

MINERALOGICAL DATA ON THE BAT GUANO DEPOSIT FROM POLOVRAGI CAVE (CĂPĂȚĂNIU MOUNTAINS, ROMANIA)

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Recent investigations in one of the most famous caves from the South Carpathians (Romania), namely the Polovragi Cave in Căpățâni Mountains, prompted to the identification of a quite representative fossil bat guano deposit, whose mineralogy was so far ignored. The cave is located on the left slope of Olteț Valley, at about 2 km upstream from the Polovragi Monastery and 200 m upstream from the end of the Olteț Gorges. The cave, which is one of the longest in Romania (having more than 9 km in length), is developed in massive limestones of Upper Jurassic – Neocomian age. The cave is typically dry, the mean temperature being of about 8°C, with small variations over the seasons. This favors the presence of an active bat colony, located mainly in the initial portion of the cave and particularly in the so-called “Bat Gallery”. Patches of slightly indurate guano cover the floor of

this gallery. The present study aims to give some preliminary mineralogical data on the main mineral species in the deposit, issued from their examination by scanning electron microscopy (SEM), inductively-coupled plasma - atomic emission spectrometry (ICP-AES) and X-ray powder diffraction (XRD).

Restricted to the guano patches, the mineral association includes hydroxylapatite, brushite, taranakite, low quartz, illite (the 2M₁ polytype), amorphous iron sesquioxides and calcite. The unit-cell parameters of selected specimens of these mineral species, refined by least-squares from X-ray powder data (Cu K_α, λ = 1.54056 Å) are given in the following Table:

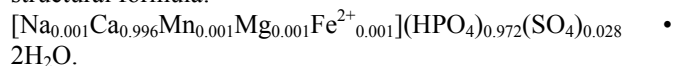
Mineral	System, S.G.	Sample	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β(°)	<i>n</i>	<i>N</i>
hydroxylapatite	<i>H</i> , P6 ₃ / <i>m</i>	PP 3 B	9.426(3)	-	6.879(3)	-	4	38
hydroxylapatite	<i>H</i> , P6 ₃ / <i>m</i>	PP 4 A	9.405(3)	-	6.867(3)	-	10	41
brushite	<i>M</i> , <i>Ia</i>	PP 1 A	5.797(2)	15.163(7)	6.228(3)	116.28(2)	7	70
taranakite	<i>R</i> , <i>R</i> $\bar{3}$ <i>c</i>	PP 1 A	8.690(3)	-	94.90(5)	-	3	88
quartz	<i>R</i> , P3 ₁ 21	PP 2 B	4.909(1)	-	5.398(2)	-	4	20
illite 2M ₁	<i>M</i> , C2/ <i>c</i>	PP 1 B	5.215(8)	8.974(6)	19.98(2)	94.27(9)	6	20
calcite	<i>R</i> , <i>R</i> $\bar{3}$ <i>c</i>	PP 4 A	4.9843(9)	-	17.037(6)	-	4	26

S.G.: space group; *n*: number of refining cycles; *N*: number of reflections used for refinement in the 2θ range 16–88° for hydroxylapatite, 5–90° for brushite, 5–66° for taranakite and 10–90° for quartz and calcite.

Hydroxylapatite occurs in the lower part of the guano pile, at the direct contact with the carbonate floor. The mineral forms white-yellow or orange crusts composed by fine platy crystals of up to 20-μm diameter and 1 μm in thickness, randomly disposed or forming post-colloidal, rosette-like aggregates. The mineral has typically a reduced crystallinity: the indices of crystallinity, calculated using the method proposed by SIMPSON (1964) are, for the two samples in the Table, 0.211 and 0.167, respectively. A ICP-AES analysis of a carefully handpicked separate, recalculated at 100 % after deduction of water in order to assess the charge balance, gave (in wt%): K₂O = 0.04, Na₂O = 0.02, CaO = 54.96, MnO = 0.08, MgO = 0.05, FeO = 0.41, P₂O₅ = 42.28, SO₃ = 0.23, H₂O = 1.93. This composition, normalized on the basis of 6 (P + S) and 26 (O,OH) per formula unit (*pfu*), leads to the chemical-structural formula: [K_{0.009}Na_{0.006}Ca_{9.824}Mn_{0.011}Mg_{0.012}Fe²⁺_{0.057}](P_{5.971}S_{0.029})O_{23.852}(OH)_{2.148}.

Brushite forms millimeter-sized snow white coatings on hydroxylapatite or small (up to 5 mm in diameter) nodules in the guano mass. The SEM study showed that the brushite aggregates are composed of finely bladed crystals, flattened on (010) and elongated toward a direction that may be [101]

or [102]. Individual crystals are up to 0.1 μm thick, 7 μm wide and 15 μm long. The ICP-AES analysis of the sample PP 1 A yielded (in wt%): Na₂O = 0.01, CaO = 32.48, MnO = 0.03, MgO = 0.02, FeO = 0.03, P₂O₅ = 40.08, SO₃ = 1.32, H₂O (as calculated for the charge balance) = 26.03. This composition, normalized on the basis of 1 (P+S) and 4 (O) in the anhydrous part of the compound, leads to the chemical-structural formula:



Taranakite occurs as dull white crusts or small veins of chalky appearance composed by clusters of crystals whose SEM examination shows roughly hexagonal forms. The individual crystals are up to 15 μm across and 1 μm thick. The mineral is typically associated with 2M₁ illite and low (alpha) quartz. The cell parameters in the Table are indicative for a variety with low ammonium content.

Reference

SIMPSON, D.R. (1964): American Mineralogist, 49: 363–376.