

1 Revision 1

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3 Fluorowardite, $\text{NaAl}_3(\text{PO}_4)_2(\text{OH})_2\text{F}_2 \cdot 2\text{H}_2\text{O}$, the fluorine analogue of wardite from the Silver Coin
4 mine, Valmy, Nevada.

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14

15 **Abstract**

16 Fluorowardite (IMA2012-016), $\text{NaAl}_3(\text{PO}_4)_2(\text{OH})_2\text{F}_2 \cdot 2\text{H}_2\text{O}$, the F analogue of wardite, is
17 a new mineral from the Silver Coin mine, Valmy, Iron Point district, Humboldt County, Nevada,
18 USA, where it occurs as a low-temperature secondary mineral in complex phosphate assemblages
19 rich in Al, Na, and F. Fluorowardite forms colorless to white or cream-colored, tetragonal-
20 pyramidal crystals up to 0.1 mm in diameter. The streak is white. Crystals are transparent to
21 translucent, with vitreous to pearly luster. The Mohs hardness is about 5, the tenacity is brittle,
22 the fracture is irregular, and crystals exhibit one perfect cleavage on {001}. The calculated
23 density is 2.760 g/cm³. Optically, fluorowardite is uniaxial positive, with $\omega = 1.576(2)$ and $\varepsilon =$

24 1.584(2) (white light) and is non-pleochroic. Electron microprobe analyses (average of 8)
25 provided: Na₂O 6.27, CaO 1.74, MgO 0.42, Al₂O₃ 35.21, Fe₂O₃ 0.72, P₂O₅ 32.49, As₂O₅ 0.64, F
26 6.76, O=F -2.85, H₂O 13.35 (structure), total 94.74 wt%. The presence of H₂O and OH and the
27 absence of CO₃ were confirmed by FTIR spectroscopy. The empirical formula (based on 14
28 anions) is: (Na_{0.87}Ca_{0.13}Mg_{0.04})_{Σ1.04}(Al_{2.96}Fe³⁺_{0.04})_{Σ3.00}(P_{1.96}As_{0.03})_{Σ1.99}O_{8.12}(OH)_{2.35}F_{1.53}·2H₂O.
29 Fluorowardite is tetragonal, $P4_12_12$, $a = 7.077(2)$, $c = 19.227(3)$ Å, $V = 962.8(5)$ Å³, and $Z = 4$.
30 The eight strongest lines in the X-ray powder diffraction pattern are [d_{obs} in Å(I)(hkl)]:
31 4.766(100)(004,103); 3.099(75)(211,203); 3.008(62)(115,212); 2.834(28)(204,213);
32 2.597(56)(205); 1.7628(32)(400,401); 1.6592(29)(multiple); and 1.5228(49)(423,2·2·10). The
33 structure of fluorowardite ($R_1 = 3.15\%$ for $435 F_o > 4\sigma F$) contains layers parallel to {001}
34 consisting of Al ϕ_6 ($\phi = \text{F, O, OH or H}_2\text{O}$) octahedra, PO₄ tetrahedra, and NaO₆(H₂O)₂ polyhedra.
35 The two independent Al ϕ_6 octahedra link by corner-sharing to form a square array. Each PO₄
36 tetrahedron shares corners with three adjacent octahedra in the same square array and a fourth
37 corner with an octahedron in the next layer. The Na atoms reside in the “cavities” in the square
38 array, forming bonds only to O atoms in the same layer. Of the two nearly identical OH sites in
39 the wardite structure, only one is occupied by F in the fluorowardite structure. This is an
40 interesting example of a structure in which OH and F are selectively incorporated into two
41 different, but similar, sites as the result of rather subtle hydrogen bonding influences.

42

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

45

46 **Introduction**

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

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

63 The name is based upon the mineral being the F analogue of wardite. Note that “fluoro-“
64 rather than “fluor-“ is used as the prefix to make pronunciation more straightforward. The new
65 mineral and name have been approved by the Commission on New Minerals, Nomenclature, and
66 Classification of the International Mineralogical Association (IMA2012-016). Two cotype
67 specimens are housed in the collections of the Mineral Sciences Department, Natural History
68 Museum of Los Angeles County, catalogue numbers 57659 and 63810. Specimen 57659 is also a
69 cotype for meurigite-Na (Kampf et al. 2009).

