

First reported sedimentary occurrence of berlinite (AlPO₄) in phosphate-bearing sediments from Cioclovina Cave, Romania—Comment

ȘTEFAN MARINCEA* AND DELIA-GEORGETA DUMITRAȘ

Department RIMTI, Geological Institute of Romania, 1 Caransebeș Street, RO-012271, Bucharest, Romania

ABSTRACT

In a recent work, Onac and White (2003) reported on berlinite, but also chlorellestadite and churchite, from the Bivouac Room, Cioclovina Cave, Romania. Our analyses of materials collected from this site failed to identify berlinite, chlorellestadite, or churchite. Due to the nature of the samples collected from the bat guano deposit at Cioclovina, many possible sources of confusion can occur. For example, separates from a mixture of taranakite, quartz, and minor illite could give the same analytical results as those reported by Onac and White (2003) for “berlinite”. For this reason, we consider that the occurrence of berlinite at Cioclovina, as well as the occurrence of other exotic species such as chlorellestadite or churchite, is not well enough substantiated and their report must be regarded with caution. Arguments to support this point of view are problems identified with the analytical techniques (EMPA, XRD), the failure of the experimental synthesis of berlinite in “dry” conditions at atmospheric pressure, and the geochemical context from Cioclovina.

INTRODUCTION

Onac and White (2003) reported the finding of berlinite, a rare high-temperature aluminum orthophosphate, in the phosphate-bearing sediments from the Cioclovina Cave, Romania (hereafter referred to as Cioclovina). After careful studies of this deposit, and particularly of the Bivouac Room, from which the quoted authors collected the material analyzed, we must disagree with their conclusions. Unfortunately, Onac and White (2003) were unable to provide splits of the material analyzed by them for re-investigation.

Aluminum orthophosphate (AlPO₄) crystallizes in seven polymorphic forms, analogues of high- and low-temperature forms of SiO₂, of which berlinite is isostructural with α -quartz (Strunz 1941; Muraoka and Kihara 1997), having a trigonal structure with space group *P*3₁21. Occurrences of berlinite are sparse and restricted to high-temperature rocks such as felsic meta- or igneous rocks, pegmatites, and hydrothermally altered rocks (Onac and White 2003; Veksler et al. 2003 and references therein).

The occurrence of berlinite in a bat guano deposit is then surprising and the analytical data reported by Onac and White (2003) are subjected to re-consideration. Our experience and previous work on phosphate assemblages from the Cioclovina Cave were used to understand the possibilities of confusion that gave rise to the mention of berlinite, as well as of two other exotic mineral species, churchite and chlorellestadite. The aim of this discussion is to re-evaluate the results reported by Onac and White (2003) in the light of our findings.

Techniques and operating conditions used to acquire the supplementary electron microprobe (EMP), X-ray powder dif-

fraction (XRD), and inductively coupled plasma-atomic emission spectrometry (ICP-AES) data needed for this discussion were essentially the same as described by Marincea et al. (2002), Marincea and Dumitraș (2003), and Dumitraș et al. (2004b). Supplementary XRD studies were carried out using a Philips PW 3710 diffractometer, under the following conditions: Mn-filtered FeK α radiation ($\lambda = 1.93735 \text{ \AA}$), 40 kV, 30 mA, step of 0.02°, 1 second per step counting time.

CHEMICAL COMPOSITION

Two different EMP analyses reported by Onac and White (2003) clearly gave results compatible with the presence of berlinite, i.e., Al:P ratios close to the ideal 1:1 for totals very close to 100 wt%.

The first problem arising from the report of Onac and White (2003) is that EMP analysis, and particularly the energy-dispersive method used by them, is not precise enough in the case of fine-grained and intergrown materials. As a rule, minerals from Cioclovina have very small dimensions: up to 7 μm were reported for taranakite (Marincea and Dumitraș 2003), up to 20 μm were mentioned for tinsleyite (Marincea et al. 2002), 1–10 μm were mentioned for brushite (Dumitraș et al. 2004b), etc. Although Onac and White (2003) did not mention the dimensions of the berlinite crystals, we suppose that they were in the range of those reported for the other phosphates. Because of the tiny crystals and the porous nature of the aggregates, microprobe results are expected to be poor; however, Onac and White (2003) reported surprisingly good analyses. In this particular case, the question is how a rastered or a defocused electron beam, which may be ideally used for analyzing phosphates in the bat-guano deposits, which are spongy and notoriously unstable under the electron beam, will avoid analytical interferences. If Onac and White

* E-mail: marincea@igr.ro

(2003) used a focused electron beam to analyze “berlinite”, it is likely that they promoted alkali migration such that, for example, ammonium-bearing taranakite or tinsleyite could be easily misidentified as berlinite.

