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Sequential dehydration of the phosphate–sulfate association from Gura Dobrogei Cave, Dobrogea, Romania

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Section S1. Representative X-ray powder data for secondary minerals from Gura Dobrogei Cave

Table S1. X-ray powder data for a selected sample of francoanellite from Gura Dobrogei Cave

	Sample GDb 11 A			(hkl)
	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I/I_o	
1	13.8797	13.7365	100	(006)
2	7.4141	7.4071	54	(012)
3	7.0936	7.0724	18	(104)
4	6.8771	6.8698	25	(0.0.12)
5	6.0857	6.0796	9	(018)
6	5.5779	5.5596	47	(1.0.10)
7	4.6481	4.6385	6	(0.0.14)
8	4.3519	4.3473	53	(110)
9	4.2963	4.2939	62	(113)
10	4.1514	4.1447	66	(116)
11	3.6832	3.6735	19	(1.1.12)
12	3.6119	3.6156	3	(0.1.20)
13	3.5409	3.5362	15	(208)
14	3.4124	3.4246	100	(0.2.10)
15	3.4124	3.4095	100	(1.1.15)
16	3.3483	3.3547	14	(1.0.22)
17	3.1581	3.1530	46	(1.1.18)
18	3.0443	3.0398	29	(0.2.16)
19	2.9118	2.9135	50	(1.1.21)
20	2.8476	2.8443	18	(211)
21	2.8476	2.8392	18	(122)
22	2.8079	2.8044	51	(125)
23	2.7774	2.7798	43	(2.0.20)
24	2.6890	2.6951	27	(1.1.24)
25	2.6890	2.6902	27	(2.1.10)
26	2.6626	2.6606	23	(1.2.11)
27	2.5633	2.5624	12	(1.2.14)
28	2.4932	2.4986	12	(1.1.27)
29	2.4932	2.4912	12	(2.1.16)
30	2.4682	2.4690	18	(306)
31	2.3630	2.3575	20	(0.3.12)
32	2.3359	2.3420	5	(1.2.20)
33	2.3033	2.3079	14	(1.0.34)
34	2.2631	2.2664	9	(2.1.22)
35	2.1697	2.1669	17	(223)
36	2.1697	2.1660	17	(1.1.33)
37	2.1449	2.1469	13	(226)
38	2.0887	2.0857	40	(312)
39	2.0887	2.0846	40	(0.1.38)
40	2.0578	2.0563	22	(137)
41	2.0211	2.0244	26	(1.3.10)
42	2.0211	2.0213	26	(2.2.15)
43	1.9645	1.9637	13	(2.2.18)
44	1.9645	1.9628	13	(0.0.42)
45	1.9347	1.9354	3	(1.3.16)
46	1.9111	1.9099	11	(1.2.32)

	Sample GDb 11 A			(hkl)
	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I/I_o	
47	1.9021	1.9016	18	(2.2.21)
48	1.8790	1.8805	17	(042)
49	1.8790	1.8797	17	(2.0.38)
50	1.8421	1.8456	19	(2.1.34)
51	1.8157	1.8181	16	(0.1.44)
52	1.8157	1.8145	16	(1.2.35)
53	1.7937	1.7930	11	(0.4.14)
54	1.7653	1.7681	9	(4.0.16)
55	1.7653	1.7643	9	(1.3.25)
56	1.7542	1.7544	15	(2.1.37)
57	1.7236	1.7253	22	(1.2.38)
58	1.7236	1.7214	22	(324)
59	1.7010	1.7037	18	(238)
60	1.7010	1.7034	18	(1.3.28)
61	1.6906	1.6917	16	(0.3.36)
62	1.6906	1.6882	16	(1.1.45)
63	1.6638	1.6667	4	(3.2.13)
64	1.6433	1.6431	32	(410)
65	1.6433	1.6424	32	(1.3.31)
66	1.6265	1.6273	8	(2.3.17)
67	1.6161	1.6173	13	(419)
68	1.5927	1.5932	22	(2.3.20)
69	1.5836	1.5860	17	(4.0.28)
70	1.5836	1.5823	17	(1.3.34)
71	1.5740	1.5743	18	(4.1.15)
72	1.5568	1.5561	18	(2.3.23)
73	1.5474	1.5466	9	(1.4.18)
74	1.5474	1.5462	9	(0.3.42)
75	1.5030	1.5045	16	(3.1.38)
76	1.5030	1.5019	16	(054)
77	1.4769	1.4762	14	(2.3.29)
78	1.4679	1.4669	14	(1.3.40)
79	1.4596	1.4611	21	(0.2.52)
80	1.4596	1.4590	21	(5.0.14)
81	1.4468	1.4484	18	(3.1.41)
82	1.4468	1.4469	18	(1.4.27)
83	1.4468	1.4447	18	(0.1.56)
84	1.4367	1.4347	12	(2.3.32)
85	1.3952	1.3979	15	(4.2.11)
86	1.3882	1.3899	15	(4.0.40)
87	1.3882	1.3884	15	(2.4.13)
88	1.3784	1.3816	6	(3.3.18)
89	1.3718	1.3723	14	(1.1.57)
90	1.3718	1.3710	14	(2.0.56)
91	1.3602	1.3600	9	(1.3.46)
92	1.3602	1.3594	9	(3.3.21)

