

MINERALS OF THE CARPATHIANS: FIRST UPDATE

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ABSTRACT

A number of rare minerals were recently discovered in different caves from Romania. Fifteen of them were identified for the first time in the Carpathians. The aim of this paper is to briefly summarize data on those mineral species published in various journals as an update to the recently published topographical mineralogical handbook of the Carpathians. Chemical and mineralogical characterization of these minerals was undertaken by X-ray powder diffraction and fluorescence analyses, energy-dispersive, atomic absorption, infrared spectrometry, thermal and electron-microprobe analyses, optical, transmission, and scanning electron microscope observations.

Key words: Cave minerals, Romania, secondary minerals, topographical mineralogy.

INTRODUCTION

Over 1000 mineral species were recently compiled in a comprehensive handbook on the Minerals of the Carpathians (Szakáll, 2002). The core of the book consists of a systematic description of 1000 valid mineral species following Dana's system of classification. Each entry describes the more important occurrences and the most interesting forms of the given mineral. Also included with the description are the size of the mineral and its color, presence of twins, and accompanying minerals. Crystallographic system and ideal formula of the mineral is given in the heading of the entry.

The following descriptive article follows the pattern of the book, providing the first update to Szakáll's book on the mineralogy of the Carpathians. The entries listed in this paper (except for jokokuite) consist of new species described from various caves in Romania. Since the fifteen minerals presented in this paper have been characterized in detail in several published articles, we are now beginning to integrate the information concerning them. By doing this, it is our hope to help the editor of the next edition of the Minerals of the Carpathians by providing quick access to this mineralogical information. The specimens discussed in this article are deposited in the Mineralogical Museum of the „Babeş-Bolyai” University and at the „Emil Racoviţă” Institute of Speleology in Cluj-Napoca and Bucharest, Romania.

MINERALS DISCOVERED BEFORE 2002

Monohydrocalcite, $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ (hexagonal), was reported to occur in the composition of white hydrated moonmilk in Humpleu and Lucia Mică caves (Bihor Mts.) (Onac and Ghergari, 1993). This mineral was identified by means of X-ray powder diffraction (XRD) and transmission electron microscope (TEM). TEM analyses revealed partial pseudomorphs of calcite after monohydrocalcite (Fig. 1).

Darapskite, $\text{Na}_3(\text{SO}_4)(\text{NO}_3) \cdot \text{H}_2\text{O}$ (monoclinic) and *nitratine*, NaNO_3 (trigonal) were found closely associated in a thin layer (~50 cm) just below a guano horizon and overlying some gravels and clays that accumulated on the floor of Şălitrari Cave (Cerna Mts.) (Diaconu and Lascu, 1999). No further information on the appearance (color, morphology etc.) of these nitrates was given. The authors suspect that the two minerals formed due to the thermomineral water activity upon guano deposits under a warm and dry cave environment.

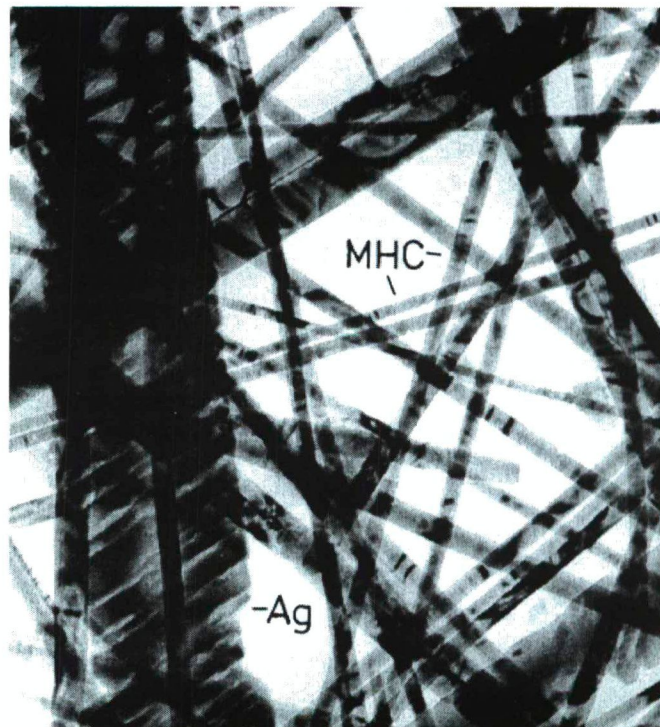


Fig. 1. Partial pseudomorphs of calcite after monohydrocalcite (Ag = aragonite; MHC = monohydrocalcite).