On the other hand, the operating conditions chosen by Onac and White (2003) are neither clearly indicated nor appropriate for analyzing bat guano materials. A lower excitation voltage (e.g., 15 kV), a defocused electron beam (e.g., 8–10 μm) and the moving of the samples during the analysis so as to minimize decomposition of the mineral under the electron beam are necessary for obtaining good analyses for such materials. These conditions were used in our works on tinsleyite and taranakite (Marincea et al. 2002; Marincea and Dumitriș 2003), but differ from the analytical conditions used by Onac and White (2003) for analyzing “berlinite”. Both electron microprobes used by these authors were operated under excessively high excitation voltages (20 kV) and low beam currents (5 or 7.5 nA) for analyzing, for example, variscite, used by Onac and White (2003) as a standard. With no indications on the counting time used by Onac and White (2003) for analyzing “berlinite”, it is difficult to establish the degree of loss of alkalis if these exist in the sample, as well as the degree of the Al and P migration.

We suppose that peak profiles for both P and Al were generated by Onac and White (2003) using data for variscite, reported as an “internal standard”. This mineral is, however, not at all suitable for use as a microprobe standard, because it is notoriously unstable under vacuum and it decomposes under the electron beam. The possible influence of Al and P migration (Autefage and Fontan 1985) and chemical bonding on the analytical results must be considered, but, first of all, taranakite or tinsleyite analyzed using variscite as a unique standard will be easily misidentified as berlinite. The standards utilized for analyzing Fe and Si, reported by Onac and White (2003) in their “berlinite”, were not mentioned. Were other elements sought, but not detected? The general lack of information on the qualitative energy-dispersion scans is one of the weak points of the papers of Onac et al. (2002) and Onac and White (2003). As a particular note, because they neglected the Fe-for-Al and Si-for-P substitutions resulting from the chemical analysis, both “berlinite” structural formulas published by Onac and White (2003) are negatively charged!

Misidentification of taranakite as berlinite under these conditions would not be surprising, and we suppose that Onac and White (2003) carried out their analyses on taranakite, which is more common in the bat guano deposits and extremely abundant in the Bivouac Room. This mineral, ideally $(\text{K}, \text{NH}_4)_3\text{Al}_5(\text{HPO}_4)_6(\text{PO}_4)_2 \cdot 18\text{H}_2\text{O}$ (Dick et al. 1998), has an Al:P ratio close enough to 1:1 to give rise to the structural formula $(\text{K}, \text{NH}_4)\text{Al}_3(\text{PO}_4)_3(\text{OH}) \cdot 9\text{H}_2\text{O}$ admitted by Onac and White (2003). This ratio would normally be modified in the electron microprobe analyses, as is the case for all highly hydrated minerals (Autefage and Fontan 1985). Taranakite with an Al:P ratio of 1:1 could be misidentified as berlinite if we ignore the presence of K and the normally lower oxide sums. Extensive migration of alkalis in highly hydrated minerals during their EMP analysis with a high-energy beam is a well-known phenomenon (Autefage 1980; Autefage and Couderc 1980, etc.).

In particular, the question remains as to whether or not taranakite loses all K when exposed to the electron beam and

if the analytical totals recorded for this mineral could give rise to confusion. Our wavelength-dispersive EMP analyses of taranakite from Cioclovina allow a careful answer to this question. Analyzing micromounts of NH_4 -bearing taranakite with the same conditions described in Marincea et al. (2002), elevated sums of “non-volatile” oxides [other than H_2O and $(\text{NH}_4)_2\text{O}$] were obtained. These sums ranged from 74.73 to 79.64 wt%, higher than the ideal 64.31 to 71.82 wt%. Using a variscite standard, the analytical totals ranged from 96.81 to 103.17 wt%! Supposing that Onac and White (2003) analyzed taranakite, their analytical totals for “berlinite” are in the range of those quoted by us. Very low or even null K contents were also recorded, in spite of the cautions taken by us to prevent burn-up of the sample. The errors were especially important if beam currents higher than 5 nA and short counting times were used. This was the principal reason for renouncing the EMP analyses in our work on taranakite from Cioclovina (Marincea and Dumitriș 2003).

X-RAY POWDER DIFFRACTION DATA

An apparently solid argument used by Onac et al. (2002) and Onac and White (2003) to support the occurrence of berlinite at Cioclovina is the X-ray powder pattern that excellently matches berlinite with cell parameters $a = 4.941(2)$ and $c = 10.887(9)$ Å, and $V = 230.1(2)$ Å³ (as refined by us). Moreover, the distinction between berlinite and quartz by XRD is very delicate and only the presence of some weak lines in the pattern of berlinite and the shifting toward higher d values of the berlinite lines could help in discriminating between the two species.

