Re-examination of berlinite (AlPO$_4$) from the Cioclovina Cave, Romania

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Abstract

Berlinite is a mineral indicative of high-temperature formation and, therefore, it would not be expected to be present in a sedimentary environment. In this study, we review the characteristics of a berlinite-bearing deposit and present a single-crystal structure investigation based on X-ray data: the refinement converged at $R1(F) = 0.0276$, $wR2(F^2) = 0.0657$ for 677 reflections ($2\theta_{MoK\alpha} \leq 70°$) and 31 variables in space-group $P3_121$ [$a = 4.9458(10)$, $c = 10.9526(20)$ Å, $V = 232.0$ Å^3, $Z = 3\{AlPO_4\}$]. The average $<T\text{-O}>$ bond distances within the two crystallographically unique TO$_4$ tetrahedra are 1.734 and 1.526 Å, respectively. From the scattering power at these T sites and the stereochemistry, the presence of an AlO$_4$ tetrahedron linked to a PO$_4$ tetrahedron is established. Consequently, the sample from Cioclovina Cave is verified as AlPO$_4$ (modification berlinite), reconfirming the first description of this mineral from a sedimentary occurrence, which underwent an obvious natural heating process.

Keywords: Berlinite, Cioclovina Cave, Romania, cave minerals

Introduction

Berlinite, AlPO$_4$, is a rare mineral with a crystal structure analogous to that of α quartz. An ordered substitution by Al and P atoms for Si atoms doubles the c unit-cell parameter; AlO$_4$ and PO$_4$ tetrahedra alternate and share corners. AlPO$_4$ compounds are known to crystallize in several other modifications characterized by distinct temperature and pressure environments. Similarities of the AlPO$_4$ phases to the isoelectronic SiO$_2$ compounds are evident (Graetsch 2002, 2003, and references therein). These compounds are of interest for multiple reasons, e.g., berlinite shows piezoelectric properties due to the space-group symmetry $P3_121$ or $P3_221$. As shown by syntheses experiments and geological settings, temperature conditions and solvents control the stability fields of the AlPO$_4$ phases in general, and especially those of berlinite (Flörke 1967; Bass and Sclar 1979; Motchany and Chavanski 2001; Veksler et al. 2003).

Onac et al. (2002) described an unusual mineral assemblage of phosphate-bearing minerals from the Cioclovina Cave, Sureanu Mountains, Romania. The cave is well known for hosting enormous amounts of phosphate-rich sediments (3 to 20 m in thickness) that once almost entirely filled some 450 m of cave passages (Breban et al. 2003). The phosphate-rich sediments are believed to have formed from large deposits of bat guano and cave bear remains. Successive cave flooding events resulted in the accumulation of large quantities of clay and sand that were either inter-bedded with bat guano horizons or completely buried the organic sediment. In some parts of the cave, the weight of the overburden sediments was significant and the underlying material was heavily compacted so that the original textures and structures were changed. We assumed that, owing to microbial processes, the temperature inside the buried guano increased until spontaneous ignition led to its combustion in some restricted parts of the cave. Combustion of bat guano in caves has been reported from several locations (Oakley 1954; Martini 1994a, 1994b, 1997; Urbani 1996). Visually, the baking of the sediments in Cioclovina Cave resulted in a change of color to dark brown. The berlinite-bearing sediment occurs only in a dead-end, side passage of the cave and shows the entire above-mentioned thermal transformation features (Onac and White 2003).

Marincea and Dumitraş's (2005) comments on that paper provide us with a welcomed opportunity to further discuss the unusual formation of a high-temperature mineral within a cave environment. At that time, the available material for further investigations was limited and especially not suitable for a phase analysis by single-crystal X-ray diffraction. Therefore, we discontinued our work until recently when a second find of the same mineral provided appropriate material for detailed single-crystal investigations.

Marincea and Dumitraş (2005) doubted the correct identification of berlinite by Onac and White (2003) for the following reasons: (1) the original X-ray powder patterns were misinterpreted; (2) unsuitable microprobe analyses led to an incorrectly determined chemical composition; (3) the unlikelihood of this species in a sedimentary environment; and (4) repetition of

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the successful synthesis of berlinite from the primary minerals failed. Below, we present a detailed single-crystal X-ray structure investigation and new chemical results to clearly demonstrate that the original description of berlinite from the Cioclovina Cave was correct.

