

Rowleyite, $[\text{Na}(\text{NH}_4, \text{K})_9\text{Cl}_4][\text{V}_2^{5+,4+}(\text{P}, \text{As})\text{O}_8]_6 \cdot n[\text{H}_2\text{O}, \text{Na}, \text{NH}_4, \text{K}, \text{Cl}]$, a new mineral with a microporous framework structure

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ABSTRACT

Rowleyite, $[\text{Na}(\text{NH}_4, \text{K})_9\text{Cl}_4][\text{V}_2^{5+,4+}(\text{P}, \text{As})\text{O}_8]_6 \cdot n[\text{H}_2\text{O}, \text{Na}, \text{NH}_4, \text{K}, \text{Cl}]$, is a new mineral species from the Rowley mine, Maricopa County, Arizona, U.S.A. It was found in an unusual low-temperature, apparently post-mining suite of phases that include various vanadates, phosphates, oxalates, and chlorides, some containing NH_4^+ . Other secondary minerals found in association with rowleyite are antipinite, fluorite, mimetite, mottramite, quartz, sal ammoniac, struvite, vanadinite, willemite, wulfenite, and several other potentially new minerals. Analyzed $\delta^{13}\text{C}$ values for the antipinite in association with rowleyite are consistent with a bat guano source. Crystals of rowleyite are very dark brownish green (appearing black) truncated octahedra up to about 50 μm in diameter. The streak is brownish green, the luster is vitreous, very thin fragments are transparent. The Mohs hardness is about 2, the tenacity is brittle, fracture is irregular, there is no cleavage, and the measured density is 2.23(2) g/cm^3 . Rowleyite is optically isotropic with $n = 1.715(5)$. Electron microprobe analyses yielded the empirical formula $[(\text{NH}_4)_{8.81}\text{Na}_{3.54}\text{K}_{2.58}]_{\Sigma 14.93}\text{Cl}_{6.29}(\text{H}_2\text{O})_{16}][(\text{V}_{9.36}^{5+}\text{V}_{2.64}^{4+})_{\Sigma 12}(\text{P}_{5.28}\text{As}_{0.72})_{\Sigma 6}\text{O}_{48}]$. Raman and infrared spectroscopy confirmed the presence of NH_4 and H_2O . Rowleyite is cubic, $Fd\bar{3}m$, with $a = 31.704(14)$ \AA , $V = 31867(42)$ \AA^3 , and $Z = 16$. The crystal structure of rowleyite ($R_1 = 0.040$ for 1218 $F_o > 4\sigma F$ reflections) contains $[\text{V}_4\text{O}_{16}]^{12+}$ polyoxovanadate units that link to one another via shared vertices with $[(\text{P}, \text{As})\text{O}_4]^{3-}$ tetrahedra to form a 3D framework possessing large interconnected channels. The channels contain a 3D ordered $[\text{Na}(\text{NH}_4, \text{K})_9\text{Cl}_4]^{6+}$ salt net, which apparently served as a template for the formation of the framework. In that respect, rowleyite can be considered a salt-inclusion solid (SIS). The rowleyite framework is among the most porous known.

Keywords: Rowleyite, new mineral species, polyoxovanadate, microporous framework, salt-inclusion solid, crystal structure, Rowley mine, Arizona