MINERAL SPECIES DESCRIBED DURING 2002-2003

Carbonates

Burbankite, $(\text{Na,Ca})_3(\text{Sr,Ba,Ce})_3(\text{CO}_3)_5$ (hexagonal) appears as a thin crust composed of sub-millimeter yellow grayish anhedral crystals. This rare anhydrous carbonate was found in association with colorless or milky white needle-like brushite and gypsum crystals in Cioclovina Cave, Șureanu Mts. (Onac et al., 2002). Its identification relies on XRD and energy dispersive spectrometry. Burbankite was precipitated under dry and either poor or no drainage conditions from alkali-rich carbonate solutions.

Glaukosphaerite, $(\text{Cu,Ni})_2(\text{CO}_3)(\text{OH})_2$ (monoclinic) occurs in the Water Cave (Peștera cu Apă) from Codreanu mine (Băița, Bihor county) as thin coatings of deep green color in association with malachite and rosasite (Onac, 2002). The diffraction data for glaukosphaerite and rosasite differ significantly, allowing them to be easily distinguish where they coexist. The calculated unit cell parameter corresponds closely to those values reported in PDF 27-178, which supports the stoichiometry. In thin section glaukosphaerite displays fibrous green spherulites and is biaxial negative.

Lansfordite, $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$ (monoclinic) was first described as a cave mineral from Valea Rea Cave (Bihor Mts.) where it appears as fine white powdery masses associated with hydromagnesite (Onac and Feier in prep.). Lansfordite seems to have precipitated from CO_3^{2-} -depleted and HCO_3^- -rich magnesium solutions at temperature below 8°C.

Norsethite, $\text{BaMg}(\text{CO}_3)_2$ (trigonal) appears as sub-millimeter well-crystallized milky white nodular aggregates on the walls of two skarn-hosted caves: Crystal (Peștera cu Cristale) and Surprise (Peștera Surpriză) in the Băița metallogenic district (Bihor county). The chemical composition of norsethite was obtained by atomic absorption spectroscopy (AAS) and its corresponding structural formula was found to be $\text{BaMgFe}_{0.01}(\text{CO}_3)_{1.99}$. There is no information on the way this mineral was precipitated in the cave environment (Onac, 2002).

Sulfates

Cesanite, $\text{Na}_3\text{Ca}_2(\text{SO}_4)_3(\text{OH})$ (hexagonal) was found closely associated with hydroxylapatite as ochre to red-brown crusts along the walls in Măgurici Cave (Someș Plateau). Cesanite is a rare sulfate and so far documented only from a single cave location (Onac et al., 2001). This hydroxylated double salt is isostructural with hydroxylapatite, with three Ca^{2+} replaced by three Na^+ and three PO_4^{3-} replaced by three SO_4^{2-} , maintaining charge balance within the structure (Onac and Vereș, 2003). Hence, the close association of the two minerals in some of the investigated samples is expected. We assume, in the absence of any data on cesanite stability at low temperature that the crystallization sequence is as follows: first to precipitate is hydroxylapatite and then cesanite from the Ca-depleted, Na- and SO_4^{2-} -enriched solutions. The presence of both gypsum and mirabilite in Măgurici Cave may have been crucial to cesanite precipitation.