X-RAY DIFFRACTION INVESTIGATIONS AND CRYSTAL-STRUCTURE REFINEMENT

Berlinite from the Cioclovina Cave forms colorless aggregates. When the translucent, well-crystallized aggregates were first collected in the "baked" sediment, we did not suspect that they would turn out to be an anhydrous phosphate. The availability of the mineral for electron microprobe analyses was limited to two small grains. The rest of the glass-like aggregates were ground for study by X-ray powder diffraction. Recently, additional well-crystallized aggregates up to 2 mm in diameter were detected within heavily compacted sediments from the "Bivouac Room" (cf. Fig. 1 in Onac and White 2003). Visually, the samples are not distinguishable from quartz, hence easily overlooked. A small chip of this material was used for single-crystal X-ray investigation (see Table 1). Determination of the unit-cell metrics showed that the sample was not quartz, as the a parameter is somewhat larger than expected for low-quartz and c is doubled. The reflections (hkl) with $l = 2n + 1$ result mainly from the distinct scattering power of the P and Al atoms and violation of the pseudo-translation vector [0 0 0.5] between the two crystallographically distinct O atom sites caused by the different space requirements of the two cations. Consequently, these reflections are weaker when compared to those with $l = 2n$ but their intensities are significant; most of these superstructure reflections could be detected. The structural parameters given by Muraoka and Kihara (1997) were used to start the structure refinement. During the refinement, some large electron densities in the difference Fourier summation led to an unexpectedly high

TABLE 1. Single-crystal X-ray data collection and structure refinement for berlinite†

a (Å)	4.9458(10)
c (Å)	10.9526(20)
V (Å^3)	232.0
Space group	$P3_121$
Z	3{AlPO$_4$}
Crystal diameter (mm^3)	$0.025 \times 0.042 \times 0.17$
Absorption coefficient μ (mm^{-1})	0.99
Scan range Δφ (at 11 distinct ω values) (°)	2
Collection time (s/°)	140
$2\theta_{max}$ (°)	70
Number of images measured	561
Crystal-detector distance (mm)	30
Data collection temperature (K)	293
Measured/unique reflections (n)	3996/677
$R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$	0.0276
$R1(F)/wR2(F^2)$* (for the 677 unique reflections)	0.0276/0.0657
$R1(F)$ [for the 629 reflections with $F_o > 4\sigma(F_o)$]	0.0246
Variable parameters (p)	31
GooF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$	1.065
Δ/σ	<0.001
Δρ$_{min}$, Δρ$_{max}$ (eÅ^{-3})	–0.33, 0.37
Extinction coefficient	0.098(15)

Notes: $R1(F) = \Sigma(||F_o| - |F_c||)/\Sigma F_o$; $wR2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^4]^{1/2}$.
$w = 1/\{\sigma^2(F_o^2) + [0.044*[\max(0,F_o^2) + 2*F_c^2/3]]^2\}$.
† Nonius Kappa-CCD four-circle diffractometer equipped with a 300 μm diameter capillary-optics collimator (graphite-monochromatized MoKα radiation). Data were corrected for background, Lorentz and polarization effects, and absorption (multi-scan method). Programs used: COLLECT (Nonius 1999), DENZO-SMN (Otwinowski and Minor 1997), and SHELXL-97 (Sheldrick 1997).

R-value. Consideration of twinning by rotation around the [001] axis improved the results; the twin law corresponds with the Dauphiné law of quartz. The twin ratio is 0.9217(11):0.0783(11). After a couple of least-squares cycles, the refinement converged satisfactorily. The fractional atomic coordinates, displacement parameters, and the recalculated interatomic distances and bond angles for berlinite are given in Tables 2 and 3, respectively.

Marincea and Dumitraş's (2005) comments on the X-ray powder diffraction section were based on the assumption that Onac and White (2003) had not found berlinite but misidentified either quartz or a mixture of other minerals. In fact, quartz and berlinite exhibit close structural similarities. Order between the larger AlO$_4$ tetrahedra and the smaller PO$_4$ tetrahedra causes $c_{berlinite} \sim 2c_{quartz}$. Hence a powder pattern taken from a berlinite sample can approximately be assigned to that of quartz, but additional weak reflections occur, some of which are observable in a pattern taken with a standard X-ray powder diffractometer. In addition, the cell volume of berlinite is larger than that of quartz, which causes a significant peak shift. In agreement with these expectations for berlinite, Onac and White (2003) observed two reflections caused by ordering of Al and P atoms; furthermore, the unit-cell volume of 230.1 Å^3 is definitely larger than the doubled unit-cell volume of low-quartz (112.35 Å^3, Tucker et al. 2001).