70

71 **Occurrence and paragenesis**

72 Fluorowardite occurs in the phosphate stope at the Silver Coin mine, Valmy, Iron Point
73 district, Humboldt County, Nevada, USA (40°55'44"N 117°19'26"W). It occurs in association
74 with alunite, barite, cacoxenite, chlorargyrite, fluorapatite, goethite, gorceixite (F-rich),
75 iangreyite, iodargyrite, jarosite, kidwellite, kintoreite/plumbogummite, krásnoite, leucophosphate,
76 lipscombite/zinlipscombite, meurigite-Na, metavariscite, millisite (F-rich), morinite, quartz,
77 rockbridgeite, strengite/variscite, and turquoise/chalcosiderite (minerals separated by slashes
78 exhibit variations in chemistry between the two species). A partial list of mineral species
79 occurring at the Silver Coin mine is given by Thomssen and Wise (2004). The Silver Coin mine
80 is the type locality for zinlipscombite (Chukanov et al. 2006), meurigite-Na (Kampf et al. 2009),
81 iangreyite (Mills et al. 2011), and krásnoite (Mills et al. 2012). Fluorowardite is a low-
82 temperature secondary mineral in complex phosphate assemblages rich in aluminium, sodium,
83 and fluorine.

84

85 **Physical and optical properties**

86 Fluorowardite occurs as colourless to white or cream-coloured, tetragonal-pyramidal
87 crystals truncated by the basal pinacoid. The forms observed are {001} (prominent and lustrous),
88 {011} and/or {012} (prominent, irregular and striated parallel to [100]), and {100} (common,
89 irregular and striated parallel to [100]); A variety of other minor forms, e.g. {114}, are observed
90 on SEM images, but are uncommon (Figs. 1 to 3). No twinning was observed. Crystals occur as
91 isolated individuals up to 0.1 mm in diameter and as drusy aggregates.

92 The streak is white. Crystals are transparent to translucent with vitreous to pearly luster.
93 Fluorowardite does not fluoresce in long or short wave ultraviolet light. The Mohs hardness is
94 about 5, the tenacity is brittle, the fracture is irregular, and crystals exhibit one perfect cleavage
95 on {001}. Attempts to measure the density by sink-float failed because of the small size of the
96 crystals and their near invisibility in available liquids. The calculated density based on the
97 empirical formula and the unit cell refined from the single-crystal data is 2.760 g/cm³.
98 Fluorowardite is unreactive and insoluble in concentrated HCl, concentrated H₂SO₄, and 70%
99 HNO₃, observed over the course of several hours. Optically, fluorowardite is uniaxial positive,
100 with $\omega = 1.576(2)$ and $\varepsilon = 1.584(2)$, measured in white light. The mineral is non-pleochroic.

101

102 **Infrared spectroscopy**

103 An FTIR spectrum (Figure 4) was obtained with a Thermo-Nicolet Model 6700
104 spectrometer equipped with a Continuum microscope. A small amount of material was crushed in
105 a diamond compression cell and analyzed in transmission through one diamond window. Band
106 assignments are according to Breitinger *et al.* (2004). The main observed bands (in
107 wavenumbers) are: 3615 and 3544 (OH stretching), 3274 and 3153 (H₂O stretching), 1659 (H₂O
108 bending), 1162 and 1131 [δ Al₂(OH)] and 1080 (PO₄ antisymmetric stretching), and 1008 (PO₄
109 symmetric stretching).

110

111 **Raman spectroscopy**

112 Raman spectroscopic micro-analyses were carried out using a Renishaw M1000 micro-
113 Raman spectrometer system. Light from a 514.5 nm argon laser was focused onto the sample
114 with a 100× objective lens, and at 100% power could provide approximately 5 mw of power at

115 the sample, in a spot size of about 1 μm . Spectral peak positions were periodically calibrated
116 against a silicon standard and rarely varied more than 1 cm^{-1} . All spectra were obtained with a
117 dual-wedge polarization scrambler inserted directly above the objective lens to minimize the
118 effects of polarization.