Onac et al. (2002) and Onac and White (2003) extensively used X-ray powder diffraction analysis in order to identify the mineral species from Cioclovina. Apparently, too much credit was given to this method: beside berlinite, some other “exotic” species, such as churchite (ideally $\text{YPO}_4 \cdot 2\text{H}_2\text{O}$) and chlorellestadite [ideally $\text{Ca}_{10}(\text{SiO}_4)_5(\text{SO}_4)_3\text{Cl}_2$], were mentioned by Onac et al. (2002) and Onac and White (2003). It is conspicuous, however, that the XRD patterns of brushite and churchite or those of hydroxylapatite and chlorellestadite are very close, precluding good XRD diagnosis of these mineral species when qualitative chemical data are lacking. As a remark, the XRD lines in the pattern of chlorellestadite are located at higher d values than the homologous lines of hydroxylapatite (see PDF 41-0479 vs. PDF 86-1023), whereas the peaks in the pattern of churchite are located at lower d values than the homologous lines for brushite (see PDFs 85-1842 and 39-1385 vs. PDF 72-0713). If hydroxylapatite was misidentified as chlorellestadite, and brushite as churchite, this suggests serious variations in the measuring conditions during the XRD experiments and raises the question of whether the “berlinite” of Onac and White (2003) is not, in reality, ordinary quartz.

Supposing that the mineral identified by X-ray as berlinite is quartz, most of the peaks reported by Onac and White (2003) for “berlinite” can be satisfactorily indexed as quartz lines on the basis of a trigonal unit cell (space group $P3_121$) having $a = 4.938(1)$ and $c = 5.465(5)$ Å, and $V = 115.2(1)$ Å³: Table 1. These unit-cell parameters are, indeed, quite large, but even larger cell parameters were calculated for α -quartz near the pressure-induced amorphous transition by Chelikowsky et al. (1991). If extreme conditions governed the mineral genesis at Cioclovina,

such transitions could occur, but this is not our view.

All but two of the lines in the XRD pattern presented by Onac et al. (2002) and Onac and White (2003) could be satisfactorily indexed by taking into account the presence of a mixture of quartz and illite 2M1 [$a = 5.233(2)$, $b = 8.997(3)$, $c = 19.845(12)$ Å, and $\beta = 95.17(3)^\circ$] (Table 1). The presence of illite in the mixture could easily give interfering lines and cause shifting of some of the lines in the pattern. Moreover, we frequently found in the guano deposit from Cioclovina mixtures of quartz and illite, sometimes containing taranakite. The remainder, low intensity, lines at 3.989 and 2.303 Å (Table 1) could be due to some other admixed phases, e.g., other clay minerals or illite polytypes.

It is noteworthy, however, that the cell parameters obtained by us for 21 quartz samples collected from the Bivouac Room [$a = 4.905(7)$ – $4.918(8)$ and $c = 5.390(4)$ – $5.414(2)$ Å], as well as their mean values [$a = 4.913(4)$ and $c = 5.403(6)$ Å], are clearly smaller than the value deduced from the XRD pattern of Onac and White (2003). Were the lines in the pattern of Onac and White (2003) shifted toward higher values? A problem is that, apparently, $\text{CuK}\alpha_1$ peaks were corrected for cell refinement by reference to silicon, which was used as internal standard (Onac and White 2003), and that excludes the shifting of the lines in the pattern of “berlinite”, as supposed for “chlorellestadite” or “churchite”. In this case, the sample analyzed by Onac and White (2003) may, indeed, be berlinite, and a presentation of the original XRD pattern, together with the standard lines, could be of great help.

GENETIC CONSIDERATIONS

There is no convincing evidence that the guano deposit at Cioclovina underwent in situ combustion, as supposed by Onac and White (2003). Monetite (Onac et al. 2002) and bassanite, recently found by us (Dumitraș et al. 2004a), are the only possible products of thermal dehydration of pre-existing mineral species (i.e., brushite and gypsum), but these species were not found in the Bivouac Room. Neither francoanellite nor, for example, whitlockite, were detected in an association where taranakite,

hydroxylapatite, ardealite, and brushite are, and probably were, notoriously abundant.

As a supplementary remark, apatite from high-temperature deposits, such as skarns, is well known to be particularly sensitive to Si-for-P substitutions (e.g., Rouse and Dunn 1982). No traces of Si were recorded in the apatite samples from the Bivouac Room, which contain, however, up to 4.66 wt% Si in the fourfold coordinated sites (Dumitraș et al., in prep).

