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THE ROLE OF FLUORINE IN VESUVIANITE: A CRYSTAL-STRUCTURE STUDY

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ABSTRACT

The crystal structures of three samples of fluorine-bearing vesuvianite have been refined to *R* indices of ~3.5% in the space group *P4/nnc* using single-crystal Mo*K*α X-ray intensity data. The same crystals were subsequently analyzed by wavelength-dispersion electron-microprobe analysis. Fluorine substitutes for (OH) at both the OH and O(10) sites in the structure. At the OH site, there is no discernable positional disorder; changes in the local bond-valence requirements accompanying the loss of the OH–O(7) hydrogen bond are satisfied by slight changes involving the coordinating cations. Bond lengths from O(7) to the *Z*(3) position remain constant, but the O(7)–*X*(3) distance contracts with increasing F-for-OH substitution in the crystal. Fluorine also substitutes for (OH) at the O(10) position. In this case, there is significant positional disorder involving both the anions at the O(10) position *and* the cations at the coordinating *Y*(3) position. Correlation of possible local arrangements with observed variations in bond lengths and chemistry allow a plausible local model to be constructed for this substitution.

Keywords: vesuvianite, crystal-structure refinement, electron- microprobe analysis, fluorine, hydroxyl.

SOMMAIRE

La structure cristalline de trois échantillons de vésuvianite contenant du fluor a été affinée jusqu'à un résidu *R* d'environ 3.5% dans le groupe spatial *P4/nnc*; nous avons utilisé des données de diffraction X obtenues sur cristal unique (rayonnement Mo*K*α. Les mêmes cristaux ont ensuite été analysés au moyen d'une microsonde électronique en dispersion d'énergie. Le fluor remplace le (OH) sur les sites OH et O(10) de la structure. Sur le site OH, il ne semble pas y avoir de désordre de position discernable; les changements dans les exigeances des valences de liaisons locales dues à la perte de la liaison hydrogène entre OH et O(10) sont satisfaits par des changements subtils impliquant les cations dans la sphère de coordinence. Les longueurs des liaisons O(7)–*Z*(3) restent constantes, mais la distance O(7)–*X*(3) diminue à mesure qu'augmente le degré de remplacement du OH par le F. Le fluor remplace l'hydroxyle dans le site O(10). La présence du F cause un désordre de position important des anions et des cations dans le site *Y*(3) en coordinence avec ces anions. Une corrélation des agencement locaux possibles avec les variations en longueurs de liaisons et en composition mènent à un modèle plausible pour expliquer cette substitution.

(Traduit par la Rédaction)

Mots-clés: vésuvianite, affinement, structure cristalline, analyse à la microsonde électronique, fluor, hydroxyle.

INTRODUCTION

Groat *et al.* (1992) reported results of a detailed chemical examination of a large number of vesuvianite samples from a wide range of localities. They showed that the chemical formula of vesuvianite can be written as $X_{19}Y_{13}Z_{18}T_{0-5}O_{68}W_{10}$, in which X = Ca, Na, *REE*, Pb^{2+}, Sb^{3+}; Y = Al, Mg, Fe^{3+}, Fe^{2+}, Ti^{4+}, Mn, Cu, Zn; Z = Si; T = B; W = OH, F, O^{2-}. They also showed that two of the most important chemical substitutions in vesuvianite are Mg + OH = Al + O^{2-} and B + Mg = 2H + Al, both of which involve hydrogen. The variable H content is thus a very important aspect of the chemistry of vesuvianite.