119 As a reference for the fluorowardite, we first obtained Raman spectra along the *a*- and *c*-
120 axes of a Rapid Creek, Yukon Territory, Canada, wardite crystal from the Caltech collection
121 (CIT-15080). In these spectra (Figures 5 and 6), we noted two strong, sharp lines at 3544 and
122 3616 cm^{-1} in the OH stretching region. In their recent spectroscopic study of wardite, Frost and
123 Xi (2012) noted similar strong lines in their IR spectra, and assigned them to the two
124 crystallographically distinct OH sites in the structure. The difference in vibrational energy in
125 these two otherwise similar sites already supports the view that they might have significantly
126 different preferences for OH, in agreement with the conclusions of the X-ray study.

127 For the fluorowardite, spectra were first collected from crystals in the microprobe section.
128 These consisted of an arc of crystals individually about 40 μm across surrounding a hemisphere
129 of material of undetermined composition, mounted in epoxy in a polished thin-section. After
130 obtaining spectra from 3 of these crystals, one determined optically to be along a *c*-axis, it
131 became obvious that, while not influencing the OH region, lines from the epoxy were
132 contributing to the spectra in the lower wavenumber regions. Next, spectra were obtained from 5
133 unoriented crystals on one sample of fluorowardite coated botryoidal matrix and 2 crystals from
134 another. The OH region of one of these crystals is shown in Figure 7.

135 For all 10 of the unoriented fluorowardite crystals measured, the ratio of the intensity of
136 the high-energy peak (3614 cm^{-1}) to the low-energy peak (3452 cm^{-1}) is less than that of the
137 lower ratio seen in the two wardite orientations. The average ratio in the unoriented crystals is

138 less than one forth the weighted average ratio seen in spectra from the oriented wardite crystal.
139 This again is consistent with the view that the F is preferentially located on only one
140 crystallographic site. The Raman spectrum of fluorowardite in the 1500-100 cm^{-1} region (Fig. 8)
141 is dominated by the phosphate bands at 1049, 1005, and 604 cm^{-1} . When Figure 8 is compared to
142 Figure 6, it can be seen that there are many similarities, and that for fluorowardite there is a
143 general broadening of several of the lines.

144

145 **Chemical composition**

146 Chemical analyses (8) were carried out using a JEOL 8200 electron microprobe in the
147 Division of Geological and Planetary Sciences, California Institute of Technology (WDS mode,
148 15 keV, 1 nA, 10-20 μm beam diameter). Standards were run at 10 nA. Quantitative elemental
149 microanalyses were processed with the CITZAF correction procedure. There was insufficient
150 material for CHN analyses, so H_2O was calculated on the basis of $\text{Al} + \text{Fe} = 3$, charge balance
151 and 14 total anions ($\text{O} + \text{F}$) *pfu*, as determined by the crystal structure analysis (see below). The
152 presence of H_2O and OH and the absence of CO_3 were further confirmed by FTIR spectroscopy
153 (see above). Note that fluorowardite is very prone to electron beam damage (melting), which
154 contributes to the low analytical total. We carefully monitored Na and F and confirmed that they
155 remained constant during the analyses. We believe that sample melting mitigated charge build up
156 at the electron penetration depth and hence eliminated any significant F or Na migration during
157 the analyses. Analytical data are given in Table 1.

158 The empirical formula (based on 14 anions) is

159 $(\text{Na}_{0.87}\text{Ca}_{0.13}\text{Mg}_{0.04})_{\Sigma 1.04}(\text{Al}_{2.96}\text{Fe}^{3+}_{0.04})_{\Sigma 3.00}(\text{P}_{1.96}\text{As}_{0.03})_{\Sigma 1.99}\text{O}_{8.12}(\text{OH})_{2.35}\text{F}_{1.53} \cdot 2\text{H}_2\text{O}$. The ideal

160 formula is $\text{NaAl}_3(\text{PO}_4)_2(\text{OH})_2\text{F}_2 \cdot 2\text{H}_2\text{O}$, which requires Na_2O 7.71, Al_2O_3 38.05, P_2O_5 35.32, F
161 9.45, H_2O 13.45, O=F -3.98, total 100 wt%.

162 The Gladstone-Dale compatibility index $1 - (K_p/K_c)$ as defined by Mandarino (1981)
163 provides a measure of the consistency among the average index of refraction, calculated density,
164 and chemical composition. For fluorowardite, the compatibility index is -0.002 based on the
165 empirical formula, within the range of superior compatibility.

