Hydroxylpyromorphite, a mineral important to lead remediation: Modern description and characterization

TRAVIS A. OLDS^{1,*}, ANTHONY R. KAMPF^{2,†}, JOHN F. RAKOVAN³, PETER C. BURNS^{4,5,‡}, Owen P. Mills⁶, and Cullen Laughlin-Yurs⁷

¹Section of Minerals and Earth Sciences, Carnegie Museum of Natural History, 4400 Forbes Avenue, Pittsburgh, Pennsylvania 15213, U.S.A.
²Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, California 90007, U.S.A.
³Department of Geology and Environmental Earth Science, Miami University, Oxford, Ohio 45056, U.S.A.
⁴Department of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, Notre Dame, Indiana 46556, U.S.A.
⁵Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, U.S.A.
⁶Applied Chemical and Morphological Analysis Laboratory, Michigan Technological University, Houghton, Michigan 49931, U.S.A.
⁷513 Iron Street, Norway, Michigan 49870, U.S.A.

ABSTRACT

Hydroxylpyromorphite, $Pb_3(PO_4)_3(OH)$, has been documented in the literature as a synthetic and naturally occurring phase for some time but has not previously been formally described as a mineral. It is fully described here for the first time using crystals collected underground in the Copps mine, Gogebic County, Michigan. Hydroxylpyromorphite occurs as aggregates of randomly oriented hexagonal prisms, primarily between about 20-35 µm in length and 6-10 µm in diameter. The mineral is colorless and translucent with vitreous luster and white streak. The Mohs hardness is $\sim 3\frac{1}{2}-4$; the tenacity is brittle, the fracture is irregular, and indistinct cleavage was observed on {001}. Electron microprobe analyses provided the empirical formula $Pb_{4.97}(PO_4)_3(OH_{0.69}F_{0.33}Cl_{0.06})_{51.08}$. The calculated density using the measured composition is 7.32 g/cm³. Powder X-ray diffraction data for the type material is compared to data previously reported for hydroxylpyromorphite from the talc mine at Rabenwald, Austria, and from Whytes Cleuch, Wanlockhead, Scotland. Hydroxylpyromorphite is hexagonal, $P6_3/m$, at 100 K, a = 9.7872(14), c = 7.3070(10) Å, V = 606.16(19) Å³, and Z = 2. The structure [$R_1 = 0.0181$ for 494 $F > 4\sigma(F)$ reflections] reveals that hydroxylpyromorphite adopts a column anion arrangement distinct from other members of the apatite supergroup due to the presence of fluorine and steric constraints imposed by stereoactive lone-pair electrons of Pb^{2+} cations. The F⁻ anion sites are displaced slightly from hydroxyl oxygen anions, which allows for stronger hydrogen-bonding interactions that may in turn stabilize the observed column-anion arrangement and overall structure. Our modern characterization of hydroxylpyromorphite provides deeper understanding to a mineral useful for remediation of lead-contaminated water.

Keywords: Hydroxylpyromorphite, apatite, crystal structure, Copps mine, infrared spectroscopy, Michigan, anion column