Table S 2. X-ray powder data for a selected sample of monetite from Gura Dobrogei Cave

	Sample GDb 5 A			(hkl)
	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I/I_o	
1	6.6240	6.6855	12	(001)
2	6.6240	6.6425	12	(010)
3	5.4112	5.4672	4	(-101)
4	4.6647	4.6639	4	(0.-1.1)
5	4.5219	4.5372	2	(110)
6	4.2227	4.2154	65	(101)
7	4.0053	4.0664	3	(-1.-1.1)
8	3.3306	3.3489	100	(-102)
9	3.3306	3.3428	100	(002)
10	3.3306	3.3339	100	(200)
11	3.0766	3.0670	12	(-120)
12	2.9435	2.9437	98	(-121)
13	2.7125	2.7200	26	(201)
14	2.5024	2.5077	11	(112)
15	2.2252	2.2248	10	(-3.-1.1)
16	2.1638	2.1617	9	(2.-2.1)
17	1.9948	1.9892	19	(212)
18	1.9948	1.9889	19	(1.-3.1)
19	1.9648	1.9678	12	(-3.-1.2)
20	1.9648	1.9656	12	(-321)
21	1.9297	1.9239	17	(-231)
22	1.8479	1.8435	17	(-223)
23	1.8371	1.8330	8	(0.-2.3)
24	1.7917	1.7989	26	(-1.-3.2)
25	1.7917	1.7940	26	(-313)
26	1.7917	1.7913	26	(-232)
27	1.7309	1.7334	16	(-2.-2.3)
28	1.7309	1.7282	16	(-104)
29	1.7208	1.7236	30	(-401)
30	1.7208	1.7230	30	(-3.-1.3)
31	1.7208	1.7191	30	(-3.-2.2)
32	1.6920	1.6964	8	(1.-2.3)
33	1.6920	1.6895	8	(-114)
34	1.6730	1.6744	18	(-204)
35	1.6730	1.6740	18	(231)
36	1.6730	1.6711	18	(-402)
37	1.6631	1.6672	17	(203)
38	1.6631	1.6670	17	(400)
39	1.6452	1.6477	10	(321)
40	1.6452	1.6468	10	(-214)
41	1.6452	1.6465	10	(-410)
42	1.6452	1.6408	10	(-140)
43	1.6154	1.6195	11	(041)
44	1.6154	1.6129	11	(0.-1.4)
45	1.6060	1.6086	9	(213)
46	1.6060	1.6039	9	(0.-4.1)
47	1.5833	1.5885	4	(-4.-1.2)
48	1.5833	1.5873	4	(033)
49	1.5833	1.5853	4	(-233)