Fluorine is a common constituent in vesuvianite; it reaches up to ~3.2 wt.% (~4.2 a.p.f.u., atoms per formula unit). The H atoms in vesuvianite are involved in fairly strong hydrogen-bonding configurations (Yoshiasa & Matsumoto 1986, Groat *et al.* 1992), and the simple substitution of F^- for $(OH)^-$ is thus expected to cause a significant perturbation on local stereochemistry. This being the case, the substitution of significant amounts of F^- for $(OH)^-$ may have an important effect on the range of other chemical substitutions in vesuvianite. In addition, the presence or absence of F^- has a spectacular effect on the infrared absorption spectra of vesuvianite (work in progress), the interpretation of which requires a detailed knowledge of the local stereochemical effects of the F^--for-$(OH)^-$ substitution. In order to shed some light on these two points, we here report on structure refinements of three crystals of F-bearing vesuvianite and compare them with the structure of low-F vesuvianite.

EXPERIMENTAL

The vesuvianite samples examined here were previously characterized by Groat *et al.* (1992), and the sample numbers used here are the same as in that study.

Collection of X-ray data

Crystals were ground into spheres using a sphere grinder to minimize differential absorption, and attached to a glass rod with "5 minute" epoxy. The crystals were mounted on a Nicolet *R3m* automated four-circle diffractometer, and the setting angles for 25 automatically aligned reflections were used to refine the orientation matrix and the (tetragonally constrained) cell dimensions; the latter are reported in Table 1, together with other information pertinent to data collection and structure refinement. Intensity data were collected over two asymmetric units (assuming *4/mmm* Laue symmetry) out to a maximum 2θ value of 60° according to the experimental procedure of Hawthorne & Groat (1985). After the normal intensity data had been collected, psi-scan data were collected for an empirical absorption-correction assuming an ellipsoidal shape of the crystals that was refined as part of the calculation. As the crystals had been ground to "spheres", the psi-scan correction produced very low *R* indices for the azimuthal data; the corrections were subsequently applied to the normal intensity data. A reflection was considered as observed if its intensity exceeds four times background based on counting statistics.

TABLE 1. PHYSICAL DATA AND INFORMATION ON REFINEMENT FOR THREE CRYSTALS OF F-BEARING VESUVIANITE

	V12	V27	V4	V33
a (Å)	15.522(1)	15.558(1)	15.563(2)	15.538(2)
c (Å)	11.802(2)	11.805(1)	11.806(2)	11.786(2)
V (Å³)	2843.3(7)	2857.4(5)	2859.5(7)	2845.6(6)
Space group	*P4/nnc*	*P4/nnc*	*P4/nnc*	*P4/nnc*
Z	4	4	4	4
F (a.p.f.u.)*	0.00	2.04	3.89	4.77
2*V* (°)	-	15(2)	0	6(5)
Crystal size (mm)	-	0.26 × 0.26 × 0.26	0.24 × 0.24 × 0.26	0.24 × 0.24 × 0.24
Radiation	-	Mo*K*α	Mo*K*α	Mo*K*α
Monochromator	-	Graphite	Graphite	Graphite
R (azimuthal) %	-	1.8	1.8	1.8
Total no. |F|	-	2108	2110	2103
No. of |F| obs	-	1949	1959	1918
R (observed) %	-	3.4	3.2	3.5
wR (observed) %	-	3.1	3.3	3.7

$R = \Sigma(|F| - |F|)/\Sigma|F|$

$wR = [\Sigma w(|F| - |F|)^2/\Sigma wF^2]^{0.5}, w = 1/\sigma^2(F)$

*Average of electron microprobe results.

Structure refinement

Scattering factors for neutral atoms were taken from the International Tables for X-ray Crystallography, Vol. IV (1974). All calculations were done with the SHELXTL system. *R* indices are of the usual form and are expressed as percentages.

The first point to consider in the refinement of vesuvianite structures is the most appropriate choice of space group. The vesuvianite structure-type can have symmetry *P4/nnc*. However, most crystals of vesuvianite show evidence of small departures from this symmetry, both in observed diffraction-intensities that violate the symmetry characteristics of *P4/nnc*, and in optical properties indicative of biaxial symmetry (Groat *et al.* 1993). For the three samples of vesuvianite examined here, the following general properties were observed: (i) only a small number of very weak reflections violate *P4/nnc* symmetry (9, 10 and 11 for V4, V27 and V33, respectively). In addition, the largest intensity of a violating reflection observed has $F/\sigma = 0.3$ for each crystal. (ii) measured 2V values (Table 1) are small, and show only minor deviations from tetragonal symmetry.