166

167 **X-ray crystallography and structure refinement**

168 Both powder and single-crystal X-ray studies were carried out using a Rigaku R-Axis
169 Rapid II curved imaging plate microdiffractometer, with monochromatized $\text{MoK}\alpha$ radiation. For
170 the powder-diffraction study, a Gandolfi-like motion on the ϕ and ω axes was used to randomize
171 the sample and observed d -spacings and intensities were derived by profile fitting using JADE
172 9.3 software. The powder data are presented in Table 2. Unit-cell parameters refined from the
173 powder data using whole pattern fitting are: $a = 7.0458(13)$, $c = 19.131(4)$ Å, and $V = 949.7(3)$
174 Å³.

175 Even after considerable effort in selecting a fluorowardite crystal for structure data
176 collection, the best crystal found was quite small ($60 \times 50 \times 35$ μm) and of marginal quality.
177 Consequently, the dataset was rather limited and much less than optimal relative to the number of
178 parameters refined. The Rigaku CrystalClear software package was used for processing the
179 structure data, including the application of an empirical multi-scan absorption correction using
180 ABSCOR (Higashi 2001). The SHELXL-97 software (Sheldrick 2008) was used for the
181 refinement of the structure. The starting atom coordinates for the structure refinement were taken
182 from the structure determination of wardite by Fanfani *et al.* (1970). Bond-valence considerations

183 clearly indicate that the O5 and O7 sites in the wardite structure are the only possible sites for F.
184 Refining both of these sites with joint occupancy by O and F showed the O7 site to be fully
185 occupied by O and the O5 (F5) site to be mostly occupied by F. H atom positions were located in
186 difference Fourier maps and were constrained to H–O distances of 0.9(3) Å and an H–H distance
187 for the H₂O of 1.45 Å. The isotropic displacement parameters ($\times 1.2$) were tied to those of the O
188 atoms to which they are associated. The location of an H site related to O7 (OH7) is further
189 corroboration that this site is OH rather than F. It should also be noted that the infrared and
190 Raman spectroscopy (see above) also support the conclusion that F preferentially occupies one of
191 these sites. In the final refinement, the occupancy of the F5 site refined to 0.84 F and 0.16 O, in
192 reasonable agreement with the EMPA, which fits an occupancy of 0.77 F and 0.23 O for the site.

193 Details of data collection and structure refinement are provided in Table 3. Fractional
194 coordinates and atom displacement parameters are provided in Table 4, selected interatomic
195 distances in Table 5, and bond valences in Table 6.

196

197 **Description of the structure**

198 The structure (Figs. 9 and 10) contains layers parallel to {001} consisting of Al ϕ_6 ($\phi = \text{F,}$
199 O, OH or H₂O) octahedra, PO₄ tetrahedra, and NaO₆(H₂O)₂ polyhedra. The two independent Al ϕ_6
200 octahedra link by corner-sharing to form a square array, in which each Al2 octahedron shares
201 four corners with Al1 octahedra and each Al1 octahedron shares two *trans* corners with Al2
202 octahedra. Each PO₄ tetrahedron shares corners with three adjacent octahedra in the same square
203 array and a fourth corner with an octahedron in the next layer. The Na atoms reside in the
204 “cavities” in the square array, forming bonds only to O atoms in the same layer. The only

205 linkages between the layers are the aforementioned tetrahedron-octahedron shared corner and
206 hydrogen bonds.

207 The F5 and OH7 sites are the shared vertices between the Al octahedra. The Al1
208 octahedron includes one F5 and one OH7 atom, which are *trans* to one another. The Al2
209 octahedron includes two *cis* F5 and two *cis* OH7 atoms arranged around the girdle of the
210 octahedron. Considering the clear preference of F for the F5 site, it is particularly intriguing that,
211 discounting hydrogen bonding, there is no clear-cut topological difference between the F5 and
212 OH7 sites.