The hypothesis of the thermal breakdown of pre-existing Al-bearing phosphates due to the combustion of guano (Onac and White 2003) is unsustainable, because it is difficult to imagine that such a phenomenon could affect and completely transform only crandallite, tinsleyite or taranakite. We have studied all these phosphates and their thermal breakdown has been carefully observed (Constantinescu et al. 1999; Marincea et al. 2002; Marincea and Dumitraș 2003). Taking into account the results of our studies and of other data from the literature (see below), it is very difficult to sustain the genesis of berlinite by thermal breakdown of a hydrous Al-bearing phosphate.

SYNTHESIS OF “BERLINITE”—COMMENTS

Onac and White (2003) reported two successful syntheses of berlinite, having as starting materials variscite and taranakite + brushite, respectively. These are, to our knowledge, the first attempts to obtain berlinite at atmospheric pressure. Various authors have successfully synthesized berlinite, but their experiments were classical hydrothermal syntheses at high pressures (Wise and Loh 1976; Bass and Sclar 1979; Gomez Morales and Rodriguez Clemente 1990; Veksler et al. 2003). The successful annealing of berlinite reported by Onac and White (2003) deserves a brief discussion.

During the thermal analysis of crandallite (Blanchard 1971), tinsleyite-leucophosphate (Marincea et al. 2002; Marincea and Dumitraș, in prep) and taranakite (Balenzano et al. 1974; Marincea and Dumitraș 2003), one of the breakdown products above 600 °C is, indeed, AlPO_4 , but it is the tetragonal polymorph, isostructural with α -cristobalite (PDF 73-1977), or the orthorhombic one, isostructural with tridymite (PDF 48-0652; Marincea and Dumitraș 2003). In all cases, AlPO_4 obtained as breakdown product up to 600 °C is X-ray amorphous. In any case, berlinite was not obtained as a cooling product.

At higher temperatures, the beta modifications of AlPO_4 -cristobalite or AlPO_4 -tridymite must occur and were identified. As well as cristobalite or tridymite (Hammonds et al. 1996) these polymorphs can be easily supercooled without reversion to structures of the quartz type, but with transitions to their α phases (Debnath and Chaudhuri 1992). It is then surprising that Onac and White (2003) obtained berlinite as a product after slow cooling of a mixture of taranakite and brushite, previously heated to 600 °C.

Particularizing for taranakite, addition of brushite to this mineral does not change the nature of its breakdown phases, but can decrease the temperatures needed for their complete amorphization, since brushite introduces a supplementary exothermic effect which increases the local temperature at ~ 500 °C (Balenzano et al. 1974; Dumitraș et al. 2004b). More data are then needed to substantiate the hypothesis of crystallization of berlinite when heating taranakite + brushite, as reported by

TABLE 1. X-ray powder diffraction data for “berlinite”: A re-interpretation

d_{meas} (Å)	Quartz		Illite 2M1 (?)		
	d_{calc} (Å)	l/l_0	(hkl)	(hkl)	d_{calc} (Å)
4.277	4.276	20	(100)	(103)	4.279
3.989	-	4	-	-	-
3.619	-	2	-	(015)	3.619
3.367	3.366	100	(101)	(024)	3.362
2.471	2.469	7	(110)	-	-
2.303	-	7	-	-	-
2.255	2.249	8	(111)	(220)	2.255
2.140	2.138	13	(200)	(206)	-
1.991	1.991	5	(201)	(143)	1.991
1.830	1.831	18	(112)	-	-
1.682	1.683	5	(022)	-	-
1.666	-	1	-	(314)	1.658
1.615	1.616	2	(210)	-	-
1.551	1.550	10	(211)	-	-
1.461	1.464	2	(113)	-	-
1.425	1.425	1	(300)	-	-
1.391	1.391	5	(122)	-	-
1.381	1.385	7	(023)	(340)	1.374
1.294	1.299	3	(014)	(410)	1.290
1.262	1.263	2	(032)	(420)	1.252
1.234	1.234	4	(220)	-	-
1.205	1.208	2	(123)	-	1.195

Onac and White (2003).

To find a possible explanation, we can only suppose that the natural taranakite from Cioclovina used by Onac and White (2003) for the experimental synthesis of berlinite was not pure enough. During our work on taranakite (Marincea and Dumitraș 2003), owing to the relatively small quantities of admixed quartz, many samples of taranakite from Cioclovina were identified as monomineralic after preliminary XRD analysis. Etching these samples with HCl proved, however, that a quartz residuum was

still present, and then the samples did not consist of pure taranakite. Supposing that Onac and White (2003) used such an impure sample in their experiments, quartz XRD peaks must occur with complete amorphization of the other heated products and could be identified as berlinite peaks.

