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Caseyite, a new mineral containing a variant of the flat-Al_{13} polyoxometalate cation

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Abstract

Caseyite, $[(V^{5+}O_2)Al_{10-x}(OH)_{20-2x}(H_2O)_{18-2x}]_2[H_2V^{4+}V^{5+}_9O_{28}][V^{5+}_{10}O_{28}]_2[(Na,K,Ca)_{2-y}(SO_4)_{2-z}\cdot(60+8x+y+4z)H_2O]$, where $x = 0–2.5$, $y = 0–2$, $z = 0–2$, is a new mineral (IMA 2019-002) occurring in low-temperature, post-mining, secondary mineral assemblages at the Burro, Packrat, and West Sunday mines in the Uravan Mineral Belt of Colorado, U.S.A. Crystals of caseyite are yellow tapering needles or blades, with a pale yellow streak, vitreous luster, brittle tenacity, curved fracture, no cleavage, Mohs hardness between 2 and 3, and 2.151 g/cm^3 calculated density. Caseyite is optically biaxial (+) with α = 1.659(3), β = 1.670(3), γ = 1.720(3) (white light), $2V = 52.6(5)°$, has strong $r < v$ dispersion, optical orientation $Z \approx \mathbf{a}$ (elongation of needles), and no pleochroism. Electron-probe microanalysis provided the empirical formula $[(V^{5+}O_2)Al_{8.94}(OH)_{17.88}(H_2O)_{15.88}]_2[H_2V^{4+}V^{5+}_9O_{28}][V^{5+}_{10}O_{28}]_2[(Na_{0.82}Ca_{0.35}K_{0.27})_{\Sigma 1.44}(SO_4)_{1.33}\cdot 70.24H_2O]$ (+0.94 H). Caseyite is monoclinic, $P2_1/n$, a = 14.123(8), b = 30.998(15), c = 21.949(11) Å, β = 97.961(8)°, V = 9516(9) Å^3, and Z = 2. The crystal structure (R_1 = 0.0654 for 9162 $I_o > 2\sigma I$ reflections) contains both normal $[V_{10}O_{28}]^{6-}$ and doubly protonated mixed-valence $[H_2V^{4+}_1V^{5+}_9O_{28}]^{5-}$ decavanadate isopolyanions, and a novel vanadoaluminate heteropolycation ("flat-$Al_{10}V\square_2$"), ideally $[(V^{5+}O_2)Al_{10}(OH)_{20}(H_2O)_{18}]^{11+}$, closely related to the technologically important flat-Al_{13} polyoxocation.

Keywords: Caseyite, new mineral, polyoxometalate, flat-Al_{13} polyoxocation, crystal structure, Packrat mine, Burro mine, West Sunday mine, Colorado