213 The H atom of the OH7 group in fluorowardite is positioned to participate in a very weak
214 hydrogen bond to O3 at an O–O distance of 3.354 Å and, although the H positions for wardite
215 have not been determined, the OH7–O3 distance of 3.38 Å in the wardite structure is also likely
216 to correspond to a weak hydrogen bond. The hydrogen bond acceptor for the OH5 group in
217 wardite is not clear. The nearest possible acceptor is OW6, at a distance of 2.83 Å, but OW6 is
218 already significantly bond-valence oversaturated (2.09 *vu* based on bond distances reported by
219 Fanfani et al. 1970) and is almost certainly a hydrogen bond donor to OH5. The other possibility
220 is O1, at a distance of 3.34 Å, but it is also bond-valence oversaturated (2.05 *vu*). The hydrogen
221 bonding in the structures of fluorowardite and wardite mainly involves the H atoms of the OW6
222 group. In both structures, the OW6 group donates one hydrogen bond to O2 (at O–O distances of
223 2.690 Å in fluorowardite and 2.64 Å in wardite) and one hydrogen bond to F5/OH5 (at O–φ
224 distances of 2.912 Å in fluorowardite and 2.83 Å in wardite). There is no possibility for even a
225 weak hydrogen bond from OW6 to OH7 in either structure.

226 It is noteworthy that the F5 site in the fluorowardite structure is significantly bond-
227 valence undersaturated (0.86 *vu*), and that it would be much more undersaturated were it not for

228 the hydrogen bond received from the OW6 group. If F occupied the OH7 site, that site would be
229 even more undersaturated than the F5 site, as it would receive no bond-strength contribution from
230 a hydrogen bond. Furthermore, if the OH7 site were occupied by F, it could not donate a
231 hydrogen bond to O3, leaving O3 highly bond-valence undersaturated (1.79 *vu*). Considering the
232 foregoing, it is clear that the hydrogen bonding in fluorowardite contributes significantly to the
233 bond-valence balance and, hence, the stability of its structure, and it can be reasoned that it
234 probably plays a significant role in the preference of F for the F5 site.

235

236 **Implications**

237 In the 117 years since wardite was first described, it has been reported to occur at dozens
238 of localities, sometimes in association with F-bearing phosphates, such as fluorapatite, morinite,
239 and fluellite; however, until now, the F-analogue of wardite has never been reported, and we are
240 unaware of any previous reports, published or unpublished, of F-bearing wardite. Fluorowardite
241 is the fifth new mineral described from the Silver Coin mine and all five of these species (the
242 others being iangreyite, krásnoite, meurigite-Na, and zinclipscorbite) occur in an unusual highly
243 F-rich phosphate assemblage. While it is likely that fluorowardite can form only in environments
244 highly enriched in F, it also seems likely that analyses of wardites occurring in only moderately
245 F-rich environments will show them to contain some F.

246

247

248 **Acknowledgements**

249 Reviewers Stuart Mills and Frédéric Hatert and Editor Keith Putirka are thanked for their
250 constructive comments on the manuscript. Work at the California Institute of Technology was

251 supported by grants from the Northern California Mineralogical Association and the National
252 Science Foundation (EAR-0947956). The remainder of this study was funded by the John Jago
253 Trelawney Endowment to the Mineral Sciences Department of the Natural History Museum of
254 Los Angeles County.

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- 290
- 291

292

FIGURE CAPTIONS

293 Figure 1. Backscatter SEM image of fluorowardite crystals growing on balls of turquoise over
294 lipscombite. The underlying material (white) is goethite.

295 Figure 2. Backscatter SEM image of fluorowardite and turquoise crystals.

296 Figure 3. Crystal drawing of fluorowardite (clinographic projection).

297 Figure 4. FTIR spectrum of fluorowardite.

298 Figure 5. Raman spectrum of wardite in the OH region taken with the laser illumination
299 down the *a*- and *c*-axes.

300 Figure 6. Raman spectrum of wardite in the lower wavenumber region obtained with the laser
301 illumination down the *a*- and *c*-axes.

302 Figure 7. Raman spectrum of fluorowardite in the OH region.

303 Figure 8. Raman spectrum of fluorowardite in the lower wavenumber region.

304 Figure 9. The structure of fluorowardite viewed along [010]. Hydrogen atoms are shown as
305 spheres. Na- ϕ and O-H bonds are shown as sticks. Hydrogen bonds are shown as single
306 lines. The outline of the unit cell is shown by thick dashed lines.

