HYDROXYLAPATITE CRUSTS ON THE CARBONATE FLOOR FROM PEŞTERA MARE DE LA BALTA (MEHEDINŢI PLATEAU, ROMANIA)

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A recent investigation carried out in one of the most attractive caves from the Mehedinţi Plateau (South Carpathians, Romania), namely Peştera Mare de la Balta ("the Big Cave" of Balta, hereafter referred to as the cave of Balta), allowed us to identify massive deposits of hydroxylapatite on the carbonate floor of the cave. These deposits, partly extended to the walls of the cave, are the result of the influence of the phosphoric solutions derived from the bat droppings on the carbonate background (limestone or moonmilk flows). The aim of this note is to give new morphologic, optical, crystallographic, chemical and infrared absorption data on hydroxylapatite from the cave. The analytical methods used in investigation were scanning electron microscopy (SEM), inductively coupled plasma-atomic emission spectrometry (ICP-AES), Fourier-transfom infrared spectrometry (FTIR) and X-ray powder diffraction (XRD).

The cave of Balta is located on the administrative territory of the homonymous village (Mehedinţi county), on the so-called "Cave Hill" (Dealul Peşterii), part of the Mehedinţi Plateau. It is a medium-sized cave (1075 m in length) consisting of two active galleries: the Passage Gallery (eastward) and the Rimstone Pools Gallery (westward). The draining water in both galleries has low levels. The cave is developed in massive limestones of Upper Jurassic – Neocomian age. The hydroxylapatite crusts investigated by us were taken off from the floor and the walls of a room located at approximately 150 m from the southern entrance of the Rimstone Pools Gallery. Restricted to these crusts, the mineral association consists of hydroxylapatite with minor quartz, illite 2*M*1 and X-ray amorphous iron sesquioxides.

Hydroxylapatite occurs as ochre to dull white aggregates composing multilayered, centimeter-sized crusts or mounds that are directly overgrown on the carbonate support. The SEM examination shows that both the crusts and the mounds are composed by thick beds of crystalline aggregates whose morphology varies from randomly disposed hexagonal laths to post-colloidal, rosette-like, deposits. Crystals are typically smaller than 10 μm and rarely attain 20 μm across.

The crystallinity indices (C.I.) calculated for many samples using the method proposed by SIMPSON (1964) are given in the following table. All but three samples in the table show very good crystallinity. The cell parameters obtained for these samples, after *n* cycles of least-squares refinement of *N* X-ray powder reflections in the 2θ range between 10 and 86° (Fe K_α, λ = 1.93735 Å) are also given in the Table 1.

The chemical composition of a selected sample (PB 45A), determined by ICP-AES, is (in wt% oxides): K_2O = 0.01, Na_2O = 0.01, CaO = 55.66, MnO = 0.01, MgO = 0.01, FeO = 0.01, P_2O_5 = 42.25, SO_3 = 0.21, H_2O (calculated) = 1.83. The resulting chemical-structural formula, calculated on the basis of basis of 6 (S+P) and 26 (O,OH) per formula unit (*pfu*), is: $[K_{0.002}Na_{0.003}Ca_{9.961}Mn_{0.001}Mg_{0.002}Fe^{2+}_{0.001}](P_{5.974}S_{0.026})O_{23.961}(OH)_{2.039}$. CO_2 was not checked for, but, as shown by the IR spectrum, is present in the sample. In fact, the FTIR spectrum of the sample PB 45 A gave a pattern typical for a hydrated carbonate-bearing hydroxylapatite, characterized by OH stretching (3570 cm^{-1}) and librational (635 cm^{-1}) bands, stretching (3414 cm^{-1}) and bending (1647 cm^{-1}) bands of molecular water, CO_3 (ν_3 1451 cm^{-1}, ν_3' 1426 cm^{-1}, ν_2 873 cm^{-1}) and PO_4 (ν_3 1082 cm^{-1}, ν_3' 1033 cm^{-1}, ν_1 962cm^{-1}, ν_4 602 cm^{-1}, ν_4' 563 cm^{-1}, ν_2 472 cm^{-1}) bands.

Reference

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

Table 1

Sample	*a* (Å)	*c* (Å)	*V* (Å^3)	*n*	*N*	C. I.
PB 17 A	9.413(2)	6.883(3)	528.2(2)	4	32	0.038
PB 18 A	9.418(2)	6.885(3)	528.9(3)	3	29	0.038
PB 18 B	9.408(6)	6.869(4)	526.6(6)	3	18	0.157
PB 20 A	9.414(3)	6.871(3)	527.4(3)	3	31	0.037
PB 22 C	9.416(4)	6.867(5)	527.3(4)	3	22	0.103
PB 23 B	9.412(3)	6.871(3)	527.1(3)	3	28	0.037
PB 26 A	9.414(3)	6.876(3)	527.8(4)	3	21	0.059
PB 27 A	9.417(5)	6.884(6)	528.8(6)	3	22	0.059
PB 45 A	9.432(9)	6.883(5)	530.3(9)	3	17	0.097