = 3, N = 19).

In both cases the calculated parameters are relatively close to those determined by WILL *et al.* (1988) for the stoechiometric α – quartz [α = 4.91239(4) Å, c = 5.40385 (7) Å and V = 112.933 Å^3].

2. GAURA UNGURULUI CAVE

This cavity, also known as the Gaura Ungurului from Pecinişca Cave has a total gallery span of 196 m (see Fig. 3), deep down into the Malm-Neocomian limestone of the Domogled massive, east of Pecinişca, a community neighboring Băile Herculane to the south.

Due to its easy access via four entrances, all situated at approximately 20 m high in relation to the western wall of the Pecinişca Gorge, (which cuts through the

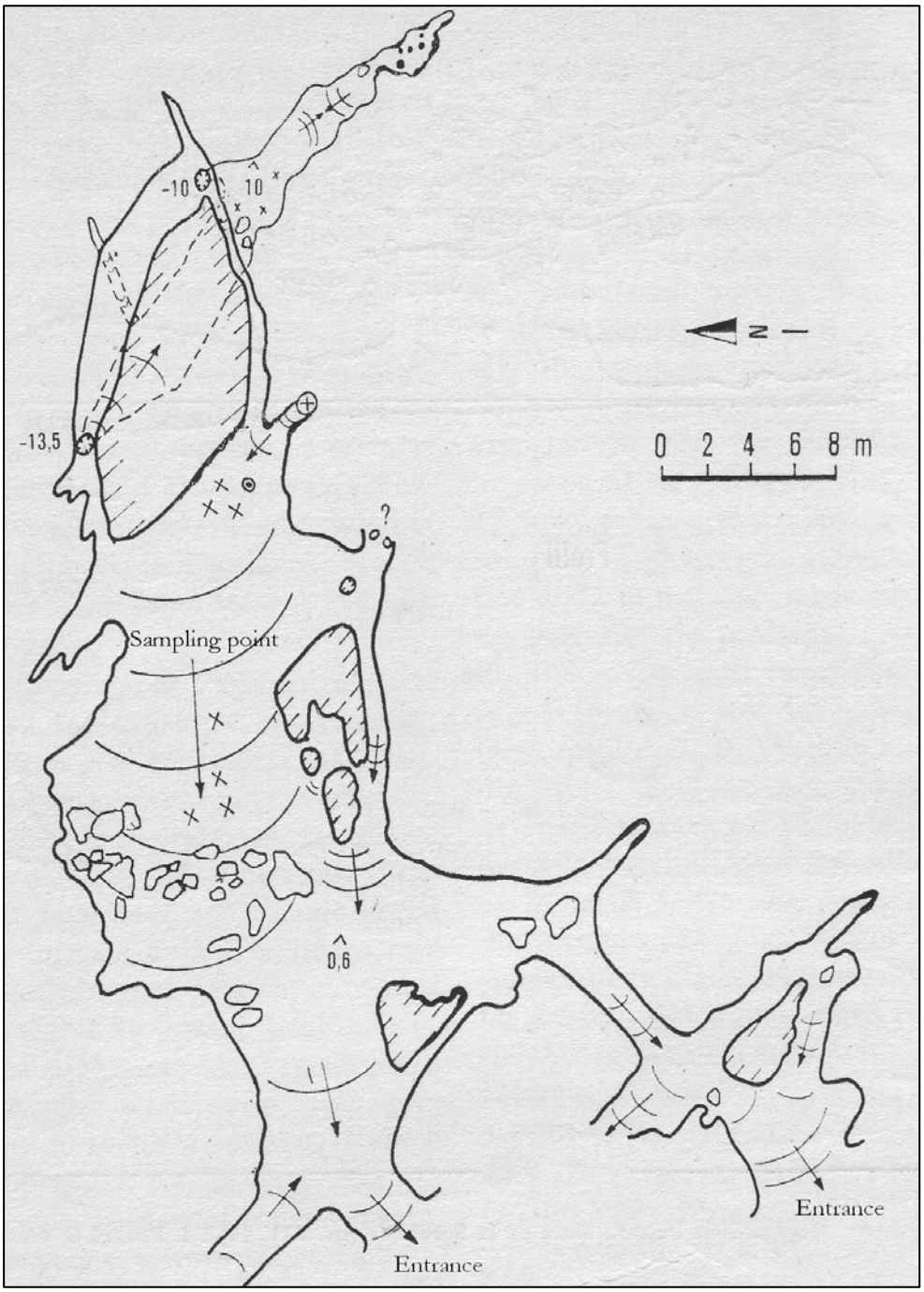

Fig. 3 – Gaura Ungurului Cave; location of the sampling point.
(Map modified after Botoşăneanu *et al*., 1967).