307 Figure 10. One layer in structure of fluorowardite viewed along [001]. Anion sites (O1, O2, O3,
308 O4, F5, OW6, and OH7) are numbered. The outline of the unit cell is shown by thick
309 dashed lines.

310

311 Table 1. Electron microprobe data for fluorowardite.
 312

Constituent	wt%	min	max	SD	Probe Standard
Na ₂ O	6.27	5.14	7.11	0.67	Amelia albite
CaO	1.74	1.11	2.20	0.33	syn. anorthite
MgO	0.42	0.20	0.77	0.17	syn. forsterite
Al ₂ O ₃	35.21	34.47	36.01	0.51	syn. anorthite
Fe ₂ O ₃	0.72	0.41	1.07	0.20	syn. fayalite
P ₂ O ₅	32.49	31.40	33.61	0.68	Durango fluorapatite
As ₂ O ₅	0.64	0.00	1.56	0.56	syn. GaAs
F	6.76	6.34	7.23	0.33	fluorophlogopite
O=F	-2.85				
H ₂ O*	13.35				
Total	94.74				

* Calculated from the structure.

313
 314

315 Table 2. Powder X-ray diffraction data for fluorowardite.
 316

I_{obs}	d_{obs}	d_{calc}	I_{calc}	hkl	I_{obs}	d_{obs}	d_{calc}	I_{calc}	hkl
9	6.639(15)	6.6116	12	101			1.7812	5	307
10	5.697(13)	5.6729	13	102			1.7614	30	400
19	5.000(7)	4.9821	31	110	32	1.7628(2)	1.7540	12	401
		4.8213	12	111			1.6979	4	403
100	4.766(2)	4.7827	44	004			1.6756	7	308
		4.7280	100	103			1.6661	5	326
4	4.397(19)	4.4187	5	112			1.6607	7	330
5	3.977(6)	3.9571	10	104	29	1.6592(4)	1.6545	4	331
8	3.929(7)	3.9260	14	113			1.6529	8	404
2	3.517(14)	3.5229	3	200			1.6506	3	413
7	3.481(8)	3.4646	20	201			1.6420	7	1·1·11
4	3.450(14)	3.4502	2	114			1.6000	4	405
75	3.099(1)	3.1091	46	211	7	1.5968(6)	1.5942	4	0·0·12
		3.0836	66	203			1.5896	5	327
62	3.008(2)	3.0345	26	115	6	1.5597(9)	1.5545	7	422
		2.9928	75	212			1.5295	20	423
28	2.834(1)	2.8365	16	204	49	1.5228(2)	1.5173	39	2·2·10
		2.8249	35	213			1.4964	3	424
3	2.692(2)	2.6856	11	116			1.4568	15	425
		2.6312	10	214			1.4405	4	1·0·13
56	2.597(1)	2.5916	70	205			1.4260	8	2·2·11
		2.5480	14	107	17	1.4210(4)	1.4182	6	408
6	2.399(2)	2.3961	7	117			1.4125	8	426
		2.3640	4	206			1.3941	5	502
7	2.329(2)	2.3311	4	301	10	1.3906(7)	1.3903	5	418
		2.3203	7	223			1.3818	4	510
7	2.268 (1)	2.2645	14	108			1.3760	3	503
9	2.166(1)	2.1700	5	312	9	1.3672(4)	1.3670	4	3·2·10
		2.1594	14	207			1.3649	6	427
28	2.109(1)	2.1081	31	304			1.3579	3	2·0·13
		2.1034	11	313	4	1.3320(4)	1.3334	7	2·1·13
8	2.078(2)	2.0876	4	225			1.3190	3	3·0·12
		2.0646	14	217	7	1.2978(3)	1.2963	11	522
13	2.022(2)	2.0350	7	109			1.2679	2	516
		2.0197	6	314	2	1.2663(7)	1.2657	2	429
		2.0016	6	305			1.2620	2	524
10	1.9644(6)	1.9630	16	226			1.2525	3	507
		1.9440	3	321			1.2470	2	3·0·13
20	1.9257(5)	1.9254	19	315	12	1.2465(3)	1.2455	6	440
		1.9146	6	322			1.2429	5	441
		1.9049	4	218	5	1.2135(4)	1.2140	7	438
6	1.8691(7)	1.8684	11	323			1.2011	4	3·3·11
		1.8410	3	227	7	1.2010(3)	1.1992	7	2·0·15
7	1.8253(9)	1.8263	2	316					
		1.8200	8	209					

Notes: Calculated lines with intensities less than 3 are not shown, unless they correspond to observed lines. Because the pattern was recorded using MoK α radiation, some significant calculated lines are contained in the shoulders of observed peaks.