As a result of these observations, the space group *P4/nnc* was used for the structure refinement of F-bearing vesuvianite. Starting parameters were those of the F-free vesuvianite V12 (Groat, Hawthorne & Ercit, in prep.), and the nomenclature of sites is that of Groat *et al.* (1992). The structures refined rapidly to convergence for an isotropic displacement model. Conversion to an anisotropic form of the displacement factors and least-squares refinement of all variables resulted in *R* indices of approximately 3.4%. At this stage, the *Y*(1) and O(10) atoms were found to be very anisotropic, and the degree of anisotropy varied from sample to sample. Consequently, these atoms were "split" into half-atoms having isotropic displacement factors constrained to be equal; it is unlikely that the split positions have equal occupancies, but this was the least biased way in which to start this phase of the refinement procedure. The refinements rapidly converged to *R* indices identical or marginally less than those for the single-atom model. However, the split-atom model greatly facilitates the interpretation of local disorder as a function of bulk and site chemistry. Final *R* indices for all refinements are given in Table 1.

The crystals all showed a small number of reflections ostensibly violating *P4/nnc* symmetry; these reflections were observed to be very weak, and we did not check them for double-diffraction effects. To examine the possibility of channel ordering [*i.e.*, splitting of *X*(4) and *Y*(1) into nonequivalent pairs of sites with differential cation order], we also refined the structures of V4 and V33 in the space group *P4/n* (*cf.* Giusepetti & Mazzi 1983, Fitzgerald *et al.* 1986, Allen & Burnham 1992). There were no significant improvements in *R* indices and no discernable ordering of cations over nonequivalent pairs of sites; the observed displacement-anisotropy at the *Y*(1) and O(10) position was still observed when these sites were split into nonequivalent pairs by the reduction in symmetry from *P4/nnc* to *P4/n*. These points indicate that the long-range structure of F-bearing vesuvianite is best described with *P4/nnc* symmetry, and that the split-site behavior is due to local order.

Electron-microprobe analysis

Subsequent to the diffraction experiments, the crystals used for the collection of the X-ray intensity data were removed from their glass fibres, mounted in Transoptic™, and polished for electron-microprobe analysis. Experimental details are given by Groat *et al.* (1992). At least ten points were analyzed on each crystal so as to get a representative composition of the whole crystal used in the collection of X-ray data. Fe^{2+}/Fe^{3+} ratios and H_2O contents are taken from Groat *et al.* (1992) and necessarily represent values for the bulk samples rather than the crystals used in the X-ray work.

RESULTS

Structure refinement

Final atomic parameters, equivalent isotropic displacement factors and anisotropic displacement factors

