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Taranakite in few fossil bat-guano deposits from caves in Southern Romania

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Taranakite, ideally $(K,NH_4)_3Al_5(HPO_4)_6(PO_4)_2 \cdot 18H_2O$, represents a quite common phosphate species in the bat guano deposits from caves, where it forms as a product of the reaction between the strongly acidic phosphatic solutions derived from the guano deposits and the clay minerals from the cave floor. This mineral species has been the focus of study because it represents one of the very few examples of well-documented $(NH_4)^+$-for-K^+ substitution, and because it has the longest crystallographic axis known so far [1]. The aim of this paper is to document the physical properties, the chemistry, the infrared behavior and principally the cell parameters of taranakite from some famous fossil bat guano deposits in caves from the Southern Carpathians and Dobrogea, as mentioned in Table 1. The mineral occurs as earthy white crusts or nodules of chalky appearance scattered locally on the *terra rossa* mass. It was also found as aggregates thinly interbedded with detrital sequences mainly composed of quartz and illite. The taranakite masses are soft, earthy-looking and porous. Individual crystals are flattened on (0001) and are up to 10 μm across, and usually smaller.

The cell parameters calculated as average of the values obtained by least-squares refinement from XRD powder data from representative samples of taranakite, using reflections in the 2θ range 5 - 90°, are given in Table 1. In all cases, the *a*:*c* ratios closely approximates the ideal value of 0.0915:1.

Table 1. Average cell parameters of taranakite from Romanian caves

Location					
Cave	*a* (Å)	*c* (Å)	*V* (Å^3)	*a*:*c*	n*
South Carpathians					
Gura Ponicovei	8.703(2)	95.03(4)	6233.1(33)	0.092:1	1
South Carpathians					
Padina Matei	8.708(9)	95.17(14)	6249.7(19)	0.091:1	3

South Carpathians
Gaura Haiducească
8.716(12)
95.20(14)
6248.1(26)
0.091:1
2
South Carpathians
Gaura cu Muscă
8.715(1)
95.09(2)
6254.3(24)
0.092:1
1
South Carpathians
Gaura Ungurului
8.660(19)
94.73(9)
6152,1(34)
0.091:1
2
South Carpathians
Cioclovina
8.687(9)
95.69(5)
6254(16)
0.091:1
3
South Carpathians
de la Războaie
8.707(14)
94.94(10)
6233(25)
0.092:1
4
South Carpathians
Polovragi
8.690(3)
95.90(5)
6264.3(75)
0.091:1
1
South Carpathians
Grigore Decapolitul
8.688(7)

			94.98(5)	6223(13)	0.091:1	6
South Carpathians	Lazului	8.702(13)	96.13(32)	6304(32)	0.091:1	3
South Carpathians	Topolniţa	8.685(17)	94.81(8)	6194(24)	0.092:1	3
South Carpathians	cu Lilieci	8.690(4)	95.8(10)	6268.1(81)	0.091:1	1
Dobrogea	Gura Dobrogei	8.694(2)	94.98(4)	6209.9(15)	0.092:1	1

* number of datasets used for averaging.

The chemical structural formulas of two of the most representative samples are:
$[K_{2.581}Na_{0.041}(NH_4)_{0.169}Ca_{0.074}Mg_{0.023}Mn_{0.004}](Al_{4.942}Fe_{0.057})(PO_4)_{1.99}(HPO_4)_{6.01}\cdot 18.07\ H_2O$ for a sample from the "Dry" Cioclovina Cave and
$[K_{2.374}Na_{0.096}(NH_4)_{0.412}Ca_{0.058}Mg_{0.047}](Al_{4.897}Fe_{0.103})(PO_4)_{2.092}(HPO_4)_{5.908}\cdot 18.172\ H_2O$ for a sample from Lazului Cave.
The band multiplicity on the IR-absorption spectrum suggests that the protonated and unprotonated phosphate groups have C_3 and C_{3v} punctual symmetries, respectively, whereas the strong imprint of the bands assumed to P-O-H vibrations suggests the local presence of $(H_2PO_4)^-$ groups. Thermal analyses showed that the molecular water is lost in two steps, before 200ºC; the dehydration is complete at 365ºC. Francoanellite was identified as a product of thermal diagenesis of taranakite only in the Gura Dobrogei Cave.

References. [1] DICK S ET AL.(1998) INORG. CHIM. ACTA 269: 47-57.