319 Table 3. Data collection and structure refinement details for fluorowardite.
 320

321	Diffractometer	Rigaku R-Axis Rapid II
322	X-ray radiation / power	MoK α ($\lambda = 0.71075$ Å) / 50 kV, 40 mA
323	Temperature	298(2) K
324	Structural Formula	(Na _{0.98} Ca _{0.02})Al ₃ P _{1.86} O ₈ (OH) _{2.32} F _{1.68} (H ₂ O) ₂
325	Space group	<i>P</i> 4 ₁ 2 ₁ 2
326	Unit cell dimensions	<i>a</i> = 7.077(2) Å <i>c</i> = 19.227(3) Å
327		
328	<i>V</i>	962.8(5) Å ³
329	<i>Z</i>	4
330	Density (for above formula)	2.738 g/cm ³
331	Absorption coefficient	0.865 mm ⁻¹
332	<i>F</i> (000)	791
333	Crystal size	60 × 50 × 35 μm
334	θ range	3.58 to 20.8°
335	Index ranges	$-7 \leq h \leq 7$, $-7 \leq k \leq 7$, $-19 \leq l \leq 18$
336	Reflections collected / unique	3412 / 498 [<i>R</i> _{int} = 0.086]
337	Reflections with <i>F</i> _o > 4 σ <i>F</i>	436
338	Completeness to $\theta = 27.46^\circ$	99.7%
339	Max. and min. transmission	0.97 and 0.95
340	Refinement method	Full-matrix least-squares on <i>F</i> ²
341	Parameters refined	104
342	GoF	1.060
343	Final <i>R</i> indices [<i>F</i> _o > 4 σ <i>F</i>]	<i>R</i> ₁ = 0.0315, <i>wR</i> ₂ = 0.0640
344	<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0387, <i>wR</i> ₂ = 0.0660
345	Flack parameter	-0.4(5)
346	Largest diff. peak / hole	+0.25 / -0.24 e/Å ³
347	<i>Notes</i> : $R_{\text{int}} = \Sigma F_o^2 - F_o^2(\text{mean}) / \Sigma [F_o^2]$. $\text{GoF} = S = \{ \Sigma [w(F_o^2 - F_c^2)^2] / (n-p) \}^{1/2}$. $R_1 = \Sigma F_o - F_c / \Sigma F_o $.	
348	$wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$. $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where <i>a</i> is 0.0283, <i>b</i> is 0, and	
349	<i>P</i> is $[2F_c^2 + \text{Max}(F_o^2, 0)] / 3$.	

350 Table 4. Atom coordinates and displacement parameters (\AA^2) for fluorowardite.
351

	x/a	y/b	z/c	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	
352											
353	P*	0.1467(3)	0.3626(2)	0.34832(8)	0.0113(8)	0.0106(14)	0.0129(13)	0.0103(11)	-0.0012(9)	0.0008(8)	0.0008(8)
354	Al1	0.4038(3)	0.1014(3)	0.25947(9)	0.0153(6)	0.0162(13)	0.0147(13)	0.0150(11)	-0.0014(9)	0.0024(9)	0.0009(8)
355	Al2	0.0953(3)	0.0953(3)	0.0000	0.0158(8)	0.0152(11)	0.0152(11)	0.0172(16)	0.0005(10)	-0.0005(10)	-0.0018(14)
356	Na*	0.3851(4)	0.3851(4)	0.5000	0.0310(16)	0.027(2)	0.027(2)	0.038(3)	-0.0034(13)	0.0034(13)	0.008(2)
357	O1	0.0296(6)	0.4144(5)	0.3066(2)	0.0160(12)	0.011(3)	0.019(3)	0.018(3)	0.004(2)	-0.004(2)	0.002(2)
358	O2	0.3046(6)	0.5121(6)	0.33587(19)	0.0196(12)	0.017(3)	0.020(3)	0.022(3)	0.000(2)	0.001(2)	-0.006(2)
359	O3	0.2131(6)	0.1666(6)	0.3224(2)	0.0213(14)	0.019(3)	0.022(3)	0.023(3)	-0.001(2)	0.003(2)	0.001(2)
360	O4	0.1041(6)	0.3547(6)	0.4267(2)	0.0197(12)	0.014(3)	0.025(3)	0.020(2)	0.000(2)	0.000(2)	0.001(2)
361	F5*	0.1263(5)	0.3470(5)	-0.03794(17)	0.0242(17)	0.024(3)	0.021(3)	0.027(2)	0.0033(19)	-0.0002(19)	0.0004(18)
362	OW6	0.1941(8)	0.0324(7)	0.1930(2)	0.0257(14)	0.028(4)	0.024(4)	0.025(3)	0.008(3)	-0.003(3)	0.005(3)
363	H6a	0.155(9)	0.104(6)	0.160(2)	0.031						
364	H6b	0.203(9)	-0.087(4)	0.180(3)	0.031						
365	OH7	0.4114(6)	0.3446(6)	0.2179(2)	0.0188(13)	0.021(3)	0.019(3)	0.017(3)	0.002(2)	0.001(2)	0.005(2)
366	H7	0.486(7)	0.327(9)	0.182(2)	0.023						