Jokokuite, $\text{Mn}^{2+}\text{SO}_4 \cdot 5\text{H}_2\text{O}$ (triclinic), is a member of the chalcantite group and forms pale pink, rosette-like aggregates (2-3 cm in diameter) intimately associated with rozenite (Fig. 2). The jokokuite crystals have a vitreous luster



Fig. 2. Rosette-like aggregates of rozenite and jokokuite in an old adit from Roșia Montană.

and show no cleavage (Onac et al., 2003). The energy-dispersive analyses (EDS) of the pink rosette-like crystals revealed Mn, S, and O to be the major elements with Fe appearing as a minor constituent. The average cell parameters obtained on the basis of 24 X-ray powder reflections are $a = 6.36(5) \text{ \AA}$, $b = 10.75(9) \text{ \AA}$, $c = 6.12(2) \text{ \AA}$, $\alpha = 98.93(1)^\circ$, $\beta = 109.96(5)^\circ$, $\gamma = 75.11(9)^\circ$, and $V = 379.81(1) \text{ \AA}^3$. These values are nearly identical to those from PDF 31-836 suggesting a pure compound.

Phosphates

Berlinite, AlPO_4 (hexagonal) was found as grayish or colorless fine crystals in vacuoles and along cracks in well-cemented clay or impregnated in the body of this clay in Cioclovina Cave (Onac et al., 2002) (Fig. 3). The XRD pattern and the hexagonal unit-cell of the Cioclovina berlinite

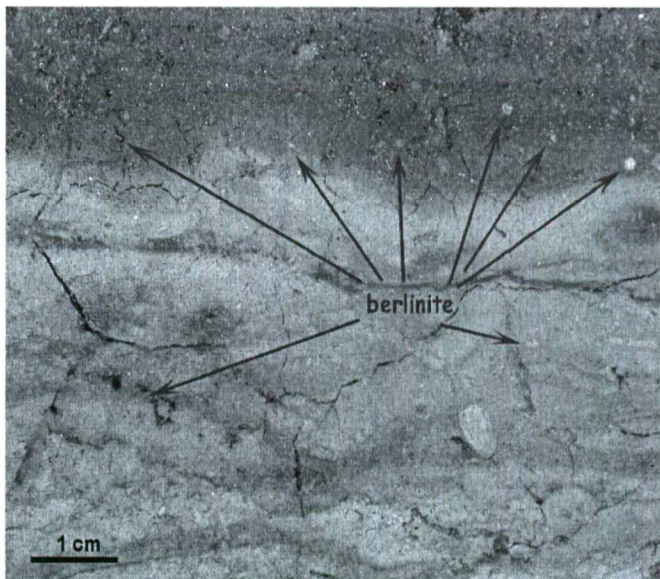


Fig. 3. Berlinite crystals within phosphate-rich sediments from Cioclovina Cave.

specimen compare well with other published determinations. The lattice parameters are $a = 4.94(4) \text{ \AA}$, $c = 10.87(1) \text{ \AA}$, $V = 230.1(3) \text{ \AA}^3$. Microprobe analyses confirmed a nearly ideal formula for berlinite. In situ guano combustion (temperature around 550°C) is responsible for the transformation of taranakite and for the dehydration of variscite into berlinite (Onac and White, 2003).

Collinsite, $\text{Ca}_2(\text{Mg,Fe}^{2+})(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (triclinic) appears as translucent millimeter thin-walled hollow spherules lining dissolution cavities within a thick hydroxylapatite crust collected from Cioclovina Cave. The mineral was identified by means of XRD and is believed to have precipitated from bat guano in damp, near-neutral pH environment (Onac et al., 2002).

Foggite, $\text{CaAl}(\text{PO}_4)(\text{OH})_2 \cdot \text{H}_2\text{O}$ (orthorhombic) occurs within black aggregates having earthy consistence that were collected from below brown-reddish crandallite-rich clays in Cioclovina Cave (Onac et al., 2002). XRD was used to identify the mineral. Foggite seems to be the result of partial decomposition of crandallite. More investigations are planned to shed light on the presence of this mineral in the cave environment.