TABLE 2. ATOMIC PARAMETERS FOR FLUORINE-BEARING VESUVIANITE CRYSTALS

		V12	V27	V4	V33
F (a.p.f.u.)		0.00	2.04	3.89	4.77
Z(1)	*x*	3/4	3/4	3/4	3/4
	y	1/4	1/4	1/4	1/4
	z	0	0	0	0
	**U*eq	60(2)	61(2)	71(3)	66(3)
Z(2)	*x*	-0.18089(4)	-0.18083(4)	-0.18110(5)	-0.18097(6)
	y	0.04110(4)	0.04030(4)	0.04051(5)	0.04035(5)
	z	0.87099(5)	0.87134(5)	0.87127(6)	0.87121(7)
	*U*eq	62(1)	62(2)	70(2)	60(2)
Z(3)	*x*	-0.08314(4)	-0.08302(4)	-0.08262(5)	-0.08293(6)
	y	-0.15084(4)	-0.15077(4)	-0.15057(5)	-0.15062(6)
	z	0.36482(5)	0.36466(6)	0.36466(6)	0.36465(7)
	*U*eq	72(1)	75(2)	80(2)	71(2)
X(1)	*x*	3/4	3/4	3/4	3/4
	y	1/4	1/4	1/4	1/4
	z	1/4	1/4	1/4	1/4
	*U*eq	76(2)	109(3)	102(3)	103(3)
X(2)	*x*	-0.18919(3)	-0.18912(3)	-0.18893(3)	-0.18908(4)
	y	0.04379(3)	0.04380(3)	0.04375(3)	0.04425(4)
	z	0.37990(4)	0.37967(4)	0.37951(5)	0.37937(6)
	*U*eq	79(1)	82(1)	85(1)	74(2)
X(3)	*x*	-0.10132(3)	-0.10004(3)	-0.10040(4)	-0.10062(4)
	y	-0.18123(3)	-0.17951(3)	-0.17965(4)	-0.17962(4)
	z	0.88698(4)	0.88558(5)	0.88627(5)	0.88753(6)
	*U*eq	169(1)	132(1)	131(2)	115(2)
X(4)	*x*	3/4	3/4	3/4	3/4
	y	3/4	3/4	3/4	3/4
	z	0.14934(15)	0.13981(21)	0.14025(25)	0.14147(26)
	*U*eq	99(3)	138(5)	170(6)	142(6)
Y(1A)	*x*	3/4	3/4	3/4	3/4
	y	3/4	3/4	3/4	3/4
	z	0.0358(1)	0.0659(3)	0.0708(3)	0.0747(4)
	*U*eq	109(3)	66(6)	63(6)	52(7)
Y(1B)	*x*	-	3/4	3/4	3/4
	y	-	3/4	3/4	3/4
	z	-	0.0333(3)	0.0392(3)	0.0436(3)
	*U*eq	-	66(6)	63(6)	52(7)
Y(2)	*x*	0	0	0	0
	y	0	0	0	0
	z	0	0	0	0
	*U*eq	72(2)	65(2)	72(3)	70(3)
Y(3)	*x*	-0.11203(4)	-0.11165(4)	-0.11277(5)	-0.11239(5)
	y	0.12089(4)	0.12058(4)	0.12102(5)	0.12085(6)
	z	0.12640(5)	0.12695(5)	0.12651(6)	0.12675(8)
	*U*eq	67(2)	74(2)	81(2)	74(3)
O(1)	*x*	-0.21915(10)	-0.21997(11)	-0.21990(12)	-0.21981(15)
	y	0.17269(9)	0.17262(10)	0.17274(12)	0.17311(14)
	z	0.08546(13)	0.08522(14)	0.08566(16)	0.08541(20)
	*U*eq	82(4)	87(4)	103(5)	98(6)
O(2)	*x*	-0.11732(10)	-0.11677(11)	-0.11682(12)	-0.11679(14)