Salištea Valley), this cave was explored by biologists since the beginning of the 20th century (MEHELY, 1900). We drew mineralogical samples from the hall directly communicating with all the entrances, whose floor is basically covered in its entirety by a thick layer of guano. Our analysis evidenced the presence of mainly taranakite, and to a much lesser extent that of quartz.

2.1. Taranakite, $K_3Al_5(HPO_4)$. $18H_2O$, represents the essential mineral found in our samples. It appears in guano deposits as streaks of white or creamy-white matter placed at the interface with detritic levels in *terra rosa* facies.

X-ray diffractograms on taranakite powders show well defined peaks; values "d" for the inter-reticular distances both calculated and measured, the relative intensities I/I_0 and Miller indices (hkl) corresponding to two significant samples, are shown in Table 4. The elemental cells parameters obtained for the two samples using refinement through least-squares method starting from sets of 121, respectively 99 diffractometric reflexes from the 2θ interval ranging from 5^0 to 86^0 (Fe$K\alpha$, filtered with Mn, λ = 1.93735 Å) are:

– sample PGU 8A: a = 8.673(2) Å, c = 94.80(3) Å, V = 6176 (3) Å^3,a:c = 0.091:1;

– sample PGU 12A: a = 8.646(2) Å, c = 94.67 (4) Å, V = 6128 (3) Å^3, a:c = 0.091:1

Numbers are similar to those supplied by FIORE and LAVIANO (1991) for the Apulia Cave in Italy (a = 8.676(6) Å, c = 95.56(8) Å).

Table 4

X-ray diffractometric data obtained for significant samples of taranakite in the Gaura Ungurului Cave

No.	Sample PGU 8 A			Sample PGU 12 A			(hkl)
	$d_{meas.}$ Å	$d_{calc.}$ Å	I / I_0	$d_{meas.}$ Å	$d_{calc.}$ Å	I / I_0	
1	15,7098	15,8007	100	15,6939	15,7741	100	(006)
2	7,9777	7,9003	29	7,8725	7,8871	35	(0.0.12)
3	7,3450	7,4183	38	7,3860	7,6987	34	(012)
4	7,1007	7,1599	10	7,1383	7,1415	7	(104)
5	5,8449	5,8872	32	5,8718	5,8737	28	(1.0.10)
6	5,0025	5,0294	8	5,0108	5,0187	9	(0.1.14)
7	4,6538	4,6520	9	4,6426	4,6424	10	(1.0.16)
8	4,3329	4,3364	18	4,3207	4,3249	15	(110)
9	4,2872	4,2961	29	4,2841	4,2848	26	(113)
10	4,1830	4,1816	6	4,1740	4,1709	4	(116)
11	4,0025	4,0099	12	3,9927	3,9998	13	(119)
12	3,7976	3,8015	89	3,7850	3,7921	85	(1.1.12)
13	3,7338	3,7378	24	3,7328	3,7306	26	(1.0.22)
14	3,5748	3,5758	49	3,5633	3,5673	46	(1.1.15)
15	3,3481	3,3477	24	3,3402	3,3401	24	(1.1.18)