In order to clarify this problem, we also tried synthesizing berlinite at atmospheric pressure. Annealing taranakite + brushite in both inert and oxid atmospheres, from 1 to 30 h and at temperatures between 350 and 600 °C, always led to the formation of X-ray amorphous products or of orthorhombic AlPO_4 (isostructural with tridymite; see Debnath and Chaudhuri 1992), monoclinic $\text{KAl}(\text{P}_2\text{O}_7)$, and tetragonal $\beta\text{-Ca}_2\text{P}_2\text{O}_7$. Specific attempts to synthesize berlinite were carried out using three different mixtures of taranakite and brushite, with an experimental time of 20 h, at a temperature of 600 °C. These conditions are identical to those reported by Onac and White (2003) for one of their successful synthesis experiments. The heating products were always orthorhombic AlPO_4 isostructural with tridymite (PDF 48-0652), monoclinic $\text{KAl}(\text{P}_2\text{O}_7)$ (PDF 70-1534), and tetragonal $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ (PDF 33-0297), their proportion being evidently controlled by the brushite/taranakite ratio in the initial mixture. The most representative pattern is depicted in Table 2, whereas the cell parameters obtained for the experimental products are given in Table 3. The two other patterns are available upon request from the first author.

Onac and White (2003) also claimed the synthesis of berlinite by heating variscite at 350-600 °C for 27 h. We suppose that the nature of the breakdown product was recognized by XRD, but the authors gave neither XRD data nor more details on the conditions of synthesis. The question following from this second reported synthesis by Onac and White (2003) is why other authors (e.g., Arlidge et al. 1963) failed to obtain berlinite under the same conditions, but instead obtained AlPO_4 -tridymite. Last, but not least, Onac and White (2003) stated that “the X-ray powder pattern of the heated variscite was that of berlinite and is indistinguishable from the natural sample”. Corroborated with their initial affirmation that “berlinite exists in several polymorphic forms, which are analogs of the silica polymorphs high and low quartz, tridymite and cristobalite,” this sentence raises the question of whether Onac and White (2003) confounded berlinite with AlPO_4 -tridymite.

TABLE 2. X-ray powder diffraction data for heating products of taranakite + brushite (experiment 1)*

d_{meas} (Å)	Pattern	AlPO_4		$\text{KAl}(\text{P}_2\text{O}_7)$		$\text{Ca}_2(\text{P}_2\text{O}_7)$	
		d_{calc} (Å)	(hkl)	d_{calc} (Å)	(hkl)	d_{calc} (Å)	(hkl)
6.0753	2	-	-	-	-	6.1092	(004)
5.6834	19	-	-	5.6821	(110)	-	-
5.1762	4	-	-	5.1680	(111)	-	-
4.4923	7	-	-	-	-	4.5116	(104)
4.3613	52	4.3671	(020)	-	-	-	-
4.1337	53	4.1276	(211)	-	-	-	-
3.8600	55	3.8487	(212)	3.8493	(002)	-	-
3.5828	3	-	-	3.5885	(112)	-	-
3.5037	3	-	-	3.5105	(200)	-	-
3.3332	34	-	-	3.3276	(121)	3.3456	(200)
3.0900	39	-	-	-	-	3.0867	(116)
3.0510	60	-	-	3.0568	(202)	3.0546	(008)
2.9162	100	-	-	2.9147	(212)	2.9065	(212)
2.7784	6	-	-	2.7787	(211)	2.7787	(108)
2.6898	10	-	-	-	-	2.6874	(124)
2.5205	10	-	-	-	-	2.5159	(109)
2.3996	5	-	-	2.4015	(231)	-	-
2.3314	6	2.3331	(410)	2.3333	(123)	-	-
2.2550	5	-	-	-	-	2.2558	(208)
2.2206	9	-	-	2.2184	(232)	2.2212	(301)
2.1562	10	-	-	2.1566	(231)	-	-
2.1312	5	2.1301	(140)	-	-	2.1376	(218)
2.0836	7	2.0819	(414)	2.0834	(322)	-	-
2.0128	5	-	-	-	-	2.0109	(1.1.11)
1.9318	4	-	-	1.9321	(204)	-	-
1.8564	3	-	-	1.8576	(241)	1.8558	(320)
1.8088	9	-	-	1.8074	(213)	1.8094	(233)
1.7740	4	-	-	-	-	1.7757	(234)
1.7347	5	-	-	1.7359	(104)	1.7395	(2.0.12)
1.6608	3	1.6620	(435)	1.6614	(413)	-	-
1.5659	2	1.5589	(346)	1.5654	(153)	1.5641	(332)
1.5053	3	-	-	1.5047	(225)	1.5076	(416)
1.4579	3	1.4580	(615)	1.4579	(153)	1.4533	(244)
1.4335	1	-	-	1.4340	(135)	1.4331	(148)
1.4234	3	-	-	1.4238	(162)	1.4243	(2.3.11)

* Mn-filtered $\text{FeK}\alpha$ radiation, $\lambda = 1.93735 \text{ \AA}$.

