Fluorwavellite, Al₃(PO₄)₂(OH)₂F·5H₂O, the fluorine analog of wavellite

ANTHONY R. KAMPF¹*, PAUL M. ADAMS², HENRY BARWOOD³†, AND BARBARA P. NASH⁴

¹Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, California 90007, U.S.A.
²126 South Helberta Avenue, no. 2, Redondo Beach, California 90277, U.S.A.
³Department of Chemistry and Physics, Troy University, 501 University Avenue, Troy, Alabama 36082, U.S.A.
⁴Department of Geology and Geophysics, University of Utah, Salt Lake City, Utah 84112, U.S.A.

ABSTRACT

Fluorwavellite (IMA2015-077), Al₃(PO₄)₂(OH)₂F·5H₂O, the F analog of wavellite, is a new mineral from the Silver Coin mine, Valmy, Iron Point district, Humboldt County, Nevada, and the Wood mine, 5 miles NE of Del Rio, Cocke County, Tennessee; at both occurrences it is a low-temperature secondary mineral. Fluorwavellite is essentially identical to wavellite in appearance and physical properties. Optically, fluorwavellite is biaxial positive, with α = 1.522(1), β = 1.531(1), and γ = 1.549(1) (white light). Electron microprobe analyses (average of nine for each co-type locality) provided the empirical formulas Al₂₉(PO₄)₆(OH)₁₈F₁₈O₂·5H₂O (+0.12 H) for the Silver Coin mine and Al₂₉(PO₄)₆(OH)₁₈F₁₈O₂·5H₂O (+0.06 H) for the Wood mine. Fluorwavellite is orthorhombic, Pcmn, with the cell parameters determined on a Wood mine crystal: a = 9.6311(4), b = 17.3731(12), c = 6.9946(3) Å, V = 1170.35(11) Å³, and Z = 4. The five strongest lines in the X-ray powder diffraction pattern are [d₀₀₁ in Å (I (hkI))]: 8.53 (100) (020,110); 5.65 (26) (101); 3.430 (28) (141,012); 3.223 (41) (240); and 2.580 (28) (331,161,232). The structure of fluorwavellite (R₁ = 3.42% for 1248 Fᵣ > 4σF reflections) is the same as that of wavellite, differing only in having one of the two independent hydroxyl sites replaced by F. A survey of F contents in wavellite-fluorwavellite from the five most common genetic types of occurrence (fluid expulsion, hydrothermal ore alteration, pegmatite phosphate alteration, residual carbonate weathering, and sedimentary leached zone) shows that F content, and the occurrence of wavellite vs. fluorwavellite, does not correlate with the type of the occurrence. It is more likely related to the fluid activity of Al, P, and F, with pH probably being an important factor. The role that wavellite and fluorwavellite play in sequestering F in the environment may be significant.

Keywords: Fluorwavellite; new mineral; crystal structure; Raman spectroscopy; infrared spectroscopy; wavellite; Silver Coin mine, Nevada, U.S.A.; Wood mine, Tennessee, U.S.A.

INTRODUCTION

Wavellite is a relatively common secondary mineral found in various deposits. Most references (e.g., Palache et al. 1951) note that it occurs most often in aluminous, low-grade metamorphic rocks, in limonite and phosphate-rock deposits, and more rarely in hydrothermal veins. Green et al. (2007) provided a synopsis of early work on the mineral. It was first recognized in the early 1780s at the High Down quarry near Barnstaple, Devon (Devonshire), England, and was formally described by Sir Humphry Davy in 1805 under the name hydrgallite. The first reliable chemical analysis was by Jöns Jacob Berzelius and was reported by William Phillips in 1823. Since then, wavellite has been found in hundreds of deposits worldwide. The end-member formula is Al₃(PO₄)₂(OH)₂·5H₂O and this is the formula for the species officially accepted by the International Mineralogical Association; but many references (e.g., Anthony et al. 2000, p. 645) give the simplified formula as Al₃(PO₄)₂(OH,F)₂·5H₂O in recognition of the commonly observed substitution of F for OH up to about 1 atom per formula unit (apfu).

Araki and Zoltai (1968) determined the structure of wavellite using a crystal from Montgomery County, Arkansas. They reported two OH sites, one of fourfold (labeled O5 here) and one of eightfold multiplicity (labeled O6 here), corresponding to one apfu and two apfu, respectively. They refined both sites as O atoms, but they did not locate H sites and they did not report a chemical analysis to confirm the absence of F. Capitelli et al. (2014) conducted a structure refinement on a crystal from Zbirov, Czech Republic, with an analyzed F content corresponding to 0.415 apfu. They located H sites related to the O5, O6, O7, and O8 sites and confirmed all F to be located at the fourfold OH site (O5), with a refined occupancy of F₀.334(4)O₅.476(4).

One of the authors (H.B.) has been analyzing wavellite from numerous localities for many years and has confirmed F contents ranging from 0.10 to 1.02 apfu. Another author (P.M.A.) noted F contents as high as 1.03 apfu for wavellite crystals from the Silver Coin mine, Humboldt County, Nevada, and 1.07 apfu for wavellite crystals from the nearby Willard mine in Pershing County. These and previously published analyses (Table 1), coupled with the findings of Capitelli et al. (2014), led us to surmise that F can fully occupy the fourfold OH site in the wavellite.