	y	0.15964(10)	0.15967(10)	0.15984(12)	0.15997(14)
	z	0.27828(12)	0.27911(14)	0.27887(15)	0.27914(19)
	*U*eq	89(4)	90(5)	99(5)	97(6)
O(3)	*x*	-0.04911(10)	-0.04923(11)	-0.04919(12)	-0.04840(14)
	y	0.22149(10)	0.22180(11)	0.22171(11)	0.22178(14)
	z	0.07643(12)	0.07596(14)	0.07559(15)	0.07583(19)
	*U*eq	83(4)	77(4)	82(5)	74(6)
O(4)	*x*	-0.06227(10)	-0.06178(10)	-0.06179(12)	-0.06142(14)
	y	0.10658(10)	0.10619(10)	0.10600(12)	0.10631(14)
	z	0.47022(12)	0.47002(14)	0.47040(15)	0.47040(18)
	*U*eq	84(4)	80(5)	85(5)	75(6)
O(5)	*x*	-0.17019(9)	-0.17033(10)	-0.16981(12)	-0.17025(14)
	y	0.01500(10)	0.01483(11)	0.01553(12)	0.01516(15)
	z	0.17833(12)	0.17876(15)	0.17865(16)	0.17909(20)
	*U*eq	99(4)	107(5)	113(5)	99(6)
O(6)	*x*	0.88108(11)	0.88181(13)	0.88244(14)	0.88171(16)
	y	-0.27075(10)	-0.27135(11)	-0.27133(13)	-0.27182(15)
	z	0.06013(13)	0.05954(15)	0.05923(17)	0.05783(19)
	*U*eq	132(4)	156(5)	165(6)	138(7)
O(7)	*x*	0.05579(10)	0.05602(11)	0.05604(12)	0.05618(15)
	y	0.17308(10)	0.17430(11)	0.17422(12)	0.17355(15)
	z	0.32192(14)	0.32218(16)	0.32198(17)	0.32117(21)
	*U*eq	115(4)	102(5)	110(5)	113(6)
O(8)	*x*	-0.06098(10)	-0.06078(10)	-0.06064(12)	-0.06060(14)
	y	-0.09101(9)	-0.09047(10)	-0.09015(12)	-0.09045(14)
	z	0.06618(13)	0.06683(14)	0.06641(16)	0.06637(19)
	*U*eq	88(4)	84(4)	93(5)	84(6)
O(9)	*x*	-0.14454(10)	-0.14426(11)	-0.14393(12)	-0.14457(14)
	y	-0.14454(10)	-0.14426(11)	-0.14393(12)	-0.14457(14)
	z	1/4	1/4	1/4	1/4
	*U*eq	102(4)	114(5)	116(5)	107(6)
O(10A)	*x*	3/4	3/4	3/4	3/4
	y	3/4	3/4	3/4	3/4
	z	0.8661(3)	0.8380(6)	0.8507(7)	0.8552(10)
	*U*eq	151(7)	127(12)	152(14)	152(16)
O(10B)	*x*	-	3/4	3/4	3/4
	y	-	3/4	3/4	3/4
	z	-	0.8824(6)	0.8812(7)	0.8764(10)
	*U*eq	-	127(12)	152(14)	152(16)
OH	*x*	-0.00480(10)	-0.00465(10)	-0.00418(12)	-0.00398(14)
	y	0.06155(10)	0.06220(10)	0.06230(11)	0.06138(14)
	z	0.13637(12)	0.13571(13)	0.13570(14)	0.13612(18)
	*U*eq	95(4)	68(4)	68(5)	59(6)

