

The crystal chemistry of ardealite from the type locality, the “dry” Cioclovina Cave, Șureanu Mountains, Romania

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Ardealite from Cioclovina was first described by Schadler (1932) from the fossil bat-guano deposit in the "dry" Cioclovina Cave (Șureanu Mountains, Romania). The mineral occurs as white pearly or earthy masses of chalky appearance. Our investigation shows that the mineral can be characterized as a P-substituted sulfate. Wet-chemical and ICP-AES analyses show a range of S/P ratios varying between 1/0.87 and 1/0.98. Although S remains the main four-fold coordinated cation in the structure, P is consistently present at concentrations between 19.10 and 20.45 wt.% P₂O₅ (0.928 – 0.992 *apfu* P). As concerning the cations, the mineral shows a very restricted range of composition. Ardealite from Cioclovina is essentially Fe-free and very low in Mn, Mg, Na and K. The indices of refraction are $\alpha = 1.530(2)$, $\beta = 1.537(2)$ and γ (calculate for $2V\gamma = 86^\circ$) = 1.543. The measured density [$D_m = 2.335(3) - 2.342(5) \text{ g/cm}^3$] agrees well with the calculated values ($D_x = 2.317 - 2.350 \text{ g/cm}^3$). The average unit cell parameters refined from 31 sets of X-ray powder data are $a = 5.719(5)$, $b = 31.012(28)$, $c = 6.249(7) \text{ \AA}$ and $\beta = 117.21(6)^\circ$. The Gladstone-Dale calculations indicate superior and excellent compatibilities, the spreading of the compatibility indices being caused by the various degrees of hydration. Thermally-assisted XRD analyses confirm that water is lost in three steps; the loss of molecular water is a two-step process and is complete before 250°C. The first thermal breakdown products are brushite and bassanite. The IR-absorption spectrum of ardealite is characterized by a splitting of the ν_3 (XO₄) fundamentals into three well-resolved bands at ~1140, 1100 and 1005 cm⁻¹, indicating distorted (XO₄) tetrahedrons for both sulfate and protonated phosphate groups. The band multiplicity on the IR-absorption spectrum ($3\nu_3 + 1\nu_1 + 3\nu_4 + 2\nu_2$) suggests that the protonated phosphate and sulfate groups have Cs punctual symmetry. The mineral derives from the reaction between calcium carbonate from the moonmilk flows or the cave floor and phosphoric solutions derived from guano, with or without hydroxylapatite as a precursor, at pH values up to 5.5.

[1] Schadler J. (1932), *Zb. Mineral. A*, 40-41.