American Mineralogist, Volume 102, pages 909–915, 2017

Fluorwavellite, $Al_3(PO_4)_2(OH)_2F{\cdot}5H_2O$, the fluorine analog of wavellite

ANTHONY R. KAMPF[1,*], PAUL M. ADAMS[2], HENRY BARWOOD[3,†], AND BARBARA P. NASH[4]

[1]Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, California 90007, U.S.A.
[2]126 South Helberta Avenue, no. 2, Redondo Beach, California 90277, U.S.A.
[3]Department of Chemistry and Physics, Troy University, 501 University Avenue, Troy, Alabama 36082, U.S.A.
[4]Department of Geology and Geophysics, University of Utah, Salt Lake City, Utah 84112, U.S.A.

ABSTRACT

Fluorwavellite (IMA2015-077), $Al_3(PO_4)_2(OH)_2F{\cdot}5H_2O$, 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 $\alpha = 1.522(1)$, $\beta = 1.531(1)$, and $\gamma = 1.549(1)$ (white light). Electron microprobe analyses (average of nine for each co-type locality) provided the empirical formulas $Al_{2.96}(PO_4)_2(OH)_{1.98}F_{1.02}{\cdot}5H_2O$ (+0.12 H) for the Silver Coin mine and $Al_{2.98}(PO_4)_2(OH)_{2.11}F_{0.89}{\cdot}5H_2O$ (+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, $V = 1170.35(11)$ Å^3, and $Z = 4$. The five strongest lines in the X-ray powder diffraction pattern are [d_{obs} in Å (I) (hkl)]: 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 (R_1 = 3.42% for 1248 $F_o > 4\sigma F$ 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 hydrargillite. 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 $Al_3(PO_4)_2(OH)_3{\cdot}5H_2O$ 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 $Al_3(PO_4)_2(OH,F)_3{\cdot}5H_2O$ 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 $F_{0.53(4)}O_{0.47(4)}$.

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] 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

---

* E-mail: akampf@nhm.org
† Deceased.

0003-004X/17/0004–909$05.00/DOI: http://dx.doi.org/10.2138/am-2017-5948

structure and that very little, if any, F occupies the eightfold OH site, or any other O site in the structure. In the present study, this was confirmed by structure refinements conducted on high-F crystals from the Silver Coin mine and from the Wood mine, Cocke County, Tennessee.

In accord with the dominant-constituent rule (cf. Nickel and Grice 1998), we have proposed that wavellites containing more than ½ F apfu qualify as a distinct mineral species, the F analog of wavellite, and that this mineral be named fluorwavellite. The new mineral and name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2015-077). One co-type specimen from each locality is housed in the collections of the Mineral Sciences Department, Natural History Museum of Los Angeles County, California, catalog numbers 65600 (Wood mine) and 65601 (Silver Coin mine).

Note that the analysis reported in Dana (189, p. 842–8432) for wavellite from Devon, England (Table[1] 1), which contains 0.43 F apfu, presumably corresponds to material from the wavellite type locality.

OCCURRENCE AND PARAGENESIS

Fluorwavellite occurs at many localities worldwide (see Table[1] 1); but the complete characterization of the species is based upon material from two mines, which should be regarded as co-type localities: the Silver Coin mine, Valmy, Iron Point district, Humboldt County, Nevada (40°55′44″N 117°19′26″W) and the Wood mine, 5 miles NE of Del Rio, Cocke County, Tennessee (35°57′52″N 82°57′36″W). At both occurrences, fluorwavellite is a low-temperature, secondary mineral.

The Silver Coin mine is a small base-metal deposit that was last worked in 1929. Since the late 1980s, the mine has been a popular site for collectors in search of rare mineral species. An extensive EDS survey of wavellites from the Silver Coin mine showed all to be the new species fluorwavellite. It is found in the Phosphate Stope, Copper Stope, and Arsenate Drift. The co-type specimen is from the Copper Stope. On this specimen, fluorwavellite is associated with barite, fluorowardite, goethite, gypsum, kidwellite, quartz, and rockbridgeite. Other species observed with fluorwavellite at the Silver Coin mine are chlorargyrite, crandallite, iangreyite, jarosite, lipscombite, metavariscite, turquoise, and variscite. A comprehensive list of mineral species occurring at the Silver Coin mine is given by Adams et al. (2015). The Silver Coin mine is the type locality for zinclipscombite (Chukanov et al. 2006), meurigite-Na (Kampf et al. 2009), iangreyite (Mills et al. 2011a), krasnoite (Mills et al. 2012), fluorowardite (Kampf et al. 2014), ferribushmakinite (Kampf et al. 2015), and crimsonite (Kampf et al. 2016).

The Wood mine is a small manganese deposit that was last worked in 1906 (Stose and Schrader 1923). The ore, consisting of massive manganese oxides, mostly pyrolusite and cryptomelane, was obtained from a small open pit, which has long been overgrown. Over the last 50 years, collectors have worked the mine dumps for specimens of wavellite and variscite (Barwood 1997), which occur in veinlets in the manganese oxides.