	Sample GDb 5 A			(hkl)
	$d_{meas.}$(Å)	$d_{calc.}$ (Å)	I/I_o	
50	1.5833	1.5835	4	(140)
51	1.5549	1.5595	4	(-124)
52	1.5549	1.5551	4	(-1.-4.1)
53	1.5549	1.5546	4	(0.-3.3)
54	1.5549	1.5539	4	(2.-3.2)
55	1.5380	1.5411	9	(-241)
56	1.5380	1.5372	9	(-420)
57	1.5380	1.5367	9	(-304)
58	1.5380	1.5352	9	(-403)
59	1.5380	1.5319	9	(104)
60	1.5221	1.5288	13	(401)
61	1.5221	1.5271	13	(141)
62	1.5221	1.5239	13	(-142)
63	1.5221	1.5211	13	(-314)
64	1.5147	1.5175	13	(3.-2.2)
65	1.5147	1.5161	13	(3.-3.1)
66	1.5147	1.5124	13	(330)
67	1.5147	1.5113	13	(4.-1.1)
68	1.5032	1.5078	9	(-1.-2.4)
69	1.5032	1.5056	9	(024)
70	1.5032	1.5008	9	(232)
71	1.4944	1.4933	7	(114)
72	1.4944	1.4922	7	(1.-1.4)
73	1.4858	1.4812	5	(-2.-3.3)
74	1.4769	1.4768	16	(223)
75	1.4769	1.4751	16	(0.-4.2)
76	1.4769	1.4742	16	(-3.-1.4)
77	1.4769	1.4741	16	(1.-3.3)
78	1.4769	1.4719	16	(-242)
79	1.4682	1.4692	3	(411)
80	1.4682	1.4682	3	(133)
81	1.4632	1.4621	8	(322)
82	1.4632	1.4610	8	(-2.-2.4)
83	1.4517	1.4541	9	(-1.-4.2)
84	1.4244	1.4268	5	(1.-4.2)
85	1.4244	1.4242	5	(4.-2.1)
86	1.4039	1.4051	10	(303)
87	1.3767	1.3804	6	(-105)
88	1.3767	1.3767	6	(-501)
89	1.3684	1.3668	6	(-404)
90	1.3684	1.3651	6	(313)
91	1.3553	1.3555	14	(-3.-3.3)
92	1.3553	1.3509	14	(-4.-2.3)
93	1.3385	1.3378	3	(2.-1.4)
94	1.3294	1.3252	5	(-2.-1.5)
95	1.3195	1.3208	6	(0.-3.4)
96	1.3195	1.3163	6	(-1.-4.3)
97	1.2916	1.2932	1	(-3.-4.1)
98	1.2654	1.2658	11	(-2.-4.3)

Section S2. Relict Minerals in the Guano Mass (Chapter 4.3)

4.3.1. Illite

Illite is a common constituent of the detrital sequences enclosed by the guano mass. It represents the most common clay mineral in the cave. In most cases, relict illite occurs in the taranakite + (francoanellite) + quartz aggregates, but the mineral can also occur as inclusions in hydroxylapatite crusts. SEM examination shows that the mineral occurs as clusters of randomly oriented irregular plates or, rarely, as aggregates of thick stacks of plates. Individual crystals are up to 10 µm wide and 1 µm thick. The XRD data match those of 2*M*1 illite; the unit cell parameters calculated for 13 representative samples are given in Table 3.

Table S 3. Crystallographic parameters of selected relict carbonates and silicates within the guano mass from Gura Dobrogei Cave.