367 * Refined site occupancies: P: 0.929(8); Na: 0.980(15) Na, 0.020(15) Ca; F5: 0.84(7) F, 0.16(7) O.
368
369

370 Table 5. Selected bond distances (Å) and angles (°) in fluorowardite.

371	P–O1	1.528(5)	Al1–O3	1.871(4)	Al2–OH7 (×2)	1.879(5)	Na–O4 (×2)	2.446(5)
372	P–O4	1.539(4)	Al1–O1	1.878(5)	Al2–O2 (×2)	1.891(4)	Na–O1 (×2)	2.458(4)
373	P–O3	1.547(5)	Al1–F5	1.894(5)	Al2–F5 (×2)	1.937(5)	Na–OW6 (×2)	2.514(6)
374	P–O2	1.557(4)	Al1–OH7	1.898(5)	<Al–φ>	1.902	Na–O3 (×2)	2.732(5)
375	<P–O>	1.543	Al1–O4	1.899(5)			<Na–O>	2.538
376			Al1–OW6	2.018(5)				
377			<Al–φ>	1.910				

378

379 Hydrogen bonds (D = donor, A = acceptor)

380	D–H	d(D–H)	d(H...A)	<DHA	d(D...A)	A	<HDH
381	OW6–H6a	0.86(3)	1.86(4)	161(6)	2.690(6)	O2	113(4)
382	OW6–H6b	0.88(3)	2.15(4)	145(5)	2.912(6)	F5	
383	OH7–H7	0.88(3)	2.47(3)	174(5)	3.354(6)	O3	

384

385

386 Table 6. Bond-valence analysis for fluorowardite. Values are expressed in valence units.

387

	O1	O2	O3	O4	F5	OW6	OH7	Σ
P	1.23	1.14	1.17	1.19				4.73
Al1	0.53		0.54	0.50	0.41	0.36	0.50	2.84
Al2		0.51 ×2→			0.36 ×2→		0.53 ×2→	2.80
Na	0.17 ×2→		0.08 ×2→	0.18 ×2→		0.15 ×2→		1.16
H6a		0.21				0.79		1.00
H6b					0.09	0.91		1.00
H7			0.07				0.93	1.00
Σ	1.93	1.86	1.86	1.87	0.86	2.21	1.96	

Notes: The bond strengths for the F5 site are based upon the refined site occupancy (0.84 F and 0.16 O).

Multiplicity is indicated by ×→. P⁵⁺–O and Al–O bond strengths are from Brese and O’Keeffe (1991). Al–F and Na–O bond strengths are from Brown and Altermatt (1985). Hydrogen-bond strengths are based on H⁺⋯O bond lengths, from Brown and Altermatt (1985); however, because X-ray diffraction locates the centroid of the electron density rather than the position of the nucleus, the determined H atom positions are too close to the donor atom by about 0.1 Å. Consequently, the H⁺⋯O/F bond lengths listed in Table 4 have been reduced by 0.1 Å for determination of the hydrogen bond strengths.

388



