While all of the samples from Silver Coin and Wood mines that we have analyzed qualify as fluorwavellite, the analyses listed in Table[1] 1 clearly indicate that both wavellite and fluorwavellite occur at many deposits and that the genetic type of the deposit does not correlate with the selective presence of either species. The occurrences of wavellite-fluorwavelite are examined in greater detail below.

PHYSICAL AND OPTICAL PROPERTIES

Fluorwavellite occurs as colorless prisms up to 1 mm long from the Silver Coin mine and up to 3 mm long from the Wood mine (Figs. 1 and 2). Crystals exhibit the forms {010}, (110}, and {101} (Fig. 3). The prisms commonly grow in radial sprays at both localities. Crystals also form bow-tie-like crystal sprays at the Silver Coin mine and dense intergrowths of subparallel prisms perpendicular to vein walls at the Wood mine. No twinning was observed.

FIGURE 1. Fluorwavellite crystals with kidwellite from the Silver Coin mine. The FOV is 1 mm across. (Color online.)

FIGURE 2. Fluorwavellite crystals from the Wood mine. The FOV is 3.5 mm across. (Color online.)

---

[1] Deposit item AM-17-45948, CIF and tables. Deposit items are free to all readers and found on the MSA web site, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2017/Apr2017_data/Apr2017_data.html).

The streak is white. Crystals are transparent with vitreous luster. The mineral does not fluoresce in long- or short-wave ultraviolet light. The Mohs hardness is about 3½, the tenacity is brittle, the fracture is uneven to conchoidal, and crystals exhibit three cleavages: one perfect on {110} and two good on {101} and {010}. The density of Wood mine crystals, measured by pycnometer, is 2.30(1) g/cm^3. The calculated density for Wood mine crystals based on the empirical formula and the unit-cell parameters from the single-crystal data are 2.345 g/cm^3. Trapped air in crystal intergrowths could account for the somewhat low value of the measured density. Fluorwavellite is insoluble in concentrated HCl and concentrated H_2SO_4, observed over the course of several hours.

Optically, fluorwavellite is biaxial positive, with α = 1.522(1), β = 1.531(1), γ = 1.549(1), measured in white light. The $2V$ measured directly on a spindle stage is 71(1)°; the calculated $2V$ is 71.2°. Weak $r > v$ dispersion was observed. The optical orientation is X = **b**; Y = **a**; Z = **c**. The mineral is non-pleochroic.

The Gladstone-Dale compatibility index $1 - (K_P/K_C)$ as defined by Mandarino (1981) provides a measure of the consistency among the average index of refraction, unit-cell parameters (used to calculate the density) and chemical composition. For fluorwavellite, the compatibility index is –0.001 based on the empirical formula, within the range of superior compatibility.

Raman and infrared spectroscopy

The Raman spectra of fluorwavellite from the Silver Coin and Wood mines were recorded with a Renishaw inVia microprobe using a 785 nm diode laser to reduce fluorescence observed with the 514 nm laser. The nominal analysis area was 5 × 50 μm. The Fourier transform infrared (FTIR) spectra were recorded using a Thermo-Nicolet model 6700 spectrometer equipped with a Continuμm microscope. The samples were analyzed in transmission mode with a micro-diamond compression cell using one diamond window as the background.

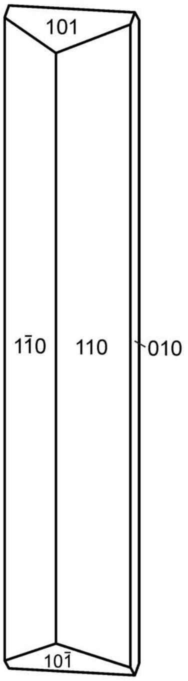

FIGURE 3. Crystal drawing of fluorwavellite (clinographic projection).

Samples from both mines yielded essentially identical results, so only the Raman and FTIR spectra for the Silver Coin samples are shown in Figures 4 and 5, respectively. Band assignments were made according to Capitelli et al. (2014). The Raman spectrum shows peaks (in cm^{-1}) at 1022 (ν_1 PO_4 symmetric stretch), 636 and 550 (ν_4 PO_4 asymmetric bend), 421 (ν_2 PO_4), and 315 and 277 (Al-O lattice vibrations). The FTIR spectrum has a sharp peak at 3521 from (OH) stretch and three broad bands at 3422, 3212, and 3092 from H_2O stretch. The H_2O bending mode was observed at 1637 and 1586 and the ν_3 (PO_4) and ν_1 (PO_4) symmetric stretchmodes at 1055 and 1022, respectively. There are no significant differences between the Raman and FTIR spectra of fluorwavellite and those of F-rich wavellite reported by Capitelli et al. (2014).

