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BRUSHITE AND HYDROXYLAPATITE IN THE CIOCLOVINA CAVE (SUREANU MOUNTAINS, ROMANIA)

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During the study of the minerals ardealite (SCHADLER, 1932) and crandallite (CONSTANTINESCU *et al.*, 1999), brushite and hydroxylapatite were abundantly found in the bat guano deposit from Cioclovina Cave, Sureanu Mountains, Romania.

Brushite generally occurs single or in irregular intergrowths with ardealite, in white earthy aggregates that overgrow hydroxylapatite or crandallite. Very thin veinlets of brushite were also recognized as infillings of some fissures that affects the hydroxylapatite mass. A wet chemical analysis of a carefully hand picked separate gave CaO = 32.06, MgO = 0.03, P_2O_5 = 40.78 and H_2O = 26.43 (all expressed in wt%). The corresponding chemical-structural formula is $(Ca_{0.995}Mg_{0.001})H_{1.008}(PO_4)\cdot 2.049\ H_2O$. The cell parameters, taken as the mean of least-squares refinements on 20 different sets of X-ray powder reflections, are a = 5.810 Å, b = 15.176 Å, c = 6.239 Å and β = 116.37°. The density of isolated grains, established by sink-float in toluene–methylene iodide solutions, is D_m = 2.325(1) g/cm^3 for a calculated value D_x = 2.328 g/cm^3. At about 200 °C (202 °C on the DTG curve and 196 °C on the DSC one, at a heating rate of 10 °C/min), the mineral breaks down into monetite [a = 6.900(3) Å, b = 6.637(3) Å, c = 6.991(4) Å, α = 96.00(3)°, β = 103.00(3)°, γ = 88.00(3)°], by losing two molecules of water in a well-defined single step. By continuing heating, monetite turns into β-$Ca_2P_2O_7$ [a = 6.686(3) Å, c = 24.089(18) Å] at 426 °C (420 °C on the DSC curve).

Hydroxylapatite occurs as aggregates of acicular or fibrous crystals composing crusts or mounds that are generally overgrown on a carbonaceous support. These aggregates are commonly corroded and coated by brushite, which fills fractures and embayments in the hydroxylapatite mass. The physical constants of a selected sample [D_x = 3.151 g/cm^3; D_m = 3.180(2) g/cm^3; ε = 1.645(2); ω = 1.653(1)], as well as the cell parameters, taken as mean of least-squares refinements on 18 different sets of X-ray powder reflections (a = 9.433 Å, c = 6.872 Å), account for the presence of a nearly stoichiometric hydroxylapatite at Cioclovina. A wet chemical analysis gave CaO = 55.10, MnO = 0.19, MgO = 0.04, Na_2O = 0.30, K_2O =0.05, P_2O_5 = 42.36 and H_2O^+ = 1.80 (all data expressed in wt%), which leads to the formula $(Ca_{4.939}Mn_{0.013}Mg_{0.005}Na_{0.049}K_{0.005})(PO_4)_3(OH)_{0.968}$, in which it is necessary to deduce a surplus of 0.018 molecules of H_2O for consuming all H in the initial analysis.

The textural relationship between different phosphate species suggest that brushite formed late, replacing hydroxylapatite and crandallite, but it predated ardealite.

References

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SCHADLER, T. (1932). Centralbl. Miner., Abt. A: 40–41.