Mineral Species	Space Group	Sample	*a* (Å)	*b* (Å)	*c* (Å)	$\beta^{(\circ)}$	*V* (Å^3)	n$^{(1)}$	N$^{(2)}$	2θ $^{(3)}$
calcite	$R\bar{3}c$	GDb 1 B	4.982(1)	-	17.041(5)	-	366.3(1)	3	25	10 - 90
calcite	$R\bar{3}c$	GDb 1 C	4.9825(9)	-	17.039(4)	-	366.3(1)	4	26	10 - 90
calcite	$R\bar{3}c$	GDb 2 B	4.983(2)	-	17.049(8)	-	366.6(3)	3	30	10 - 90
calcite	$R\bar{3}c$	GDb 4 C	4.9812(9)	-	17.031(5)	-	366.0(1)	3	26	10 - 90
calcite	$R\bar{3}c$	GDb 10 A	4.9849(6)	-	17.047(3)	-	366.84(9)	3	28	10 - 90
calcite	$R\bar{3}c$	GDb 13 A	4.989(3)	-	17.076(9)	-	368.1(6)	3	20	10 - 90
calcite	$R\bar{3}c$	GDb 14 A	4.981(2)	-	17.029(9)	-	365.9(2)	3	23	10 - 90
illite	*C*2/*c*	GDb 1 A	5.214(3)	9.023(5)	20.138(9)	95.80(3)	942.6(7)	6	46	10 - 90
illite	*C*2/*c*	GDb 2 A	5.177(2)	9.066(3)	20.202(7)	94.95(2)	944.6(4)	4	58	5 - 90
illite	*C*2/*c*	GDb 2 B	5.226(3)	9.016(4)	20.137(8)	95.62(2)	944.2(5)	6	90	5 - 90
illite	*C*2/*c*	GDb 4 A	5.212(4)	9.012(5)	20.125(9)	95.72(3)	940.5(6)	6	61	5 - 90
illite	*C*2/*c*	GDb 4 B	5.216(5)	9.013(5)	20.184(9)	95.54(4)	944.5(8)	5	51	5 - 90
illite	*C*2/*c*	GDb 5 B	5.211(3)	9.018(6)	20.142(9)	95.69(3)	941.9(7)	6	45	5 - 90
illite	*C*2/*c*	GDb 6 B	5.227(4)	9.008(6)	20.116(9)	95.07(5)	943.4(7)	3	53	5 - 90
illite	*C*2/*c*	GDb 9 A	5.207(5)	9.017(5)	20.124(9)	95.33(4)	940.8(8)	4	37	5 - 90
illite	*C*2/*c*	GDb 9 B	5.217(3)	9.019(4)	20.115(9)	95.66(2)	941.9(5)	10	64	5 - 90
illite	*C*2/*c*	GDb 11 B	5.201(5)	9.018(5)	19.99(2)	95.15(6)	934.0(9)	3	85	5 - 90
illite	*C*2/*c*	GDb 11 C	5.226(5)	9.037(9)	20.109(9)	95.30(5)	945.7(9)	5	52	5 - 90
illite	*C*2/*c*	GDb 12 A	5.224(3)	9.007(3)	20.145(8)	95.79(2)	943.0(5)	10	63	5 - 90
illite	*C*2/*c*	GDb 13 B	5.211(4)	9.027(5)	20.108(9)	95.60(3)	941.4(6)	10	82	5 - 90
kaolinite	*Cc*	GDb 11 C	5.146(2)	8.910(6)	14.549(7)	100.20(2)	656.5(4)	5	61	5 - 90
quartz	$P\,3_221$	GDb 2 B	4.912(1)	-	5.398(2)	-	112.78(6)	4	21	5 - 90
quartz	$P\,3_221$	GDb 3 B	4.918(1)	-	5.400(2)	-	113.12(5)	5	22	5 - 90
quartz	$P\,3_221$	GDb 4 A	4.908(2)	-	5.404(4)	-	112.76(9)	3	21	5 - 90
quartz	$P\,3_221$	GDb 4 B	4.910(2)	-	5.406(3)	-	112.88(7)	3	20	5 - 90
quartz	$P\,3_221$	GDb 6 B	4.916(1)	-	5.401(1)	-	113.06(5)	4	22	5 - 90
quartz	$P\,3_221$	GDb 8 A	4.912(1)	-	5.395(3)	-	112.73(7)	3	21	5 - 90
quartz	$P\,3_221$	GDb 8 B	4.909(1)	-	5.407(1)	-	112.85(3)	4	20	5 - 90
quartz	$P\,3_221$	GDb 9 A	4.919(1)	-	5.402(1)	-	113.21(2)	3	22	5 - 90
quartz	$P\,3_221$	GDb 12 A	4.910(1)	-	5.396(3)	-	112.65(6)	4	20	5 - 90

(1) Number of cycles of refinement; (2) Number of reflections used for refinement; (3) Range of 2θ angles used in collecting the reflections.