Chemical composition

Electron probe microanalyses (EPMA; nine spots on three crystals for each co-type locality) were carried out using a Cameca SX-50 electron microprobe in the Department of Geology and Geophysics at the University of Utah (WDS mode, 15 kV, 10 nA, 10 μm beam diameter). Raw X-ray intensities were corrected for matrix effects with a $\phi(\rho z)$ algorithm (Pouchou and Pichoir 1991). CHN analyses provided 22.84 wt% H_2O

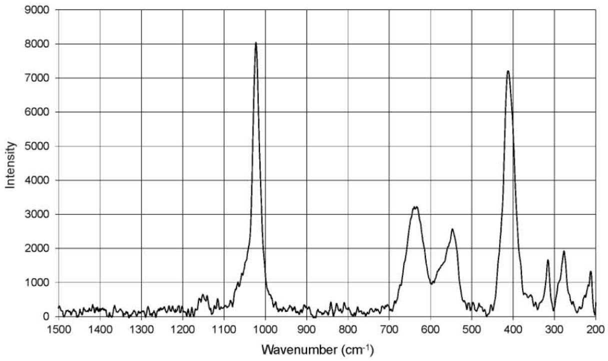

FIGURE 4. Raman spectra of fluorwavellite from the Silver Coin mine.

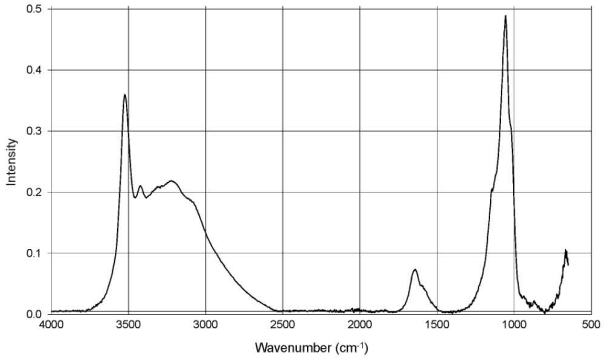

FIGURE 5. FTIR spectrum of fluorwavellite from the Silver Coin mine.

for material from the Wood mine; however, impurities almost certainly contribute to the lower than expected value. There was insufficient material for CHN analyses of Silver Coin material. Consequently, we have calculated H_2O for both Wood mine and Silver Coin mine analyses on the basis of P = 2 apfu, charge balance, and 16 O+F apfu, as determined by the crystal-structure analysis (see below). Analytical data are given in Table 2.

The empirical formulas (based on 16 O+F) are $Al_{2.96}(PO_4)_2(OH)_{1.98}F_{1.02}\cdot 5H_2O$ (+0.12 H for charge balance) for the Silver Coin mine analyses and $Al_{2.98}(PO_4)_2(OH)_{2.11}F_{0.89}\cdot 5H_2O$ (+0.06 H for charge balance) for the Wood mine analyses. The end-member formula is $Al_3(PO_4)_2(OH)_2F\cdot 5H_2O$, which requires Al_2O_3 36.94, P_2O_5 34.29, H_2O 26.11, F 4.59, F=O –1.93, total 100 wt%.

The survey of F contents in wavellites in Table[1] 1 includes the aforementioned analyses, other new analyses by EPMA and by scanning electron microscope wavelength-dispersive spectrometry (SEM-WDS), as well as analyses reported by other investigators. The EPMA analyses were conducted on a Cameca SX-40 (15kV and 10 nA) in the Geology Department at Indiana University and the SEM-WDS analyses were conducted on a JEOL 7600F field emission SEM equipped with an Oxford WAVE WDS (10 kV, 5.5 nA, and a 12 μm spot size).

X-ray crystallography and structure refinement

Both powder and single-crystal X-ray studies were carried out using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer, with monochromatized Mo*K*α radiation. For the powder-diffraction study, a Gandolfi-like motion on the φ and ω axes was used to randomize the sample and observed *d*-values and intensities were derived by profile fitting using JADE 2010 software (Materials Data, Inc.). The powder data are presented in Table[1] 3. Unit-cell parameters refined from the powder data using whole pattern fitting are: $a = 9.6482(16)$, $b = 17.362(3)$, $c = 6.9848(11)$ Å, and $V = 1170.0(3)$ Å^3.

Structure refinements were performed using data obtained from crystals from both the Silver Coin mine and the Wood mine. The results were very similar; however, because the refinement based on the data for the Wood mine crystal was better, it is the only one reported here. The Rigaku CrystalClear software package was used for processing of structure data, including the application of an empirical multi-scan absorption correction using ABSCOR (Higashi 2001). SHELXL-2013 software (Sheldrick 2015) was used for the refinement of the structure with neutral-atom scattering factors. The starting atom coordinates for the structure refinement were taken from the structure determination of wavellite by Capitelli et al. (2014). The O5 and O6 sites in the wavellite structure, each shared between two Al atoms, are clearly either OH or F. The occupancy of the O5(F5) site refined to $F_{0.90}O_{0.10}$, while the O6 site refined to full occupancy by O. The H atom site associated with the O6 site was located in a difference Fourier map, as were H sites associated with the O7 and O8 sites, corresponding to H_2O groups. The H sites were then refined with soft restraints of 0.82(3) Å on the O–H distances and 1.30(3) Å on the H–H distances and with the U_{eq} of each H tied to that of its O atom (×1.5 for OH and ×1.2 for H_2O). Details of data collection and structure refinement are provided in Table 4. Fractional coordinates and atom displacement parameters are provided in Table[1] 5, selected interatomic distances in Table[1] 6, and bond valences in Table[1] 7. (CIF available[1].)

