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First reported sedimentary occurrence of berlinite ($AlPO_4$) in phosphate-bearing sediments from Cioclovina Cave, Romania

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ABSTRACT

This paper describes the first reported occurrence of berlinite ($AlPO_4$) formed entirely under sedimentary conditions. Berlinite appears as grayish or colorless fine crystals in vacuoles and along cracks in heavily compacted, phosphate-rich sediments within the Cioclovina Cave in Romania. The X-ray powder diffraction pattern and the hexagonal unit-cell of the Cioclovina berlinite specimen compare well with other published determinations. The lattice parameters are $a = 4.94(4)$, $c = 10.87(1)$ Å, $V = 230.1(3)$ Å^3. Microprobe analyses confirmed a nearly ideal formula for berlinite. In situ guano combustion is responsible for the transformation of taranakite and for the dehydration of variscite into berlinite. Berlinite was successfully synthesized from these two minerals at atmospheric pressure and temperatures ranging from 350 to 600 °C.

INTRODUCTION

Berlinite, $AlPO_4$, is a rare high-temperature aluminum phosphate mineral first described by Blomstrand (1868) from the Westanå iron mine in Sweden. Huttenlocher (1935) determined its quartz-like crystal structure. Later, based on a specimen collected from the type locality, the first complete crystallographic description was undertaken by Strunz (1941). Since its discovery, berlinite has been documented from only a few localities worldwide. In all these occurrences the mineral is found in association with metamorphic or hydrothermally altered rocks (Gallagher and Gerards 1963; Reif et al. 1989; Duggan et al. 1990; Ek and Nysten 1990; Matsubara et al. 1999). The formation of berlinite in such geologic environments is consistent with the experimental data obtained by Wise and Loh (1976) and Bass and Sclar (1979) in the system Al_2O_3-$AlPO_4$-H_2O.

Berlinite exists in several polymorphic forms, which are analogs of the silica polymorphs high and low quartz, tridymite, and cristobalite (Muraoka and Kihara 1997). It has a three-dimensional framework structure composed of alternating corner-sharing AlO_4 and PO_4 tetrahedra. It has also been argued, based on infrared and Raman spectra, that these structures are composed of $(PO_4)^{3-}$ tetrahedra “isolated” from each other by Al^{3+} (Rokita et al. 2000). In recent years, structural analogs of quartz, such as berlinite, have attracted special attention as promising piezoelectric materials. Therefore, a large number of papers dealing with synthesis of berlinite (Kolb and Laudise 1982; Shvansky et al. 1997; Motchany and Chvanski 2001) and its crystal structure and physical properties (Muraoka and Kihara 1997; Christie and Chelikowsky 1998) have been published.

This paper describes the occurrence and formation of berlinite under sedimentary conditions in a highly unusual cave setting (Cioclovina Cave, Romania).

SITE DESCRIPTION

Cioclovina Cave is situated in the west-southwest side of the Sureanu Mountains in Romania (Fig. 1) and is developed in Lower Cretaceous-aged limestones. It consists of a long fossil passage, much of which was almost entirely filled by an impressive phosphate deposit. Between 1912 and 1941, more than 30,000 m^3 of guano-derived phosphate sediments were mined and used as fertilizer. This deposit contains a fascinating assemblage of minerals that includes, apart from many rare and/or unusual phosphates (e.g., berlinite, chlorellestadite, churchite, leucophosphite, foggite, sampleite, etc.), several carbonates, silicates, sulfates, halides, and hydroxide species (Onac et al. 2002). Cioclovina Cave is also the type locality for ardealite (Halla 1931; Schadler 1932).

Most of the minerals identified within the phosphate deposit form crusts, nodules, aggregates of tiny crystals, and earthy masses. Berlinite appears as grayish or colorless sub-millimeter crystals in vacuoles or along cracks in heavily compacted, magenta- to brown-colored phosphate-rich sediments from the Bivouac Room (Fig. 1). Visually berlinite crystals are indistinguishable from quartz.

