Phoxite, \((\text{NH}_4)_2\text{Mg}_2(\text{C}_2\text{O}_4)(\text{PO}_3\text{OH})_2(\text{H}_2\text{O})_4\), the first phosphate-oxalate mineral

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ABSTRACT

Phoxite, \((\text{NH}_4)_2\text{Mg}_2(\text{C}_2\text{O}_4)(\text{PO}_3\text{OH})_2(\text{H}_2\text{O})_4\), 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, aphithitalite, 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); \(2\ell = 16(1)\); dispersion \(r < v\); slight; orientation \(Y = b\), \(X^\alpha a = 9^\circ\) in obtuse \(\beta\). Electron microprobe analyses yielded the empirical formula \([\text{NH}_4\text{H}_7\text{K}_{17}]\text{Mg}_{20}\text{C}_2\text{O}_{40}\text{PO}_{11}\text{OH})_2(\text{H}_2\text{O})_4\), with the C and H content inferred from the crystal structure. Raman spectroscopy confirmed the presence of NH\(_4\) and C\(_2\)O\(_4\). Phoxite is monoclinic, \(P2_1/c\) with \(a = 7.2962(3)\), \(b = 13.5993(4)\), \(c = 7.8334(6)\) Å, \(\beta = 108.271(8)^\circ\), \(V = 738.07(7)\) Å\(^3\), and \(Z = 2\). In the crystal structure of phoxite (\(R_I = 0.0275\) for 1147 \(I > 2\sigma(I)\) reflections), bidentate linkages between C\(_2\)O\(_4\) groups and Mg-centered octahedra yield chains, which link to one another via PO\(_4\)OH tetrahedra to create undulating \([\text{Mg}_2\text{C}_2\text{O}_4(\text{PO}_3\text{OH})_2(\text{H}_2\text{O})_4]^-\) 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

INTRODUCTION

In our investigations of post-mining mineralization in mines of the southwestern U.S., we encountered an unusual and still actively forming bat guano assemblage at depth (125 feet) in the Rowley mine near Theba, Arizona. Previously, from this assemblage, we reported on the new mineral rowleyite, which has a microporous vanadate-phosphate framework structure (Kampf et al. 2017). Herein, we report on the new mineral phoxite, \((\text{NH}_4)_2\text{Mg}_2(\text{C}_2\text{O}_4)(\text{PO}_3\text{OH})_2(\text{H}_2\text{O})_4\), which is the first mineral found to contain both phosphate and oxalate groups.

Oxalate minerals are relatively rare. While they sometimes form abiotically, they most commonly occur in connection with biological systems. Some plants (e.g., \textit{Tragia ramosa}) use calcium oxalate as a natural defense against pests and in other biochemical processes (e.g., metal detoxification and calcium regulation; Nakata 2003). Engineered calcium oxalate crystals are being studied as a novel pesticide for chewing pests (e.g., locusts) (Nakata 2015). Oxalate materials could even be employed simultaneously as pesticides and fertilizers, enriching the soil with ammonium (similar to zeolite uses; Bernardi et al. 2016; Eroglu et al. 2017) and phosphate, while providing essential oxalate ingredients to enhance natural defense mechanisms in plants. Recent developments in metal organic framework synthesis have predominantly used Fe\(^{2+}\)-based amine-templated oxalate phosphates with some success (cf. Rehákůvá et al. 2004; Anstoetz et al. 2015; Usman et al. 2018). However, iron release can decrease soil pH and, therefore, be problematic in areas with already acidic soils. A synthetic phase corresponding to phoxite might be useful in agriculture applications with either high or low acidic soils or in soils with saline or alkaline waters. We are currently investigating methods of synthesis, ion-exchange mechanisms for common metal nutrients, and dissolution properties in phoxite, with an eye toward natural soil remediation and enhanced time-release fertilization for increased crop yield with minimal soil treatment.

Biologically induced mineralization can involve various processes among which is the deposition of excretion from birds or bats on rock surfaces to form incrustations of guano. Bat guano is generally rich in ammonium oxalate (and urate) and phosphates, as well as cations such as K, Na, Ca, Mg, and Fe. Clearly, the new mineral is compositionally consistent with formation in a guano deposit; however, it is surprising that no other mineral containing both essential phosphate and oxalate has previously

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