TABLE 2. Analytical data (wt%) for fluorwavellite

Const.	Silver Coin mine			Wood mine			Probe
	Mean	Range	S.D.	Mean	Range	S.D.	Standard
Al_2O_3	36.79	36.35–37.07	0.22	36.68	36.42–37.09	0.21	sanidine
P_2O_5	34.66	33.90–35.51	0.50	34.31	33.50–34.95	0.42	apatite
F	4.74	4.48–4.96	0.17	4.08	3.58–4.46	0.26	syn. CaF_2
H_2O[a]	26.65			26.52			
F=O	–2.00			–1.72			
Total	100.84		99.87				

[a] Based on the structure.

DESCRIPTION OF THE STRUCTURE

As for wavellite, the structure of fluorwavellite (Fig. 6) contains two different chains of corner-sharing $Al\varphi_6$ (φ = F, O, OH or H_2O) octahedra along [001]; one chain consists of all $Al1\varphi_6$ octahedra and the other of $Al2\varphi_6$ octahedra. These chains are linked to one another by corner-sharing with PO_4 tetrahedra (Fig. 7). The result is a framework structure with channels along [001]. Within these channels are disordered H_2O groups located at half-occupied O9 and O10 sites, 0.895(9) Å apart. Note that the H sites associated with these disordered H_2O groups cannot generally be located in refinements of the wavellite structure.

In the wavellite structure (and specifically in our refinement of the fluorwavellite structure), the O5/F5 and O6 sites are similar in that each is a linking corner between two $Al\varphi_6$ octahedra; O5/F5 links $Al1\varphi_6$ octahedra and the O6 site links Al2 φ_6 octahedra. The environments of these sites differ in several important respects: (1) the Al1–O5/F5 distances are much shorter than the Al2–O6 distances; (2) the chain of $Al2\varphi_6$ octahedra is significantly more kinked than the chain of $Al1\varphi_6$ octahedra (see Fig. 7) and (3) the O6 site is within reach of a potential hydrogen bond acceptor (O3 at 2.859 Å), while the closest potential hydrogen bond acceptor to O5/F5 is quite distant (O4 at 3.198 Å). (Note that the kinking

TABLE 4. Data collection and structure refinement details for fluorwavellite from the Wood mine

Diffractometer	Rigaku R-Axis Rapid II
X-ray radiation/power	Mo*K*α (λ = 0.71075 Å)/50 kV, 40 mA
Temperature	293(2) K
Structural formula	$Al_3(PO_4)_2(OH)_2[F_{0.90}(OH)_{0.10}]\cdot 5H_2O$
Space group	*Pcmn*
Unit-cell parameters	$a = 9.6311(4)$ Å $b = 17.3731(12)$ Å $c = 6.9946(3)$ Å
V	1170.35(11) Å^3
Z	4
Density (for above formula)	2.353 g/cm^3
Absorption coefficient	0.701 mm^{-1}
F(000)	843.6
Crystal size	130 × 75 × 45 μm
θ range	3.60 to 27.49°
Index ranges	$-12 \leq h \leq 12, -22 \leq k \leq 22, -9 \leq l \leq 6$
Reflections collected/unique	6066/1376 [$R_{int} = 0.035$]
Reflections with $F_o > 4\sigma F$	1248
Completeness to θ = 27.49°	99.3%
Min. and max. transmission	0.914 and 0.969
Refinement method	Full-matrix least-squares on F^2
Parameters refined/restraints	124/7
GoF	1.082
R indices [$F_o > 4\sigma F$]	$R_1 = 0.0342$, $wR_2 = 0.0946$
R indices (all data)	$R_1 = 0.0370$, $wR_2 = 0.0970$
Largest diff. peak/hole	+0.66/–0.44 *e*/A^3

Note: $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma[F_o^2]$. GoF = $\Sigma = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$. $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where *a* is 0.0716, *b* is 0.1059, and *P* is $[2F_c^2 + \text{Max}(F_o^2,0)]/3$.

of the $Al2\varphi_6$ chain facilitates the close approach of the O6 site to the O3 site.) The hydrogen bond between O6 and O3 clearly contributes to the stability of the structure and this explains why OH preferentially occupies the O6 site, and conversely why F is preferred at the O5/F5 site. In their report on the structure refinement of an F-rich wavellite, Capitelli et al. (2014) also reported that all F is accommodated at the O5 site.

GENETIC TYPES OF WAVELLITE OCCURRENCES

Our survey of F contents in wavellites (Table[1] 1) indicates that nearly all wavellites contain significant amounts of F and that many, if not most, are fluorwavellite. As of August 2016, there are 389 wavellite localities listed on Mindat (www.mindat.org/min-4250.html). It appears that, taken together, wavellite and fluorwavellite are the most common F-bearing phosphate minerals, outside of the apatite group, in near-surface environments. Along with members of the crandallite group, wavellite is the most common product of weathering/alteration of phosphorites and aluminous phosphatic rocks. Vast blanket deposits of both minerals exist worldwide where meteoric water leaches clay-rich phosphorites. Concentrations of wavellite have even been mined for phosphorus and aluminum salts in Pennsylvania at Moore's Mill, Cumberland County (Stose 1907; Gordon 1922) and St. Clair County, Alabama (Schrader et al. 1917).