**U*eq = *U*eq x 10^4 (Å^2)

are given in Tables 2 and 3, respectively. For the relevant atomic positions, results are given for both the single-site and the split-site models. Tables of structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. Selected interatomic distances are given in Table 4, where they are compared with corresponding values from a fluorine-free vesuvianite (V12, taken from Groat *et al.*, in prep.). Site-scattering in terms of equivalent electrons are given in Table 5;

TABLE 3. ANISOTROPIC DISPLACEMENT FACTORS FOR FLUORINE-BEARING VESUVIANITE CRYSTALS

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
			V27			
Z(1)	63(3)	63(3)	58(6)	0	0	0
Z(2)	56(3)	66(3)	65(3)	7(2)	-2(3)	-1(2)
Z(3)	114(3)	51(3)	60(3)	-2(2)	1(2)	1(2)
X(1)	143(5)	103(5)	81(4)	0	0	0
X(2)	70(2)	99(2)	77(2)	3(2)	-7(2)	10(2)
X(3)	113(2)	99(2)	184(3)	-26(2)	-49(2)	26(2)
X(4)	69(5)	69(5)	256(12)	0	0	0
Y(2)	61(4)	58(4)	75(4)	3(4)	2(4)	6(4)
Y(3)	84(3)	71(3)	69(3)	-4(2)	13(3)	-7(2)
O(1)	121(8)	70(8)	72(8)	4(6)	1(7)	8(6)
O(2)	85(8)	86(8)	97(8)	0(6)	-22(7)	-11(6)
O(3)	87(8)	70(7)	76(8)	-5(6)	-3(6)	-5(6)
O(4)	87(8)	72(8)	80(8)	9(6)	-9(6)	7(6)
O(5)	101(8)	142(9)	81(8)	-9(7)	14(7)	47(7)
O(6)	275(10)	89(8)	100(8)	27(7)	26(8)	40(7)
O(7)	83(8)	109(8)	112(8)	-7(7)	6(7)	17(6)
O(8)	71(7)	75(7)	105(8)	14(6)	27(6)	7(6)
O(9)	139(7)	139(7)	70(10)	6(7)	-6(7)	-24(9)
OH	56(7)	90(7)	57(7)	-11(6)	-2(6)	-7(6)
			V4			
Z(1)	75(4)	75(4)	61(4)	0	0	0
Z(2)	63(3)	80(3)	69(3)	5(3)	-2(3)	-3(2)
Z(3)	117(3)	58(3)	67(3)	1(2)	2(3)	5(3)
X(1)	158(5)	86(5)	65(4)	0	0	0
X(2)	75(2)	104(2)	77(2)	4(2)	-5(2)	7(2)
X(3)	117(3)	104(3)	174(3)	-20(2)	-41(2)	22(2)
X(4)	104(7)	104(7)	272(14)	0	0	0
Y(2)	69(5)	62(5)	86(4)	5(4)	6(4)	1(4)
Y(3)	84(4)	81(4)	77(3)	-9(3)	9(3)	0(3)
O(1)	136(9)	85(8)	91(8)	3(7)	-2(7)	5(7)
O(2)	90(9)	105(9)	101(9)	10(7)	-27(7)	-6(7)
O(3)	104(9)	68(8)	78(8)	0(7)	-8(7)	0(7)
O(4)	96(9)	73(9)	88(9)	11(7)	-10(7)	-6(7)
O(5)	106(9)	139(10)	139(10)	98(9)	-7(8)	10(7)
O(6)	254(11)	116(10)	125(9)	32(8)	32(8)	46(8)
O(7)	92(9)	126(9)	112(9)	4(8)	15(7)	18(7)
O(8)	77(8)	92(9)	114(9)	10(7)	28(7)	15(7)
O(9)	142(8)	142(8)	70(11)	4(8)	-4(8)	16(11)
OH	70(8)	84(8)	51(7)	-10(6)	-6(6)	-20(7)
			V33			
Z(1)	68(5)	68(5)	60(7)	0	0	0
Z(2)	55(4)	60(4)	66(4)	5(3)	-4(3)	4(3)
Z(3)	99(4)	51(4)	62(4)	1(3)	1(3)	-3(3)
X(1)	170(7)	77(6)	65(5)	0	0	0
X(2)	63(3)	90(3)	72(3)	1(2)	-5(2)	9(2)
X(3)	93(3)	84(3)	170(3)	-20(3)	-35(3)	13(2)
X(4)	111(8)	111(8)	171(15)	0	0	0
Y(2)	57(6)	64(6)	90(6)	7(5)	-1(5)	8(5)
Y(3)	77(4)	72(4)	76(4)	-1(3)	8(3)	-6(3)
O(1)	129(11)	75(10)	94(10)	21(9)	7(9)	8(9)
O(2)	96(10)	88(11)	109(11)	-3(9)	-39(9)	-18(8)
O(3)	97(11)	59(10)	68(10)	0(8)	13(8)	7(8)
O(4)	75(10)	68(10)	85(11)	17(8)	8(8)	3(8)
O(5)	86(11)	123(11)	91(11)	-15(9)	19(9)	39(9)
O(6)	202(13)	103(12)	110(11)	30(9)	30(10)	32(9)
O(7)	70(10)	152(12)	114(11)	23(10)	13(9)	19(9)
O(8)	67(10)	79(10)	105(11)	13(8)	22(8)	1(8)
O(9)	120(9)	120(9)	83(13)	4(10)	-4(10)	-38(13)
OH	58(10)	85(10)	38(9)	-4(8)	-11(8)	-13(8)