CRYSTALLOGRAPHY

X-ray diffraction data were obtained using a Scintag Pad V diffractometer (45 kV and 40 mA), using Ni-filtered Cu radiation. Silicon was added as an internal standard. The step-scan data were continuously collected over the range 3 to 85° 2θ using a step interval of 0.025° 2θ. The X-ray diffraction data (Table 1) for the powdered samples are in good agreement with those given on PDF 10-423 for synthetic berlinite. The lattice

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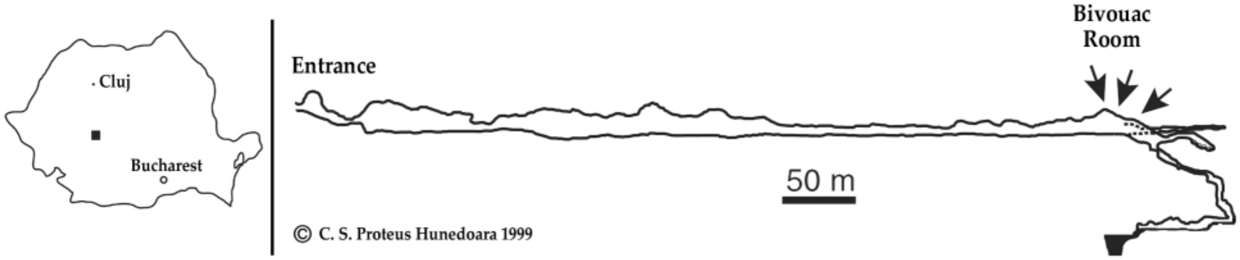

FIGURE 1. Simplified map showing the location of Cioclovina Cave and berlinite sample locations (arrows).

TABLE 1. Powder diffraction data for berlinite

d (Å)	*I*	*hkl*
4.277	20	100
3.989	4	101
3.619	2	003
3.367	100	102
2.471	7	110
2.303	7	104
2.255	8	112
2.140	13	200
1.991	5	202
1.830	18	114
1.682	5	204
1.666	1	106
1.615	2	210
1.551	10	212
1.461	2	116
1.425	1	300
1.391	5	214, 206
1.381	7	302
1.294	3	215
1.262	2	304
1.234	4	220
1.205	2	222

Note: $a = 4.94(4)$, $c = 10.87(1)$ Å, $V = 230.1(3)$ Å^3.

parameters for Cioclovina Cave berlinite, based on least-squares refinement of 22 XRD reflections using the UnitCell Program of Holland and Redfern (1997), were $a = 4.94(4)$, $c = 10.87(1)$ Å, $V = 230.1(3)$ Å^3. These parameters compare well with other published determinations for synthetic or natural berlinite from various worldwide locations (Strunz 1941; Gallagher and Gerards 1963; Ek and Nysten 1990). However, the value of c for Cioclovina Cave berlinite is significantly smaller than the range of 10.91–10.97 Å reported for other specimens. One possibility is the substitution of 2 Si^{4+} for $Al^{3+} + P^{5+}$ (2 c for quartz = 10.84 Å). The compositional data (Table 2) shows 0.11 wt% SiO_2, which seems insufficient to account for the shift in cell parameter.

CHEMICAL COMPOSITION

The chemical composition of berlinite was determined by means of a Jeol JXA-8600 electron microprobe at the University of Bristol (U.K.), operated at 20 kV accelerating voltage and 5 nA beam current. Synthetic variscite, $AlPO_4·2H_2O$, served as a standard.

The average of seven individual analyses gave the composition shown in Table 2. On the basis of 4 O atoms, the compositional formula $Al_{0.995}P_{0.999}O_4$ was calculated. Within the precision of measurements this corresponds to the nearly ideal formula of berlinite, $AlPO_4$.