Wavellite (including fluorwavellite) is formed in a wide variety of environments. Most reported occurrences of wavellite are of five general genetic types, which we refer to here as fluid expulsion, hydrothermal ore alteration, pegmatite phosphate alteration, residual carbonate weathering, and sedimentary leached zone. Rarer occurrences are carbonatites/syenites (four listed on Mindat) and guano deposits (one listed on Mindat). There were also 37 localities listed on Mindat that did not contain sufficient information to identify the type of occurrence.

Fluid expulsion occurrences of wavellite form in veins derived from fluid expelled during low grade metamorphism. These types of deposits are widespread and include many of the better known locations for wavellite specimens, including the Devon, England type locality and the noteworthy wavellite occurrences in Garland, Montgomery, and Saline counties, Arkansas (Barwood and Delinde 1989). Most slate-hosted occurrences worldwide are of this type. Of the 389 localities on Mindat, 52 are of this type.

Hydrothermal ore alteration occurrences of wavellite derive from low-grade hydrothermal alteration of phosphatic rocks and alteration of apatite in ore veins (e.g., Silver Coin mine, Nevada; Llallagua, Bolivia), blanket deposits from rising volcanic solutions such as epithermal gold deposits (e.g., Carlin trend, Nevada) and acid phosphosulfate deposits (Bajnóczi et al. 2004) are common worldwide wherever they have been exposed by mining. Of the 389 localities listed on Mindat, 137 are of this type.

Pegmatite phosphate alteration occurrences of wavellite result from the alteration of aluminous primary phosphates, usually amblygonite-montebrasite, in pegmatites. Noteworthy occurrences are those at Montebras, France, and Hagendorf, Germany (Dill and Weber 2009). Of the 389 localities listed on Mindat, 19 are of this type.

Residual carbonate weathering occurrences of wavellite result from the meteoric weathering of phosphatic limestones and glauconitic sandstones and cherts, and lateritic weathering of limestone-hosted karst deposits (Hall et al. 1997; Deady et al. 2014). Widespread and numerous examples are found in old iron and manganese mines, and in bauxite deposits throughout the eastern United States (e.g., Wood mine, Tennessee) and central Europe. Of 389 localities on Mindat, 74 are of this type.

Sedimentary leached zone occurrences of wavellite derive from the meteoric weathering of phosphate-rich rocks (phosphorites) and carbonatites. Noteworthy examples of such deposits are found in Florida and Senegal (Van Kauwenbergh et al. 1990; Flicoteaux and Lucas 1984). Of the 389 occurrences listed on Mindat, 42 are of this type.

The genetic classification of all of the wavellite-fluorwavellite samples in our survey is indicated in the last column of Table[1] 1. It is clear from this survey that F content, and the occurrence of wavellite vs. fluorwavellite, does not correlate with the genetic type of the occurrence. Rather, it is more likely related to the fluid activity of Al, P, and F (likely also coupled with S and Fe). A noteworthy example is provided by the crystals from Slate

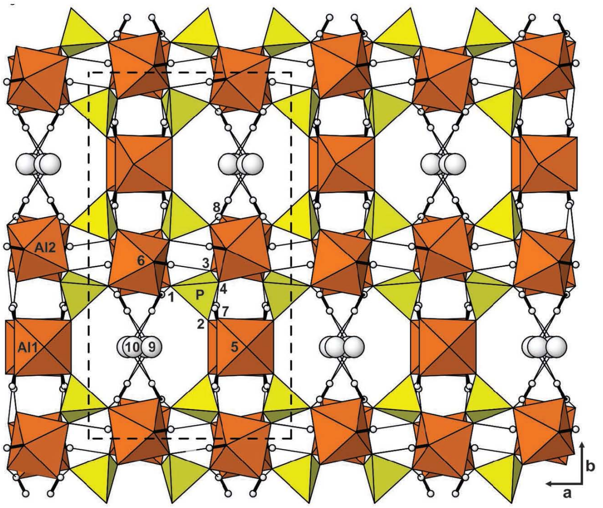

FIGURE 6. The structure of fluorwavellite viewed along [001]. O–H bonds are thick black lines; H···O (hydrogen) bonds are thin black lines. O/F sites are numbered. (Color online.)

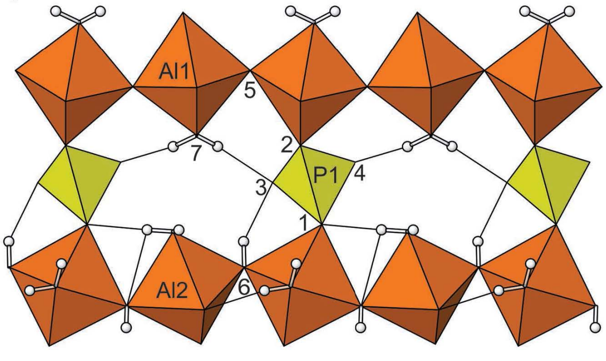

FIGURE 7. Two different corner-linked chains of $Al\varphi_6$ (φ = F, O, OH or H_2O) octahedra in the structure of fluorwavellite. O–H bonds are thick black lines; H···O (hydrogen) bonds are thin black lines. O/F sites are numbered. (Color online.)

