Fluorowardite, NaAl$_3$(PO$_4$)$_2$(OH)$_6$F$_2$·2H$_2$O, 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)$_6$F$_2$·2H$_2$O, 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 perfectcleavage on {001}. The calculated density is 2.760 g/cm$^3$. Optically, fluorowardite is uniaxial positive, with $\omega = 1.576(2)$ and $\epsilon = 1.584(2)$ (white light) and is non-pleochroic. Electron microprobe analyses (average of 8) provided: Na$_2$O 6.27, CaO 1.74, MgO 0.42, Al$_2$O$_3$, 35.21, Fe$_2$O$_3$, 0.72, P$_2$O$_5$, 32.49, As$_2$O$_5$, 0.64, F 6.76, O=F 2.85, H$_2$O 13.35 (structure), total 94.74 wt.%. The presence of H$_2$O and OH and the absence of CO$_3$ were confirmed by FTIR spectroscopy. The empirical formula (based on 14 anions) is: (Na$_{0.9}$Ca$_{0.1}$Mg$_{0.03}$)$_{21.98}$(Al$_{2.96}$Fe$_{0.04}$)$_{21.98}$(P$_{3.16}$As$_{0.03}$)$_{21.98}$O$_{5.12}$(OH)$_{2.83}$F$_{1.51}$; 2H$_2$O. Fluorowardite is tetragonal, $P_{4}$2$_{1}$2, $a$ = 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 $d_{hkl}$ in Å (hkl): 4.766(100)(004,103); 3.999(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$_{2}$O$_{4}$ ($\varphi$ = F, O, OH or H$_2$O) octahedra, PO$_{4}$ tetrahedra, and NaO$_{3}$(H$_2$O)$_{2}$ polyhedra. The two independent Al$_{2}$O$_{4}$ 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

INTRODUCTION

Wardite, NaAl$_3$(PO$_4$)$_2$(OH)$_6$·2H$_2$O, was first described by Davison (1896) from cavities in variscite nodules from Utah. Although not specifically mentioned in that paper, the type locality is the well-known Clay Canyon deposit near Fairfield in Utah County, which is also the type locality for englischite, gordonite, millisite, montgomeryite, and overite. Since that time, wardite has been reported from many other localities worldwide, but has previously not been reported to contain significant amounts of F. The structure of wardite was solved by Fanfani et al. (1970) using a crystal from the type locality. They reported the structure to include two distinct OH sites.

The recognition of wardite crystals in an F-rich secondary phosphate assemblage at the Silver Coin mine near Valmy, Nevada, led us to extensively survey wardite crystals for high F contents that could correspond to the F analog. We found F to be present in most of the wardite crystals in this assemblage, with contents reaching levels sufficient to take the place of nearly half of the OH in the structure. The refinement of the structure of one of these crystals (see below) showed the F to selectively occupy one of the OH sites, where it is strongly dominant over OH. While it is not entirely clear whether it is possible for both OH sites to be dominated by F, its dominance at one of the sites is sufficient to qualify the phase as a new mineral and the F analog of wardite.

The name is based upon the mineral being the F analog of wardite. Note that “fluoro-” rather than “fluor-” is used as the prefix to make pronunciation more straightforward. The new mineral and name have been approved by the Commission on