TABLE 3. Cell parameters of the thermal breakdown products of taranakite + brushite *

Phase	$\text{KAl}(\text{P}_2\text{O}_7)$				AlPO_4			$\text{Ca}_2(\text{P}_2\text{O}_7)$		brushite/taranakite initial ratio
	a (Å)	b (Å)	c (Å)	β (°)	a (Å)	b (Å)	c (Å)	a (Å)	c (Å)	
Experiment 1	7.316(3)	9.673(4)	8.022(2)	106.33(2)	9.684(9)	8.734(8)	18.45(8)	6.691(6)	24.44(2)	1/1
Experiment 2	7.283(6)	9.674(8)	8.000(6)	106.44(4)	9.654(9)	8.675(9)	18.26(3)	6.689(6)	24.28(3)	1/0.76
Experiment 3	7.307(9)	9.668(9)	8.018(6)	106.21(5)	9.629(9)	8.713(9)	18.32(4)	6.682(6)	24.35(3)	1/5

* Mn-filtered $\text{FeK}\alpha$ radiation, $\lambda = 1.93735 \text{ \AA}$.

TABLE 4. Ba, Sr, Y, and selected REEs in calcium phosphates from Cioclovina (ppm)*

Element	hydroxylapatite (n = 20)				brushite (n = 13)				ardealite (n = 5)			
	Min.	Max.	Mean	St. dev.	Min.	Max.	Mean	St. dev.	Min.	Max.	Mean	St. dev.
Ba	4.20	40.80	12.90	10.39	0.74	14.70	2.73	3.73	0.88	20.00	6.65	8.11
Sr	29.00	182.00	76.20	37.41	2.10	20.00	8.49	4.92	4.80	39.00	15.16	13.59
Y	0.14	22.30	5.36	6.10	0.20	5.78	1.09	1.73	0.19	1.82	0.98	0.60
La	0.14	17.30	4.25	4.32	0.27	5.07	1.00	1.33	0.00	3.18	1.54	1.44
Ce	0.83	6.89	2.81	1.61	0.00	8.64	2.53	2.32	0.00	7.82	2.06	3.40
Eu	0.07	0.38	0.18	0.09	0.00	0.22	0.10	0.07	0.14	0.25	0.19	0.05
Yb	0.00	0.88	0.19	0.24	0.00	0.20	0.02	0.06	0.00	0.07	0.02	0.03

* ICP-AES analyses.

OTHER EXOTIC MINERAL SPECIES

The crystal-chemical properties of Ca-phosphates, especially hydroxylapatite (Elliott 1994; Fleet and Pan 2000), but also brushite and ardealite, make them efficient traps for rare earth elements (REE), Sr, Ba, and Y if these elements are present in the system. Our analyses of these phosphates (Table 4) do not show any evidence of massive substitution of Ca by Sr, Ba, Y, or REE at Cioclovina. This should be, however, the normal behavior of these species in the case of their association with REE-bearing minerals such as churchite or with Sr-, Ba-, and REE-rich species such as burbankite, mentioned by Onac et al. (2002).

From the REE-bearing species, only churchite (ideally $\text{YPO}_4 \cdot 2\text{H}_2\text{O}$, but REE-rich species such as churchite-Nd or churchite-Dy are also known) was mentioned by Onac and White (2003), and this deserves a brief comment. It is noteworthy that churchite and brushite have similar structures. Possibilities of confusion stemming from the structural similarities are then evident and raises the question of whether churchite could really exist at Cioclovina.