16	3,2754	3,2842	29	3,2726	3,2762	26	(2.0.14)
17	3,1755	3,1720	19	3,1670	3,1644	20	(0.2.16)
18	3,1298	3,1274	71	3,1225	3,1205	76	(1.1.21)
19	2,9478	2,9436	16	2,9324	3,9369	17	(2.0.20)
20	2,9191	2,9202	7	2,9073	2,9140	8	(1.1.24)
21	2,7730	2,7785	12	2,7689	2,7711	12	(217)
22	2,7230	2,7289	22	2,7183	2,7232	26	(1.1.27)
23	2,7230	2,7195	22	2,7131	2,7125	21	(2.1.10)
24	2,6127	2,6161	31	2,6055	2,6104	34	(2.0.26)
25	2,5589	2,5602	11	2,5521	2,5538	12	(2.1.16)
26	2,5260	2,5299	7	2,5224	2,5237	7	(1.2.17)
27	2,4698	2,4728	4	2,4659	2,4662	5	(306)
28	2,4335	2,4355	1	2,4255	2,4296	1	(1.2.20)
29	2,3835	2,3866	23	2,3812	2,3805	23	(0.3.12)
30	2,3373	2,3380	6	2,3318	2,3325	7	(1.2.23)
31	2,2553	2,2602	7	2,2525	2,2562	10	(1.0.40)
32	2,2553	2,2572	7	2,2525	2,2534	10	(0.0.42)
33	2,1409	2,1435	7	2,1392	2,1387	7	(1.2.29)
34	2,1139	2,1147	4	2,1091	2,1096	4	(3.0.24)
35	2,0833	2,0826	8	2,0780	2,0771	7	(131)
36	2,0343	2,0346	5	2,0298	2,0293	5	(1.3.10)
37	1,8998	1,9007	7	1,8987	1,8961	6	(2.2.24)
38	1,8998	1,9021	7	1,8987	1,8980	6	(2.1.37)
39	1,8428	1,8419	3	1,8389	1,8371	4	(4.0.10)
40	1,8428	1,8448	3	1,8389	1,8404	4	(2.2.27)
41	1,7969	1,7974	6	1,7959	1,7941	10	(1.1.48)
42	1,7744	1,7742	7	1,7722	1,7754	7	(1.3.28)
43	1,7409	1,7413	3	1,7381	1,7377	5	(2.1.43)
44	1,6776	1,6765	3	1,6751	1,6729	6	(0.3.42)
45	1,6406	1,6390	7	1,6389	1,6346	7	(410)
46	1,6406	1,6368	7	1,6389	1,6325	7	(143)
47	1,6204	1,6194	5	1,6197	1,6153	6	(2.3.20)
48	1,5661	1,5650	3	1,5642	1,5609	3	(1.4.18)
49	1,5661	1,5647	3	1,5642	1,5612	3	(1.3.40)
50	1,5148	1,5142	2	1,5148	1,5108	1	(1.3.43)
51	1,4858	1,4846	2	1,4842	1,4819	3	(1.1.60)
52	1,4325	1,4320	1	1,4318	1,4283	2	(5.0.20)
53	1,4325	1,4320	1	1,4318	1,4283	2	(339)
54	1,4228	1,4217	3	1,4158	1,4191	7	(1.1.63)

2.2. Quartz, *αSiO₂* is practically omnipresent in association with the taranakite aggregates, in whose mass it is evidenced as coralloid aggregates.

The elemental cells values determined after "n" refinement cycles [using the least-squares method for quartz in association with the taranakite, departing from a standard number of 15 cycles attributable univocally to quartz, situated in the "d" values interval ranging from 4.3 and 1.3 Å (Fe$K\alpha$, λ = 1.93735 Å)] are:

– sample PGU 2A: α = 4.905(2) Å, c = 5.399(4) Å, V = 112.50(9) Å^3, (n = 3)
– sample PGU 8B: α = 4.907(1) Å, c = 5.402(3) Å, V = 112.64(6) Å^3, (n = 4).

These are reasonably close to those determined by WILL *et al* (1988) for the stoechiometric α – quartz [α = 4.91239(4) Å, c = 5.40385(7) Å, V = 112.933 Å^3].

3. HOŢILOR CAVE IN BĂILE HERCULANE (THE GROTA HAIDUCILOR CAVE)

The Hoţilor Cave in Băile Herculane is situated on the western slope of the Cerna Gorge, at approximately 25 m from the valley thalweg, dug in the same Malm-Neocomian limestone facies.

The total length of the cavity is only 143 m (Fig. 4), of which only the central hall presented interest to us. From here we took samples from the stratified levels opened by an old archaeological site that were later analyzed through X-ray diffractometry. The analysis evidenced a main mineral, and a subordinate one: hydroxylapatite and α-quartz.