Mountain, California, examined in this study, which show zoning from F-rich cores (>3.9% F) to F-poor rims (<0.5% F).

The role of pH in the formation of wavellite and fluorwavellite

Aluminum in soils and sediments is normally highly insoluble; however, under highly acidic or alkaline conditions, it forms various soluble complexes. In natural waters, aquo, $(OH)^-$, F^-, and organic complexes are the most important (Driscoll and Schecher 1990; Driscoll et al. 2001). Using fluorescence spectroscopy, one of the authors (HB) has detected traces of organic phases in wavellite. It is also well known that pH controls Al polymerization in soils (Huang and Keller 1972). It is reasonable to assume that pH also plays a significant role in the formation of wavellite and fluorwavellite.

In soils, Al has two ranges of solubility, below pH 6 and above pH 8. Under very acid conditions (<pH 3), monomeric Al^{3+} is the dominant ion in solution. As the pH rises, hydrolyzed OH^- complexes become more prominent. All forms of soluble Al reach a minimal solubility around pH 6.5 (Driscoll and Schecher 1990). Wavellite is generally insoluble in acid solutions (allowing specimens to be routinely cleaned with oxalic acid and hydrochloric acid solutions). At elevated pH (>9), wavellite and fluorwavellite are readily soluble and could contribute to the release of F into the environment. Such highly alkaline conditions are rare; consequently, wavellite and fluorwavellite are more likely to act as sinks, rather than sources of F.

Fluorine in soils and sediments is invariably coupled to Al complexes. Studies have shown that the maxima for soluble Al in soils also coincides with maximum absorption of F in the range of pH 4.8–6.5 (Arnesen and Krogstad 1998; Wenzel and Blum 1992). Aluminum in soils and sediments is mostly associated with clay minerals and they have been shown to react strongly with F. Replacement of OH in kaolinites by F has been demonstrated (Zhang et al. 2007), and this may have a bearing on the formation of fluorwavellite. In solution, F is entirely bound by Al complexes below pH 5. As the pH rises, hydroxyl complexes of Al form, resulting in more free F in solution (Skjelkvale 1994). The role of F released from apatite is not well defined for any of the wavellite forming systems discussed in this paper.

Phosphorus in wavellite-forming systems is ultimately derived from apatite sources. The phosphate anion in solution is entirely pH dependent. Reaction of phosphate with Fe, Al, and Ca occurs over specific pH regions (Goldberg and Sposito 1984). Maximum absorption of P by iron occurs around pH 3.5 and extends up to around pH 5.5. Phosphorus sorption by aluminum begins around pH 4, peaks at around pH 5.5, and tapers off to nil around pH 7. Calcium fixation begins around pH 6 and extends above pH 9. Studies of the mobility of P and Al in lateritic deposits are consistent with these constraints (Huang and Keller 1972; Vieillard et al. 1979). Practical observations of the sequence of mineralization in supergene Fe deposits is also consistent with the sequence of pH and availability of Fe, Al, and P outlined here (Dill et al. 2009).

Implications

Our survey of F contents shows that the occurrence of wavellite vs. fluorwavellite does not correlate with the genetic type of the occurrence. Coupled with our refinement of the fluorwavellite structure, we have also shown that a complete solid solution exists between wavellite and fluorwavellite, and we have defined an apparent limit for the F content of wavellite-fluorwavellite of about one F apfu. Considering that wavellite and fluorwavellite are the most common F-bearing phosphate minerals, outside of the apatite group, in near-surface environments, our findings can be used to understand the occurrence of fluorine in natural systems.

The genesis of wavellite-fluorwavellite is more complex than previously recognized. The role of P and Al availability is only partially understood and the role that hydroxyl, sulfate, organic, and fluoro Al complexes play is less well defined, but recognized. The specific fields of soluble and complexed Al, Fe, F, and P that lead to the formation of wavellite-fluorwavellite need much more study. What is well documented is that pH is clearly critical to the formation, stability, and solubility of wavellite-fluorwavellite. As noted above, at elevated pH (>9), wavellite-fluorwavellite is readily soluble and could contribute to the release of F into the environment; however, because such highly alkaline conditions are rare, wavellite-fluorwavellite is more likely to act as a sink, rather than a source of F. The role that wavellite-fluorwavellite plays in sequestering F in the environment is likely to be significant and deserves further study.

Acknowledgments

Reviewers Ferdinando Bosi and Ian Gray are thanked for their constructive comments on the manuscript. Anatoly Kasatkin is thanked for analyses of fluorwavellite samples in the collection of the Fersman Museum. A portion of this study was funded by the John Jago Trelawney Endowment to the Mineral Sciences Department of the Natural History Museum of Los Angeles County.

