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Fluorowardite, $NaAl_3(PO_4)_2(OH)_2F_2 \cdot 2H_2O$, the fluorine analog of wardite from the Silver Coin mine, Valmy, Nevada

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Abstract

Fluorowardite (IMA2012-016), $NaAl_3(PO_4)_2(OH)_2F_2 \cdot 2H_2O$, the F analog of wardite, is a new mineral from the Silver Coin mine, Valmy, Iron Point district, Humboldt County, Nevada, U.S.A., where it occurs as a low-temperature secondary mineral in complex phosphate assemblages rich in Al, Na, and F. Fluorowardite forms colorless to white or cream-colored, tetragonal-pyramidal crystals up to 0.1 mm in diameter. The streak is white. Crystals are transparent to translucent, with vitreous to pearly luster. The Mohs hardness is about 5, the tenacity is brittle, the fracture is irregular, and crystals exhibit one perfect cleavage on {001}. The calculated density is 2.760 g/cm^3. Optically, fluorowardite is uniaxial positive, with $\omega = 1.576(2)$ and $\varepsilon = 1.584(2)$ (white light) and is non-pleochroic. Electron microprobe analyses (average of 8) provided: Na_2O 6.27, CaO 1.74, MgO 0.42, Al_2O_3 35.21, Fe_2O_3 0.72, P_2O_5 32.49, As_2O_5 0.64, F 6.76, O=F –2.85, H_2O 13.35 (structure), total 94.74 wt%. The presence of H_2O and OH and the absence of CO_3 were confirmed by FTIR spectroscopy. The empirical formula (based on 14 anions) is: $(Na_{0.87}Ca_{0.13}Mg_{0.04})_{\Sigma 1.04}(Al_{2.96}Fe^{3+}_{0.04})_{\Sigma 3.00}(P_{1.96}As_{0.03})_{\Sigma 1.99}O_{8.12}(OH)_{2.35}F_{1.53} \cdot 2H_2O$. Fluorowardite is tetragonal, $P4_12_12$, $a = 7.077(2)$, $c = 19.227(3)$ Å, $V = 962.8(5)$ Å^3, and $Z = 4$. The eight strongest lines in the X-ray powder diffraction pattern are [d_{obs} in Å(I)(hkl)]: 4.766(100)(004,103); 3.099(75)(211,203); 3.008(62)(115,212); 2.834(28)(204,213); 2.597(56)(205); 1.7628(32)(400,401); 1.6592(29)(multiple); and 1.5228(49)(423, 2·2·10). The structure of fluorowardite ($R_1 = 3.15\%$ for 435 $F_o > 4\sigma F$) contains layers parallel to {001} consisting of $Al\varphi_6$ (φ = F, O, OH or H_2O) octahedra, PO_4 tetrahedra, and $NaO_6(H_2O)_2$ polyhedra. The two independent $Al\varphi_6$ octahedra link by corner-sharing to form a square array. Each PO_4 tetrahedron shares corners with three adjacent octahedra in the same square array and a fourth corner with an octahedron in the next layer. The Na atoms reside in the "cavities" in the square array, forming bonds only to O atoms in the same layer. Of the two nearly identical OH sites in the wardite structure, only one is occupied by F in the fluorowardite structure. This is an interesting example of a structure in which OH and F are selectively incorporated into two different, but similar, sites as the result of rather subtle hydrogen bonding influences.

Keywords: Fluorowardite; new mineral; crystal structure; hydrogen bonding; FTIR spectroscopy; Raman spectroscopy; electron microprobe analysis; Silver Coin mine, Valmy, Nevada