The occurrences of churchite known so far are largely restricted to weathered chert, shale, limestone, granitic pegmatite, and vein deposits (Lottermoser 1987 and references therein) or to lateritic weathered mantles of carbonatites (Lottermoser 1987, 1990; Lapin 1992). In all cases, this mineral is associated with other REE-bearing species, usually secondary apatite (e.g., Lottermoser 1990). If the REE contents in apatite are in the range of those measured by us (Table 4), the report of churchite at Cioclovina is very doubtful, in spite of a supposed extreme mobility of the REE from an unmentioned source. Chemical analyses are obligatory to sustain the assumption of Onac and White (2003) that churchite exists at Cioclovina. As a substitute, Onac et al. (2002) gave a SEM microphotograph of a supposed churchite aggregate obviously showing platy crystals identical with those observed by us for brushite (Dumitraș et al. 2004b), and in evident contrast with the tufts and sheaves of acicular aggregates reported by the previous authors (e.g., Lottermoser 1987)!

Chlorellestadite is another "exotic" mineral species mentioned by Onac and White (2003) at Cioclovina and its hypothetical occurrence was used as an argument to support the genesis of berlinite by guano combustion. However, in a P-rich environment such that at Cioclovina, Si-substituted (chlor?)apatite and not chlorellestadite would be expected to occur. The silicate-sulfate status of chlorellestadite being well established (Rouse and Dunn 1982) we could expect that, in a P-rich environment, this mineral species at least associates with a high-temperature phosphate.

Pliego-Cuervo and Glasser (1978) and Neubauer and Pöllmann (1992, 1995) successfully synthesized chlorellestadite as a high-temperature phase, and the presence of this mineral in self-combusted sedimentary sequences is not unexpected. It is to note, however, that the presence of Si in the "berlinite" of Onac and White (2003) indicates the overall presence of silica and high temperature silicate phases such as wollastonite, gehlenite, spurrite would be expected to occur. But such phases, or their hydrothermal or weathering products (e.g., scawtite, xonotlite, tobermorite etc.), were not found in any of the samples examined by us and were not reported by Onac and White (2003). Last, but not least, considering the temperatures of chlorellestadite synthesis (800–1100 °C according to Pliego-Cuervo and Glasser

1978; 500–1050 °C according to Neubauer and Pöllmann, 1992; 700–1000 °C according to Neubauer and Pöllmann, 1995), we are surprised that at Cioclovina this mineral, if present, associates with berlinite, and not with AlPO_4 -tridymite or even AlPO_4 -cristobalite.

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REFERENCES CITED

- Arlidge, E.Z., Farmer, V.C., Mitchell, B.D., and Mitchell, W.A. (1963) Infra-red, X-ray and thermal analysis of some aluminium and ferric phosphates. *Journal of Applied Chemistry*, 13, 17–27.
- Autefage, F. (1980) Variations de la teneur en sodium et de potassium dans des minéraux au cours de leur analyse à la microsonde électronique. *Bulletin de Minéralogie*, 103, 48–53.
- Autefage, F. and Couderc, J.-J. (1980) Étude du mécanisme de la migration du sodium et du potassium au cours de leur analyse à la microsonde électronique. *Bulletin de Minéralogie*, 103, 623–629.
- Autefage, F. and Fontan, F. (1985) Comportement de minéraux hydratés au cours de leur analyse à la microsonde électronique. *Bulletin de Minéralogie*, 108, 293–304.
- Balenzano, F., Dell'Anna, L., and Di Piero, M. (1974) Ricerche mineralogiche su alcuni fosfati rinvenuti nelle grotte di Castellana (Bari): strengite aluminifera, vivianite, taranakite, brushite e idrossiapatite. *Rendiconti della Società Italiana di Mineralogia e Petrologia*, 30, 543–573.
- Bass, J.D. and Sclar, C.B. (1979) The stability of trolleite and the Al_2O_3 - AlPO_4 - H_2O phase diagram. *American Mineralogist*, 64, 1175–1183.
- Blanchard, F.N. (1971) Thermal analysis of crandallite. *Quarterly Journal of the Florida Academy of Sciences*, 34, 1–9.
- Chelikowsky, J.R., Troullier, N., Martin, J.L., and King, H.E. Jr. (1991) Pressure dependence of the structural properties of α -quartz near the amorphous transition. *Physical Review B*, 44, 489–497.
- Constantinescu, E., Marincea, S., and Craciun, C. (1999) Crandallite in the phosphate association from Cioclovina cave (Sureanu Mts., Romania). In N. Anastasiu and G. Ilinca, Eds., *Mineralogy in the System of Earth Sciences*, p. 1–5. Imperial College Press, London.
- Debnath, R. and Chaudhuri, J. (1992) Surface-bound titania-induced selective growth and stabilization of tridymite aluminum phosphate. *Journal of Solid State Chemistry*, 97, 163–168.
- Dick, S., Gossner, U., Weiss, A., Robl, C., Grossman, G., Ohms, G., and Zeiske, T. (1998) Taranakite—the mineral with the longest crystallographic axis. *Inorganica Chimica Acta*, 269, 47–57.
- Dumitraș, D.G., Hatert, F., Bilal, E., and Marincea, Ș. (2004a) Gypsum and basanite in the bat guano deposit from the "dry" Cioclovina cave (Sureanu Mountains, Romania). *Romanian Journal of Mineral Deposits*, 81 (Special Issue), 84–87.
- Dumitraș D.G., Marincea, S., and Fransolet, A.M. (2004b) Brushite in the bat guano deposit from the "dry" Cioclovina Cave (Sureanu Mountains, Romania). *Neues Jahrbuch für Mineralogie, Monatshefte*, 1, 45–64.
- Elliott, J.C. (1994) Structure and Chemistry of the Apatites and Other Calcium Orthophosphates. Elsevier, Amsterdam, The Netherlands.
- Fleet, M.E. and Pan, Y. (2000) Site preference of rare earth elements in hydroxyapatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$. *Journal of Solid State Chemistry*, 149, 391–398.
- Gomez Morales, J. and Rodriguez Clemente, R. (1990) Sintesis de fosfatos de aluminio en soluciones acuosas diluidas. *Boletín de la Sociedad Española de Mineralogía*, 13, 1–9.
- Hammonds, K.D., Dove, M.T., Giddy, A.P., Heine, V., and Winkler, B. (1996) Rigid-unit phonon modes and structural phase transitions in framework silicates. *American Mineralogist*, 81, 1057–1079.
- Lapin, A.V. (1992) Churchite from lateritic weathered mantles on carbonatites and the behavior of rare earths in the supergene alteration zone. *Akademia Nauk Russian Doklady, Earth Sciences Section*, 327, 135–139.
- Lottermoser, B.G. (1987) Churchite from the Mt. Weld carbonatite laterite, Western