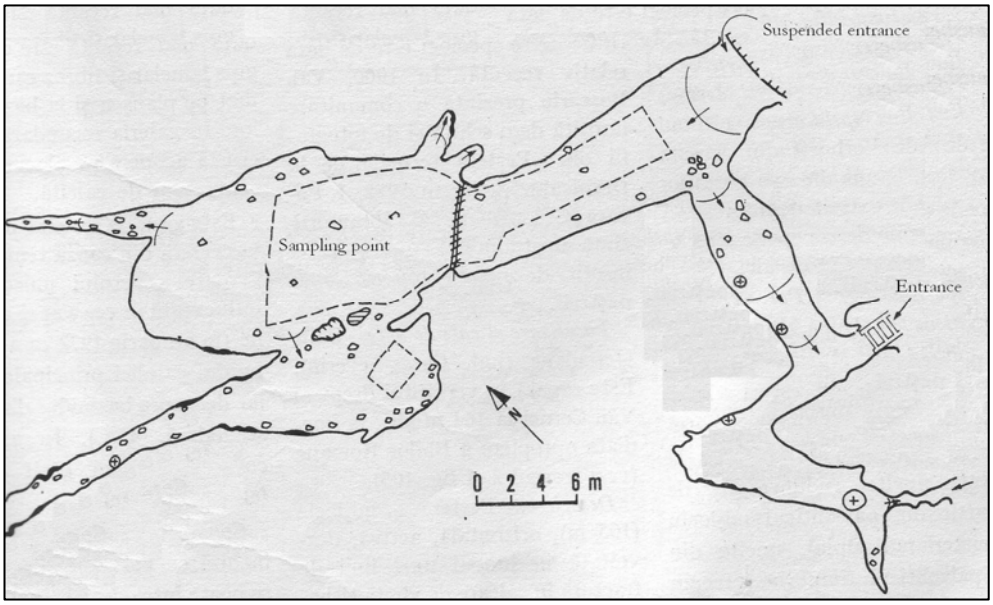

Fig. 4 – Hoţilor Cave; location of the sampling point.
(Map modified after Botoşăneanu *et al.,* 1967).

3.1. Hydroxylapatite, $Ca_5(PO_4)_3(OH)$ appears as a yellow or ochre dull crust. It is just slightly crystallized, with crystallinity indices calculated using the

method proposed by SIMPSON (1964) higher than 0.2. The measured and calculated inter-reticular distances, the Miller indices (hkl) and the relative intensities for the main diffractometric reflexes we obtained on a representative sample taken from Hoților Cave (samples PH 2A) are presented in Table 5.

Table 5

X-Ray Diffractometry data obtained from a significant sample of hydroxylapatite from the Hoților Cave in Băile Herculane

No.	Sample PH 2 A			(hkl)
	$d_{meas.}$ Å	$d_{calc.}$ Å	I / I_0	
1	5,2881	5,2518	3	(101)
2	3,8637	3,8820	8	(111)
3	3,4329	3,4336	35	(002)
4	3,1810	3,1643	95	(102)
5	2,8036	2,8109	100	(211)
6	2,7746	2,7738	58	(112)
7	2,6277	2,6259	18	(202)
8	1,9912	1,9958	10	(203)
9	1,9415	1,9410	21	(222)
10	1,8720	1,8700	14	(230)
11	1,8340	1,8374	28	(213)
12	1,8051	1,8043	75	(321)
13	1,7791	1,7787	19	(410)
14	1,7533	1,7524	13	(402)
15	1,7533	1,7506	13	(303)
16	1,7160	1,7168	22	(004)
17	1,6370	1,6422	7	(322)
18	1,5394	1,5404	41	(240)
19	1,5025	1,5031	9	(241)
20	1,4496	1,4482	11	(323)
21	1,3812	1,3869	17	(224)

Fe *Kα* radiation filtered with Mn (λ =1,93735 Å), $2\theta = 10^0 – 86^0$.

The elemental cells parameters determined for the above-said sample [a = 9.412(5) Å, c =6.867(6), V = 526.9(6) Å^3] are relatively close to those determined for the stoechiometric hydroxylapatite by BRUNET *et al.* (1999), [a = 9.421(2) Å, c = 6.882(3) Å].

3.2. Quartz, αSiO$_2$ appears in the form of crystalline aggregates of milky-white color, embedded in the hydroxylapatite crust.

The elemental cells parameters determined after three refinement cycles using the least-squares method, starting from 15 cycles attributable univocally to

quartz in an analyzed sample, lying in the interval 2θ ranging from 10 to 87° (Fe *Kα*, λ = 1.93735 Å) are: a = 4.908(2) Å, c = 5.400(4) Å, V = 112.64(7) Å^3. Numbers are relatively close to those determined by WILL *at al.* (1988) for the stoechiometric *α*-quartz (a = 4.9123(4), c = 5.4085 and V = 112.933 Å^3).

The present paper adds the mineralogical data to the previous information concerning biospeleology, archaeology and thermalism (POVARĂ *et al.,* 1972, BOTOŞĂNEANU *et al.* etc.) of the caves from the Băile Herculane area.

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