



Rare minerals in the phosphate-rich deposit from the Cioclovina Cave, Romania

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The Cioclovina Cave hosts an unusual mineral assemblage, including berlinite, churchite-Y, leucophosphite, foggite, sampleite, taranakite, tinsleyite, or crandallite; it is the type locality of ardealite. The cave is well known for hosting over 30,000 m³ of phosphate-rich sediments. Successive cave flooding events resulted in the accumulation of large quantities of clay and sand that were inter-bedded with bat guano horizons or completely buried the organic sediment.

On special interest is the occurrence of the minerals berlinite and hydroxyllestadite because they indicate high-temperatures during formation and hence their presence within a sedimentary environment is extremely surprising. The single-crystal X-ray study clearly identifies that the sample under investigation is berlinite: the refinement converged at $R1(F) = 0.0276$, $wR2(F^2) = 0.0657$ for 677 reflections ($2\eta_{MoK\alpha} \leq 70^\circ$) and 31 variables in space-group $P3_121$ ($a = 4.9458(10)$, $c = 10.9526(20)$ Å, $V = 232.0$ Å³, $Z = 3\{\text{AlPO}_4\}$). Hydroxyllestadite was also investigated by single-crystal X-ray experiments ($R1(F) = 0.038$ for 783 reflections up to $2\eta_{MoK\alpha} = 70^\circ$ and 42 variables, space-group symmetry $P6_3/m$, $a = 9.496(2)$, $c = 6.920(2)$ Å, $V = 540.4$ Å³, and $Z = 1$). Furthermore, the refinement of the atomic position for the $Z = (\text{OH}, \text{Cl}, \text{F})$ atoms was used as an indicator for the chemical composition.

It is likely that both minerals formed due to intense thermal process (guano combustion) that affected a phosphatized, silica-rich carbonate-mudstone sedimentary sequence occurring in a restricted area within the cave.