Marincea and Dumitraş (2005) interpreted the pattern published by Onac and White (2003) as possibly being that of quartz. The two additional reflections with d-values of 3.619 and 1.666 Å and intensities of 1 and 2% of the strongest peak in the pattern, respectively, were assigned to illite 2M. Not taking into account that some X-ray powder patterns may sometimes be wrongly interpreted, it is unrealistic to assume that two (weak) reflections of a pattern fit exactly into a lattice refined from the 2θ values of 20 reflections (12 of them have a larger intensity but the remaining 8 reflections are of the same or weaker intensity). Illite also exhibits additional reflections in the range of the collected pattern. We have to emphasize that identification of a chemical compound or even a mineral based on only two reflections is more than suspect. Moreover, a misinterpretation of brushite, Ca(PO$_3$OH)·2H$_2$O, for churchite-(Y), YPO$_4$·2H$_2$O, and of hydroxyl-apatite, Ca$_5$(PO$_4$)$_3$(OH), for chlorellestadite, Ca$_5$[(Si,P,S)O$_4$]$_3$(Cl,OH,F), was assumed by Marincea and Dumitraş (2005); however, shifts opposite from those observed are required for these mineral pairs. Due to the fact that Si was used as an internal standard in the original powder patterns, an opposite peak shift for distinct diagrams and moreover for two phases within one pattern should be excluded.

CHEMICAL COMPOSITION

Marincea and Dumitraş (2005) doubted that the electron microprobe compositions in the original study corresponded to berlinite. Their arguments were based mainly on a misinterpretation of the chemical analysis due to an incorrect microprobe analyses by both independent investigations published by Onac and White (2003). They argue that an excitation voltage that was too high, low beam current and focused electron beam would have promoted loss of alkali elements and consequently, ammonium-bearing taranakite or tinsleyite were misidentified as berlinite. Furthermore, they criticized the choice of variscite as an internal standard due to a possible decomposition under

TABLE 2. Fractional atomic coordinates and displacement parameters for berlinite

Atom	Wyckoff letter	site symmetry	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Al	3(a)	2	0.46649(11)	0	1/3	0.01152(18)	0.00976(23)	0.01031(20)	−0.00043(15)	½ U_{23}	½ U_{22}	0.01073(13)
P	3(b)	2	0.46689(9)	0	5/6	0.01225(17)	0.00970(20)	0.01054(18)	−0.00031(13)	½ U_{23}	½ U_{22}	0.01111(13)
O1	6(c)	1	0.4157(2)	0.2911(2)	0.39763(8)	0.0228(5)	0.0166(4)	0.0160(3)	−0.00438(3)	−0.0028(3)	0.0122(4)	0.01740(18)
O2	6(c)	1	0.4150(3)	0.2575(2)	0.88400(8)	0.0225(5)	0.0161(4)	0.0172(4)	−0.0048(3)	−0.0041(3)	0.0125(4)	0.01733(19)

Note: The anisotropic displacement parameters are defined as: exp $[-2\pi^2 \sum^3_{i=1} \sum^3_{j=1} U_{ij} a^*_i a^*_j h_i h_j]$, U_{eq} according to Fischer and Tillmanns (1987).

the electron beam.

The electron-microprobe analyses published by Onac and White (2003) gave totals of 99.96 and 99.68 wt%, respectively. The analytical formula reported was $Al_{0.993}P_{0.998}O_4$, consistent with expectations for berlinite. For this study, we performed an additional microprobe analysis using the new material, with the same analytical protocol, except for the standards. Natural garnet was used for Al, Fe, and Si, whereas fluorapatite replaced variscite for P. The mean of five analyses (total = 99.99 wt%) from a single berlinite grain yielded the chemical formula: $Al_{0.998}(P_{1.002}Si_{0.001})_{\Sigma=1.003}O_4$ (normalized on the basis of 4 O atoms per formula unit), thus confirming the presence of berlinite.

EXOTIC MINERAL SPECIES

Onac and White's (2003) note that, "This deposit contains a fascinating assemblage of minerals that includes, apart from many rare and/or unusual phosphates (e.g., berlinite, churchite, leucophosphite, foggite, …) …" was intended to highlight the unique mineralogy of the phosphate deposit in the Cioclovina Cave. However, Marincea and Dumitraş's (2005) comment that "the occurrence of other exotic species such as chlorellestadite or churchite, is not well enough substantiated and their report must be regarded with caution" prompted us to carry out additional studies. Optical observations with a polarizing microscope, X-ray powder patterns, electron-microprobe investigations, and Fourier-transform infrared analyses confirmed the presence of churchite-(Y) and foggite, $CaAl(PO_4)(OH)_2·H_2O$, in the guano-related phosphate deposit from the Cioclovina Cave (Onac et al. 2005). However, it was indeed inaccurate when mentioning chlorellestadite within the unusual mineral assemblage (Onac et al. 2002; Onac and White 2003). A recent microanalytical, structural, and vibrational spectroscopy study confirmed the mineral earlier referred too as chlorellestadite is in fact hydroxylellestadite, $Ca_5[(Si,P,S)O_4]_3(OH,F,Cl)$ but showing significant substitution of OH by Cl and F (Onac et al. 2006).