TABLE 2. Chemical composition of Cioclovina Cave berlinite (wt%)

Oxide	Bristol Probe	Bern Probe
Al_2O_3	41.64	41.47
P_2O_5	58.18	58.0
SiO_2	0.11	0.14
Fe_2O_3	0.03	0.07
Total	99.96	99.68

Replicate analyses on splits from the same sample were also done at the University of Bern (Switzerland) using a CamScan CS4 instrument equipped with a Pioneer light element detector and a Voyager 4 EDS-image acquisition system. Operating conditions were 20 kV, 7.5 nA and variscite was used as an internal standard. The average chemical composition from five replicate analyses yielded similar values (Table 2), giving the following compositional formula: $Al_{0.993}P_{0.998}O_4$

DISCUSSION

The identification of berlinite among many other mineral phases in the phosphate-bearing sediments from the Cioclovina Cave was unexpected. Until now, berlinite was documented only from relatively high-temperature and high-pressure volcanic and metamorphic environments.

Two features of the berlinite-bearing sediment in the Bivouac Room must be addressed: the highly compacted nature of the deposit and the fact that a heating process has significantly altered the texture or fabric of the rock; these features have obliterated the outlines of the original sedimentary grains. In addition, fragments of charred materials have also been found within the phosphate-bearing sediments in the vicinity of the berlinite sampling site. Due to several flooding events, large quantities of detrital sediments (mostly clay and sand) were transported into the cave. In some sections of the cave the guano deposit was totally buried. This phenomenon caused the compaction of both guano and sediment deposits. At the same time, owing to microbial processes, the temperature inside the guano deposit increased until spontaneous ignition led to its combustion. Under these circumstances we presume some of the phosphate minerals precipitating within the guano deposit may have been transformed into berlinite. Other compounds formed by combustion of guano were previously reported by Martini (1994, 1997) in caves from Namibia.

Three of the phosphates that have previously been documented from Cioclovina Cave, taranakite $(K,NH_4)Al_3(PO_4)_3(OH)\cdot9H_2O$, tinsleyite $KAl_2(PO_4)_2(OH)\cdot H_2O$, and crandallite $CaAl_3(PO_4)_2(OH)_5\cdot H_2O$ (Constantinescu et al. 1999; Marincea et al. 2002), may be potential sources for berlinite. During the process of guano sediment combustion, NH_4 plus Ca and K oxides were expelled and the aluminum orthophosphate was formed. However, variscite, $AlPO_4\cdot2H_2O$, is the stable form of aluminum phosphate and if it ever existed along with the above-mentioned minerals, its dehydration has ultimately led to berlinite.

To test whether the formation of berlinite was possible under such conditions, a natural sample of taranakite from the Cioclovina Cave and reagent-grade hydrated aluminum phosphate (variscite) with a purity greater than 97% were used to synthesize berlinite. The chemical composition of the taranakite was confirmed using an electron microprobe and the X-ray powder diffraction data are in good agreement with those published in PDF 29-981.

The two samples (variscite and taranakite) were independently heated in the temperature range from 350 to 600 °C for 27 and 20 hours respectively at atmospheric pressure. The X-ray powder diffraction pattern of the heated variscite was that of berlinite and is indistinguishable from the natural sample. Taranakite also underwent a dehydration process, but berlinite did not form. We repeated the experiment under the same conditions but added small amounts of brushite ($CaHPO_4\cdot2H_2O$). This time the synthesis of berlinite was successful. The lattice parameters of both synthetic heated products, calculated from the 24 main reflections in the range $15° < 2\theta < 70°$, were found to be very close to those determined for the natural berlinite sample.

In summary, field, petrographic, and experimental data on the Cioclovina Cave berlinite are consistent with an origin caused by combustion of buried phosphate-bearing clay sediments at relatively high temperature (~550 °C). This is apparently the first recorded occurrence of this mineral, formed entirely under sedimentary conditions.

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