# CALCIUM PHOSPHATES IN THE BAT GUANO DEPOSIT FROM PEŞTERA MARE DE LA MEREŞTI, PERŞANI MOUNTAINS, ROMANIA

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The cave from Mereşti (Peştera Mare de la Mereşti) is located at the northern margin of Perşani Mountains, in the Vârghiş Gorges, at about 18 km north–northwest of Baraolt, Covasna County, Romania. The cave, which has, including the divergent galleries, 1527 m in length, is developed in Tithonian-Neocomian algal micritic limestones with calcarenite levels. A bat guano deposit, with limited extension, was identified inside the cave.

Calcium phosphates (*i.e.*, hydroxylapatite, carbonate-hydroxylapatite, brushite and ardealite) are the most representative mineral species in the bat guano pile, but the associated minerals also include calcite, gypsum, alpha (low) quartz, illite and interstratified kaolinite-illite.

**Hydroxylapatite**, or more precisely carbonate-hydroxylapatite, is the most common mineral species in the lower part of the guano pile. It occurs as creamy white crusts composed of fine platy crystals up to 15 μm in diameter and 1 μm in thickness.

An inductively coupled plasma - atomic emission spectrometry (ICP-AES) analysis of a carefully handpicked separate, recalculated to 100% after the deduction of water in order to assess the charge balance, gave (in wt.%) the following results: $K_2O$ = 0.01, $Na_2O$ = 0.01, CaO = 54.87, MnO = 0.03, MgO = 0.27, FeO = 0.39, $P_2O_5$ = 42.03, $SO_3$ = 0.53, $H_2O$ = 1.86. This composition, normalized on the basis of 6 (P + S) and 26 (O,OH) per formula unit (*pfu*), leads to the chemical-structural formula:
$[K_{0.002}Na_{0.003}Ca_{9.804}Mn_{0.004}Mg_{0.067}Fe^{2+}_{0.054}](P_{5.934}S_{0.066})O_{23.929}(OH)_{2.071}$.

Note that the presence of carbonate substituting for phosphate groups was ignored, because $CO_2$ was not checked for. The infrared spectrum of the same sample gave, however, a pattern typical for carbonate-hydroxylapatite, characterized by OH stretching (3570 $cm^{-1}$) and librational (635 $cm^{-1}$) bands, $CO_3$ ($\nu_3$ 1466 $cm^{-1}$, $\nu_3$' ~1430 $cm^{-1}$, $\nu_2$ 872 $cm^{-1}$) bands, and $PO_4$ ($\nu_3$ 1086 $cm^{-1}$, $\nu_3$' 1042 $cm^{-1}$, $\nu_1$ 955 $cm^{-1}$, $\nu_4$ 604 $cm^{-1}$, $\nu_4$' 564 $cm^{-1}$, $\nu_2$ 472 $cm^{-1}$) bands.

The cell parameters obtained by least-squares refinement of 59 X-ray powder (XRD) reflections obtained for a representative sample are $a$ = 9.438(3) Å, $c$ = 6.868(3) Å and $V$ = 529.8(3) $Å^3$.

**Brushite** occurs as snow white powdery coating on hydroxylapatite or as nodular earthy masses (several mm to 2 cm in diameter) in the bat guano mass, in which case the mineral is generally surrounded by hydroxylapatite. In terms of the composition and stoichiometry, the Mereşti material closely matches the $CaHPO_4 \cdot 2H_2O$ end-member. Its mean composition, taken as an average of five ICP-AES analyses of samples whose purity was proved by XRD analysis is (in wt.%): $K_2O$ = 0.02, $Na_2O$ = 0.02, CaO = 32.09, MnO = 0.07, MgO = 0.21, FeO = 0.16, $P_2O_5$ = 40.26, $SO_3$ = 1.11, $H_2O$ (as calculated for the charge balance) = 26.05. This composition, normalized on the basis of 2 (P+S) and 8 (O) in the anhydrous part of the compound, leads to the chemical-structural formula:
$[K_{0.001}Na_{0.002}Ca_{1.969}Mn_{0.003}Mg_{0.018}Fe^{2+}_{0.008}](HPO_4)_{1.952}(SO_4)_{0.048} \cdot 4H_2O$.

The average unit-cell parameters, taken as mean of the values obtained by least-squares refinements from 7 sets of X-ray powder data including 51-93 reflections unequivocally attributable to brushite are $a$ = 5.812(5) Å, $b$ = 15.169(5) Å, $c$ = 6.239(4) Å and $\beta$ = 116.35(13)°.

**Ardealite** occurs as cream white, thin and porous crusts that overcoat hydroxylapatite or as small nodules, up to 0.5 cm in diameter, surrounded by a mass composed of hydroxylapatite and brushite.

The average ICP-AES composition, obtained as mean of three individual analyses of representative samples yielded (in wt.%): $K_2O$ = 0.01, $Na_2O$ = 0.01, CaO = 32.45, MnO = 0.02, FeO = 0.05, MgO = 0.04, $P_2O_5$ = 21.05, $SO_3$ = 22.76, $H_2O$ (calculated in order to assess the charge balance) = 23.60. The resulting chemical-structural formula, calculated on the basis of basis of 2 (S+P) and 8 (O) in the anhydrous part of the compound, is:
$[K_{0.001}Na_{0.001}Ca_{1.992}Mg_{0.004}Fe^{2+}_{0.002}](HPO_4)_{1.021}(SO_4)_{0.979} \cdot 4H_2O$.

The cell parameters, taken as mean of least-squares refinements on 6 different sets of X-ray powder reflections, are $a$ = 5.718(3) Å, $b$ = 30.998(24) Å, $c$ = 6.248(5) Å and $\beta$ = 117.17(5)°.

The textural relationships between the three calcium phosphates, observed by scanning electron microscopy and energy-dispersive electron microprobe analysis suggests that their sequence of crystallization was from (carbonate-) hydroxylapatite to brushite and finally ardealite. All the three species clearly resulted from the reaction between the strongly acidic solutions derived from the guano mass and the cave floor or *moonmilk* flows.