

CALCIUM PHOSPHATES IN THE BAT GUANO DEPOSIT FROM PEȘTERA MARE DE LA MEREȘTI, PERȘANI MOUNTAINS, ROMANIA

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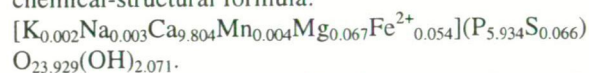
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The cave from Merești (Peștera Mare de la Merești) is located at the northern margin of Perșani Mountains, in the Vârghiș Gorges, at about 18 km north-northwest of Baraolt, Covasna County, Romania. The cave, which has, including the divergent galleries, 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: K₂O = 0.01, Na₂O = 0.01, CaO = 54.87, MnO = 0.03, MgO = 0.27, FeO = 0.39, P₂O₅ = 42.03, SO₃ = 0.53, H₂O = 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:

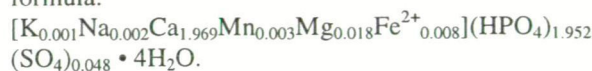


Note that the presence of carbonate substituting for phosphate groups was ignored, because CO₂ was not checked for. The infrared spectrum of the same sample gave, however, a pattern typical for carbonate-hydroxylapatite, characterized by OH stretching (3570 cm⁻¹) and librational (635 cm⁻¹) bands, CO₃ (ν₃ 1466 cm⁻¹, ν₃' ~1430 cm⁻¹, ν₂ 872 cm⁻¹) bands, and PO₄ (ν₃ 1086 cm⁻¹, ν₃' 1042 cm⁻¹, ν₁ 955 cm⁻¹, ν₄ 604 cm⁻¹, ν₄' 564 cm⁻¹, ν₂ 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) Å³.

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

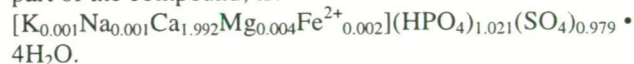
of the composition and stoichiometry, the Merești material closely matches the CaHPO₄·2H₂O end-member. Its mean composition, taken as an average of five ICP-AES analyses of samples whose purity was proved by XRD analysis is (in wt.%): K₂O = 0.02, Na₂O = 0.02, CaO = 32.09, MnO = 0.07, MgO = 0.21, FeO = 0.16, P₂O₅ = 40.26, SO₃ = 1.11, H₂O (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:



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 β = 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.%): K₂O = 0.01, Na₂O = 0.01, CaO = 32.45, MnO = 0.02, FeO = 0.05, MgO = 0.04, P₂O₅ = 21.05, SO₃ = 22.76, H₂O (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:



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 β = 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.