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Phoxite, $(NH_4)_2Mg_2(C_2O_4)(PO_3OH)_2(H_2O)_4$, the first phosphate-oxalate mineral

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ABSTRACT

Phoxite, $(NH_4)_2Mg_2(C_2O_4)(PO_3OH)_2(H_2O)_4$, is a new mineral species from the Rowley mine, Maricopa County, Arizona, U.S.A., and it has potential uses in agricultural applications for soil conditioning, fertilizing, and as a natural pesticide. It was found in an unusual bat-guano-related, post-mining assemblage of phases that include a variety of vanadates, phosphates, oxalates, and chlorides, some containing NH_4^+. Other secondary minerals found in association with phoxite are antipinite, aphthitalite, bassanite, struvite, thenardite, and weddellite. Crystals of phoxite are colorless composite blades up to about 0.4 mm. The streak is white, and the luster is vitreous to oily. The Mohs hardness is 2½, the tenacity is brittle, fracture is irregular, there is fair {100} cleavage, and the measured density is 1.98(2) g/cm^3. Phoxite is optically biaxial (–) with $\alpha = 1.499(1)$, $\beta = 1.541(1)$, $\gamma = 1.542(1)$ (white light); $2V = 16(1)°$; dispersion $r < v$, slight; orientation $Y = \mathbf{b}$, $X \wedge \mathbf{a} \approx 9°$ in obtuse β. Electron microprobe analyses yielded the empirical formula $[(NH_4)_{1.77}K_{0.23}]_{\Sigma 2}Mg_{2.00}(C_2O_4)(PO_3OH)_2(H_2O)_4$, with the C and H content inferred from the crystal structure. Raman spectroscopy confirmed the presence of NH_4 and C_2O_4. Phoxite is monoclinic, $P2_1/c$, with $a = 7.2962(3)$, $b = 13.5993(4)$, $c = 7.8334(6)$ Å, $\beta = 108.271(8)°$, $V = 738.07(7)$ Å^3, and $Z = 2$. In the crystal structure of phoxite ($R_1 = 0.0275$ for 1147 $I_o > 2\sigma I$ reflections), bidentate linkages between C_2O_4 groups and Mg-centered octahedra yield chains, which link to one another via PO_3OH tetrahedra to create undulating $[Mg_2(C_2O_4)(PO_3OH)_2(H_2O)_4]^{2-}$ sheets. Strong hydrogen bonds link the sheets into a "soft framework," with channels containing NH_4^+. The NH_4^+ forms both ordered hydrogen bonds and electrostatic bonds with O atoms in the framework. Phoxite is the first mineral known to contain both phosphate and oxalate groups as essential components.

Keywords: Phoxite, new mineral species, phosphate, oxalate, crystal structure, Rowley mine, Arizona