References cited

Adams, P.M., Wise, W., and Kampf, A.R. (2015) The Silver Coin mine, Iron Point district, Humboldt County, Nevada. Mineralogical Record, 46, 701–728.

Anthony, J.W., Bideaux, R.A., Bladh, K.W., and Nichols, M.C., Eds. (2000) Handbook of Mineralogy, Volume 4. Arsenates, Vanadates, Phosphates. Mineral Data Publishing, Tucson, Arizona, 680 pp.

Araki, T., and Zoltai, T. (1968) The crystal structure of wavellite. Zeitschrift für Kristallographie, 127, 21–33.

Arnesen, A.K.M., and Krogstad, T. (1998) Sorption and desorption of fluoride in soil polluted from the aluminum smelter at Ardal (Western Norway). Water, Air, and Soil Pollution, 103, 357–373.

Bajnóczi, B., Seres-Hartai, E., and Nagy, G. (2004) Phosphate-bearing minerals in the advanced argillic alteration zones of high-sulphidation type ore deposits in the Carpatho-Pannonian Region. Acta Mineralogica-Petrographica, Szeged, 45, 81–92.

Barwood, H. (1997) Red and pink variscite from the Wood mine, Cocke County, Tennessee. Rocks & Minerals, 72, 268–270.

Barwood, H., and Delinde, H. (1989) Arkansas phosphate minerals: a review and update. Rocks and Minerals, 64, 294–299.

Bergendahl, M.H. (1955) Wavellite spherulites in the Bone Valley formation of central Florida. American Mineralogist, 40, 497–504.

Brese, N.E., and O'Keeffe, M. (1991) Bond-valence parameters for solids. Acta Crystallographica, B47, 192–197.

Brown, I.D., and Altermatt, D. (1985) Bond-valence parameters from a systematic analysis of the inorganic crystal structure database. Acta Crystallographica, B41, 244–247.

Capitelli, F., Della Ventura, G., Bellatreccia, F., Sodo, A., Saviano, M., Ghiara, M.R., and Rossi, M. (2014) Crystal-chemical study of wavellite from Zbirov, Czech Republic. Mineralogical Magazine, 78, 1057–1070.

Chukanov, N.V., Pekov, I.V., Möckel, S., Zadov, A.E., and V.T. Dubinchuk. (2006) Zinclipscombite $ZnFe_2^{3+}(PO_4)_2(OH)_2$—a new mineral. Proceedings of the Russian Mineralogical Society, 135, 13–18.

Dana, E.S. (1892) The System of Mineralogy of James Dwight Dana 1837–1868, 6th ed., p. 842–843. Wiley, New York.

Deady, E., Mouchos, E., Goodenough, K., Williamson, B., and Wall, F. (2014) Rare earth elements in karst-bauxites: a novel untapped European resource? In ERES 2014: 1st European Rare Earth Resources Conference, Milos, 4–7 September,

2014. British Geological Survey/EURARE (www.eurare.eu), 364–375.

Dill, H.G., and Weber, B. (2009) Pleystein-City on Pegmatite. 4th International Symposium on Granitic Pegmatites, Recife, Brazil.

Dill, H.G., Weber, B., and Kaufhold, S. (2009) The origin of siderite-goethite-phosphate mineralization in the karst-related fault bound iron ore deposit Auerbach, Germany, a clue to the timing of hypogene and supergene Fe-Al phosphates in NE Bavaria. Neues Jahrbuch für Mineralogie Abhandlungen, 186, 283–307.

Driscoll, C.T., and Schecher, W.D. (1990) The chemistry of aluminum in the environment. Environmental Geochemical Health, 12(1), 28–49.

Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Butler, T.J., Cronan, C.S., Eager, C., Lambert, K.F., Likens, G.E., Stoddard, J.L., and Weathers, K.C. (2001) Acidic deposition in the Northeastern United States: Sources and inputs, ecosystem effects and management strategies. BioScience, 51, 180–193.

Flicoteaux, R., and Lucas, J. (1984) Weathering of phosphate minerals. In J.O. Nriagu et al., Eds., Phosphate Minerals, p. 290–317. Springer-Verlag, Berlin.

Goldberg, S., and Sposito, G. (1984) A chemical model of phosphate adsorption by soils: II Noncalcareous soils. Soil Science Society of America Journal, 48, 779–783.

Gordon, S.G. (1922) W.L. Newman mine, Pennsylvania. Mineralogy of Pennsylvania, 1, p. 136–138. Special Publication 1, The Academy of Natural Sciences of Philadelphia.

Green, D.I., Cotterell, T.F., Jones, I., Cox, D., and Cleevely, R. (2007) Wavellite: its discovery and occurrences in the British Isles. U.K. Journal of Mines & Minerals, 28, 11–30.

Hall, R.B., Foord, E.E., Keller, D.J., and Keller, W.D. (1997) Phosphates in some Missouri refractory clays. Clays and Clay Minerals, 45, 353–364.

Higashi, T. (2001) ABSCOR. Rigaku Corporation, Tokyo.

Huang, W.H., and Keller, W.D. (1972) Geological mechanics for the dissolution, transport and deposition of aluminum in the zone of weathering. Clays and Clay Minerals, 20, 69–74.