Francoanellite, $\text{H}_6(\text{K,Na})_3(\text{Al, Fe}^{3+})_5(\text{PO}_4)_8 \cdot 13\text{H}_2\text{O}$ (trigonal) forms soft and unctuous to the touch, white nodular aggregates (3 to 50 mm in diameter) and earthy masses in the lower part of the fresh guano that overlies the argillaceous floor deposits in Măgurici Cave. XRD indicated that the mineral is francoanellite. Its XRD patterns exhibit similar d -values with taranakite except at the initial part of the diffraction spectra ($2\theta < 20^\circ$). The difference in water content between the two hydrated phosphates leads to a noticeable variation of the c value (97.6 \AA for taranakite and 83.2 \AA for francoanellite). The a values, however, are identical (8.70 \AA) for both minerals (Onac and Vereş, 2003). All francoanellite samples inspected by means of SEM revealed the presence of thousands of pseudo-hexagonal crystals (Fig. 4). The partial dehydration of taranakite has resulted in the precipitation of francoanellite.

Leucophosphite, $\text{KFe}_2^{3+}(\text{PO}_4)_2(\text{OH}) \cdot 2\text{H}_2\text{O}$ (monoclinic) forms thin pale yellowish-brown crusts (less than 1 mm thick) within white taranakite veins in a section below the Bivouac Room, Cioclovina Cave (Onac et al., 2002). XRD was used to identify the mineral. Leucophosphite may be the final product of the reaction between H_3PO_4 (derived from the leached guano) and illite in the presence of iron hydroxides.

Phosphammite, $(\text{NH}_4)_2\text{HPO}_4$ (monoclinic?) occurs as sparse, colorless, and transparent anhedral crystals (0.5 mm in size) in the lower part of a dry decomposed guano deposit hosted in Măgurici Cave (Onac and Vereş, 2003). The XRD data and the unit cell of the Măgurici specimen showed a striking similarity to that of artificial phosphammite as recorded in the PDF 29-111. This similarity indicates an almost pure compound. As in the other known occurrence (Bridge, 1973), phosphammite was precipitated in an early stage from the liquid fraction of guano. This unusual occurrence of phosphammite in a cave from a temperate region provides evidence that the highly soluble phosphate mineral may persist even in relatively moist environments as long as the temperature "within" the dry fossil guano deposit is almost twice the annual average within the cave.

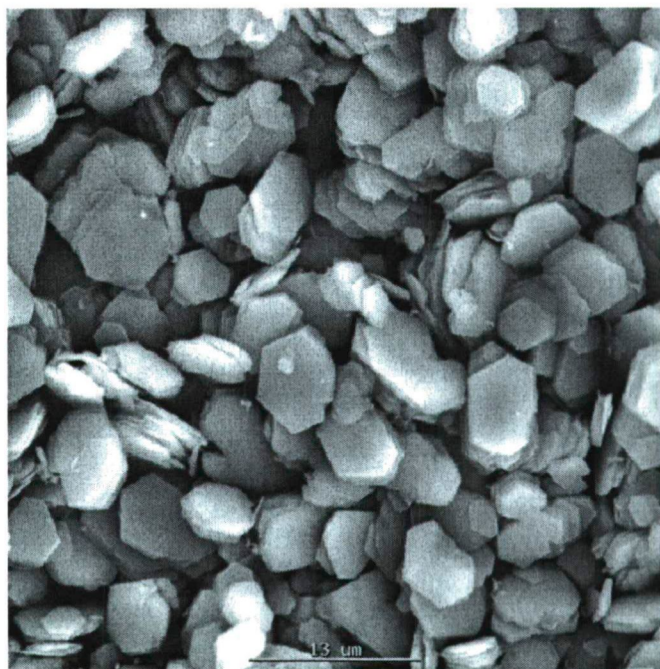


Fig. 4. SEM image of pseudo-hexagonal crystals of francoanellite from Măgurici Cave.

Tinsleyite, $\text{KAl}_2(\text{PO}_4)(\text{OH}) \cdot 2\text{H}_2\text{O}$ (monoclinic) appears as an early diagenetic mineral, in small quantities, as composite aggregates in the bat guano deposit in Cioclovina Cave. The mineral association (tinsleyite, quartz, and K-bearing clay minerals) suggests that highly concentrated phosphoric acid solutions from guano reacted with illite to form quartz and tinsleyite (Marincea et al., 2002).

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