SYNTHESIS OF BERLINITE

Onac and White (2003) obtained the trigonal modification of $AlPO_4$ after heating variscite or an admixture of taranakite + brushite from 350 to 600 °C. However, Marincea and Dumitraş (2005) failed to synthesize berlinite under similar conditions; they observed only an orthorhombic modification of $AlPO_4$ with some other phosphates. Again, they concluded that some admixture of quartz (with the starting materials) led to misinterpretation of the X-ray powder patterns. In support of this contention it is worth mentioning that synthesis of berlinite under ambient pressure conditions is not new. Flörke (1967) investigated the crystallization and phase transitions of $AlPO_4$ up to 1400 °C. He obtained a trigonal phase (in analogy to the mineral berlinite) below ~700 °C; above that temperature, $AlPO_4$ crystallizes in

TABLE 3. Bond distances (Å) for berlinite

Al-O1[0, ii]	1.7301(10)	P-O1[i, iv]	1.5270(9)
Al-O2[i, v]	1.7381(10)	P-O2[0, iii]	1.5242(11)
O1[0]-Al-O1[ii]	111.72(8)	O1[i]-P-O1[iv]	108.82(8)
O1[0]-Al-O2[i]	107.29(3)	O1[i]-P-O2[0]	109.08(4)
O1[0]-Al-O2[v]	109.45(5)	O1[i]-P-O2[iii]	110.83(6)
O1[ii]-Al-O2[i]	109.45(5)	O1[iv]-P-O2[0]	110.83(6)
O1[ii]-Al-O2[v]	107.29(3)	O1[iv]-P-O2[iii]	109.08(4)
O2[i]-Al-O2[v]	111.70(8)	O2[0]-P-O2[iii]	108.20(8)

Notes: Symmetry code: [0] x, y, z; [i] $-x+1, -x+y, -z+4/3$; [ii] $x-y, -y, -z+2/3$; [iii] $x-y, -y, -z+5/3$; [iv] $-y+1, x+y, z+1/3$; [v] $-y+1, -x-y, z-2/3$.

analogy to tridymite, and cristobalite and an incommensurate phase as well. Flörke (1967) also discussed the influence of alkali elements, NH_4^+, and admixtures of SiO_2. Bass and Sclar (1979) heated synthetic reagent grade $AlPO_4·2H_2O$ at 550 °C for about 20 h to a constant weight and obtained a trigonal modification of $AlPO_4$ equivalent to berlinite as proved by a 114.6 mm diameter Debye-Scherrer X-ray camera. Their reported unit-cell parameters [a = 4.947(1), c = 10.951(3) Å] agree with that obtained during the present work within the accuracy of the experiments. The distinct results of the tempering investigations might have been caused by different peak temperatures reached due to temperature gradients within the oven and/or inaccurate sensitivity of the temperature control. It seems that Onac and White (2003) tempered somewhat below the stability field of the orthorhombic modification of $AlPO_4$, whereas Marincea and Dumitraş (2005) were above the stability field of trigonal $AlPO_4$. Consequently, the latter failed to obtain a berlinite-like phase. Also, the influence of some impurities might have supported stabilization of the distinct phases (cf. Flörke 1967).

CONCLUDING REMARKS

For a final decision about the occurrence of berlinite in the Cioclovina Cave, a single-crystal structure investigation was performed. This method allows specification of the crystal structure and it gives some hints of the chemical composition; both are required for the correct definition of a phase. In full agreement with Onac and White (2003), the single-crystal X-ray analysis proved the occurrence of berlinite, $AlPO_4$. The average <M-O> bond distances within the two crystallographically different MO_4 tetrahedra are 1.734 and 1.526 Å, respectively. The MO_4 tetrahedra exhibit only small distortions; as expected the AlO_4 tetrahedra are somewhat less regular [O-Al-O bond angles between 107.29(3) and 111.72(8)°] as compared to the PO_4 tetrahedra [O-P-O bond angles between 108.20(8) and 100.83(6)°]. The bridging angles Al-O1-P and Al-O2-P are 142.62(7)° and 142.26(7)°, respectively. The features of the crystal structure determined during this work agree with those found by Sowa et al. (1990) and Muraoka and Kihara (1997) for $AlPO_4$ samples synthesized under ambient conditions (cf. also Cora et al. 2003).

The presence of berlinite along with hydroxylellestadite is a strong indicator that the heavily compacted phosphate-bearing clay sediments underwent natural heating process, probably caused by in situ guano combustion. It is difficult to imagine any other process able to generate the high-temperature environment needed for the genesis of these two minerals within the cave.

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