The XRD patterns were alternatively indexed accepting the 1*M*, 2*M*1 and 2*M*2 polytypism of the mineral. As the best fitting between the measured and the calculated XRD pattern was obtained for the monoclinic *C*2/*c* symmetry, this space group was accepted for the unit cell calculations. Consequently, the illite polytype from Gura Dobrogei is most probably the 2*M*1 one. The unit cell parameters in Table 3 are in reasonable agreement with those refined for 2*M*1 polytypes of illite: *a*

= 5.193(5) – 5.21(1) Å, b = 8.994(5) – 9.00(1) Å, c = 20.08(1) - 20.10(10) Å, β = 95.8 - 95.83° (Drits et al., 1993).

4.3.2. Kaolinite

Kaolinite occurs scarcely in the clayey mass composing the *terra rossa*, where the mineral is closely admixed with illite and quartz, in powdery ochre to reddish brown sequences, whose color is given by amorphous gels of iron oxi-hydroxides. The X-ray powder pattern of a kaolinite separate was analyzed by the fitting method, after the indexing in both the monoclinic 2*M* and triclinic 1*A* hypotheses of symmetry, in the space groups *Cc* and *C*1, respectively. As the differences between the measured and calculated inter-reticular distances are minimal in the *Cc* hypothesis of symmetry, it seems reasonable to consider that the kaolinite polytype from Gura Dobrogei is the 2*M* one. The monoclinic symmetry of kaolinite from Gura Dobrogei is also supported by the fact that the reflections corresponding to (131) and $(1\,\overline{3}\,1)$ in the XRD pattern are not well resolved, being represented by a unique peak which is indicative of an ordered kaolinite (Fialips et al., 2000, and references therein). The unit cell parameters refined for the most representative sample are given in Table 3. They are close to those calculated for the 2*M* kaolinite by the PDF (ICDD) file 01-075-0938 (a = 5.148 Å, b = 8.920 Å; c = 14.535 Å, β = 100.20°).

4.3.3. Quartz

Quartz occurs as milky-white clusters of crystals, embedded in the guano layers. It generally associates with taranakite, illite and francoanellite, but can also occur as inclusion in the hydroxylapatite or gypsum crusts. The individual crystals composing the quartz aggregates are up to 10 µm in diameter.

The unit cell parameters obtained by least-squares refinement for a number of representative samples are given in Table 3. Some other XRD patterns are available under request from the first author, increasing the number of unit cell refinements to 17. The mean unit cell parameters, obtained as average of the 17 sets of data, are: a = 4.912(5) Å, c = 5.402(8) Å and V = 112.9(2) Å^3. These values, as well as the individual values in Table 3, are very close to the unit cell parameters refined for the synthetic alpha-quartz by Will et al. (1988): a = 4.91239(4) Å, c = 5.40385(7) Å and V = 112.933 Å^3; this suggests that both the authigenic and allogenic quartz from Gura Dobrogei was crystallized at low pressures and temperatures (*e.g.*, Brice, 1980, Levien et al, 1980).

References

Brice, J.C.: The lattice constants of α-quartz. J. Mat. Sci., 15, 161-167, https://doi.org/10.1007/BF00552441, 1980.

Drits, V.A., Weber, L.F., Salyn, A.L., and Tsipursky, S.I.: X-ray identification of one-layer illite varieties: application to the study of illites around uranium deposits of Canada. Clays and Clay Minerals, 41, 3, 389-398, https://doi.org/10.1346/CCMN.1993.0410316, 1993.

Fialips, C.-I., Petit, S., Decarreau, A., and Beaufort, D.: Influence of synthesis pH on kaolinite "crystallinity" and surface properties. Clays and Clay Minerals, 48, 2, 173-184, https://doi.org/10.1346/CCMN.2000.0480203, 2000.

Levien, L., Prewitt, C.T., and Weidner, D.J.: Structure and elastic properties of quartz at pressure. Am. Mineral., 65, 920-930, 1980.

Will, G., Bellotto, M., Parish, W., and Hart, M.: Crystal structures of quartz and magnesium

germanate by profile analysis of synchrotron-radiation high-resolution powder data. J. Appl. Cryst., 21, 182-191, https://doi.org/10.1107/S0021889887011567, 1988.