- Australia. *Mineralogical Magazine*, 51, 468–469.
- — (1990) Rare-earth element mineralization within the Mt. Weld carbonatite laterite, Western Australia. *Lithos*, 24, 151–167.
- Marincea, Ș. and Dumitraș, D. (2003) The occurrence of taranakite in the “dry” Cioclovina Cave (Sureanu Mountains, Romania). *Neues Jahrbuch für Mineralogie, Monatshefte*, 3, 127–144.
- Marincea, Ș., Dumitraș, D., and Gibert, R. (2002) Tinsleyite in the “dry” Cioclovina Cave (Sureanu Mountains, Romania): The second world occurrence. *European Journal of Mineralogy*, 14, 157–164.
- Muraoka, Y. and Kihara, K. (1997) The temperature dependence of the crystal structure of berlinite, a quartz-type form of AlPO_4 . *Physics and Chemistry of Minerals*, 24, 243–253.
- Neubauer, J. and Pöllmann, H. (1992) Synthesis and characterization of chloride bearing silico-sulfate-apatites. *Neues Jahrbuch für Mineralogie, Monatshefte*, 7, 295–310.
- — (1995) Solid solution series of silico-sulphate-chloride-apatites. *Neues Jahrbuch für Mineralogie, Abhandlungen*, 168, 237–258.
- Onac, B.P. and White, W.B. (2003) First reported sedimentary occurrence of berlinite (AlPO_4) in phosphate-bearing sediments from Cioclovina Cave, Romania. *American Mineralogist*, 88, 1395–1397.
- Onac, B.P., Breban, R., Kearns, J., and Tamas, T. (2002) Unusual minerals related to phosphate deposits in Cioclovina Cave, Sureanu Mts. (Romania). *Theoretical and Applied Karstology*, 15, 27–34.
- Pliego-Cuervo, Y. and Glasser, F.P. (1978) Phase relations and crystal chemistry of apatite and silicocarnotite solid solutions. *Cement and Concrete Research*, 8, 519–524.
- Rouse, R.C. and Dunn, P.J. (1982) A contribution to the crystal chemistry of ellestadite and the silicate sulfate apatites. *American Mineralogist*, 67, 90–96.
- Strunz, H. (1941) Isotypie von Berlinit mit Quarz. *Zeitschrift für Kristallographie*, 103, 228–229.
- Veksler, I.V., Thomas, R., and Wirth, R. (2003) Crystallization of AlPO_4 - SiO_2 solid solutions from granitic melts and implications for P-rich melt inclusions in pegmatitic quartz. *American Mineralogist*, 88, 1724–1730.
- Wise, W.S. and Loh, S.E. (1976) Equilibria and origin of minerals in the system Al_2O_3 - AlPO_4 - H_2O . *American Mineralogist*, 61, 409–413.

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