Jacob, K.D., Hill, W.L., Marshall, H.L., and Reynolds, D.S. (1933) The composition and distribution of phosphate rock with special reference to the United States. U.S. Department of Agriculture Technical Bulletin, 364, p 40.

Kampf, A.R., Adams, P.M., Kolitsch, U., and Steele, I.M. (2009) Meurigite-Na, a new species, and the relationship between phosphofibrite and meurigite. American Mineralogist, 94, 720–727.

Kampf, A.R., Adams, P.M., Housley, R.M., and Rossman, G.R. (2014) Fluorowardite, $NaAl_3(PO_4)_2F_2(OH)_2(H_2O)_2$, the fluorine analogue of wardite from the Silver Coin mine, Valmy, Nevada. American Mineralogist, 98, 804–810.

Kampf, A.R., Adams, P.M., Nash, B.P., and Marty, J. (2015) Ferribushmakinite, $Pb_2Fe^{3+}(PO_4)(VO_4)(OH)$, the Fe^{3+} analogue of bushmakinite from the Silver Coin mine, Valmy, Nevada. Mineralogical Magazine, 79, 661–669.

Kampf, A.R., Adams, P.A., Mills, S.J., and Nash, B.P. (2016) Crimsonite, $PbFe^{3+}_2(PO_4)_2(OH)_2$, the phosphate analogue of carminite from the Silver Coin mine, Valmy, Nevada, USA. Mineralogical Magazine, 80, 925–935.

Mäkelä, K. (1969) Wavellite from Kittilä, Finnish Lapland. Bulletin of the Geological Society of Finland, 41, 193–197.

Mandarino, J.A. (1981) The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. Canadian Mineralogist, 19, 441–450.

Matsubara, S., Aito, S., and Kato, A. (1988) Phosphate minerals in chert from Toyoda, Kochi, City, Japan. Journal of Mineralogy Petrology and Economic Geology, 83, 141–149.

Mills, S.J., Kampf, A.R., Sejkora, J., Adams, P.M., Birch, W.D., and Plášil, J. (2011a) Iangreyite: a new secondary phosphate mineral closely related to perhamite. Mineralogical Magazine, 75, 329–338.

Mills, S.J., Ma, C., and Birch, W.D. (2011b) A contribution to understanding the complex nature of peisleyite. Mineralogical Magazine, 75, 2733–2737.

Mills, S.J., Sejkora, J., Kampf, A.R., Grey, I.E., Bastow, T.J., Ball, N.A., Adams, P.M., Raudsepp, M., and Cooper, M.A. (2012) Krásnoite, the fluorophosphate analogue of perhamite, from the Huber open pit, Czech Republic and the Silver Coin mine, Nevada. Mineralogical Magazine, 76, 625–634.

Nickel, E.H., and Grice, J.D. (1998) The IMA Commission on New Minerals and Mineral Names: Procedures and guidelines on mineral nomenclature. Canadian Mineralogist, 36, 913–926.

Palache, C., Berman, H., and Frondel, C. (1951) In Dana's System of Mineralogy, 7th ed., vol. II, pp. 962–964. Wiley, New York.

Pouchou, J.-L., and Pichoir, F. (1991) Quantitative analysis of homogeneous or stratified microvolumes applying the model "PAP." In K.F.J. Heinrich and D.E. Newbury, Eds., Electron Probe Quantitation, p. 3l–75. Plenum Press, New York.

Schrader, F.C., Stone, R.W., and Sanford, S. (1917) Useful minerals of the United States. U.S. Geological Survey Bulletin 624, p. 15.

Sheldrick, G.M. (2015) Crystal Structure refinement with *SHELX*. Acta Crystallographica, C71, 3–8.

Skjelkvale, B.L. (1994) Factors influencing fluoride in Norwegian lakes. Water Air Soil Pollution, 77, 151–167.

Stose, G.W. (1907) Phosphorus ore at Mt. Holly Springs, Pennsylvania. U.S. Geological Survey Bulletin 315, 474–483.

Stose, G.W., and Schrader, F.C. (1923) Manganese deposits of east Tennessee. U.S. Geological Survey Bulletin 737, 154 p.

Van Kauwenbergh, S.J., Cathcart J.B., and McClellan, G.H. (1990) Mineralogy and alteration of the phosphate deposits of Florida. U.S.Geological Survey Bulletin 1914, 46 pp.

Vieillard, P., Tardy, Y., and Nahon, D. (1979) Stability fields of clays and aluminum phosphates: paragenesis in lateritic weathering of argillaceous phosphatic sediments. American Mineralogist, 64, 626–634.

Wenzel, W.W., and Blum, W.E.H. (1992) Fluorine speciation and mobility in F-contaminated soil. Soil Science, 153, 357–364.

Zhang, H., Baoyu, S., Penghua, L., and Wei, Z. (2007) Experimental study of fluorine transport rules in unsaturated stratified soil. Journal of China University of Mining and Technology, 17, 382–386.

Manuscript received September 6, 2016
Manuscript accepted November 17, 2016
Manuscript handled by G. Diego Gatta