*U_{ij} = U_{ij} x 10^4

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) IN F-BEARING VESUVIANITE CRYSTALS

		V12	V27	V4	V33
F (a.p.f.u.)		0.00	2.04	3.89	4.77
Z(1)-O(1)a	×4	1.639(3)	1.637(2)	1.640(2)	1.631(2)
<Z(1)-O>		1.639	1.637	1.640	1.631
Z(2)-O(2)b		1.645(2)	1.646(2)	1.646(2)	1.641(2)
Z(2)-O(3)c		1.643(2)	1.643(2)	1.644(2)	1.640(2)
Z(2)-O(4)b		1.676(2)	1.678(2)	1.687(2)	1.679(2)
Z(2)-O(7)b		1.617(2)	1.611(2)	1.616(2)	1.616(2)
<Z(2)-O>		1.645	1.645	1.648	1.644
Z(3)-O(5)d		1.634(2)	1.634(2)	1.637(2)	1.636(3)
Z(3)-O(6)e		1.605(2)	1.603(2)	1.606(2)	1.608(3)
Z(3)-O(8)d		1.620(2)	1.621(2)	1.623(2)	1.622(3)
Z(3)-O(9)		1.660(1)	1.658(1)	1.659(1)	1.659(2)
<Z(3)-O>		1.630	1.629	1.631	1.631
X(1)-O(1)a	×4	2.333(2)	2.335(2)	2.331(2)	2.327(2)
X(1)-O(2)a	×4	2.514(2)	2.528(2)	2.527(2)	2.522(2)
<X(1)-O>		2.424	2.432	2.429	2.425
X(2)-O(1)f		2.489(2)	2.488(2)	2.492(2)	2.487(2)
X(2)-O(2)		2.433(2)	2.434(2)	2.436(2)	2.427(2)
X(2)-O(3)b		2.375(2)	2.374(2)	2.372(2)	2.372(2)
X(2)-O(4)		2.443(2)	2.451(2)	2.451(2)	2.453(2)
X(2)-O(5)		2.439(2)	2.432(2)	2.431(2)	2.422(2)
X(2)-O(5)f		2.332(2)	2.337(2)	2.345(2)	2.336(2)
X(2)-O(6)o		2.913(2)	2.917(2)	2.910(2)	2.929(3)
X(2)-O(8)d		2.318(2)	2.324(2)	2.326(2)	2.326(2)
<X(2)-O> [8]		2.468	2.470	2.470	2.469
<X(2)-O> [7]		2.404	2.406	2.408	2.403
X(3)-O(3)j		2.455(2)	2.456(2)	2.459(2)	2.444(2)
X(3)-O(6)p		2.487(2)	2.518(2)	2.505(2)	2.482(2)
X(3)-O(6)l		3.010(2)	3.022(2)	3.015(2)	2.978(2)
X(3)-O(7)j		2.569(2)	2.547(2)	2.555(2)	2.556(3)
X(3)-O(7)m		2.491(2)	2.492(2)	2.495(2)	2.509(2)
X(3)-O(7)b		2.371(2)	2.363(2)	2.366(5)	2.361(2)
X(3)-O(8)k		2.613(2)	2.621(2)	2.617(2)	2.599(2)
X(3)-O(10A)q	×1/2	2.556(1)	2.638(2)	2.607(1)	2.594(2)
X(3)-O(10B)q	×1/2	-	2.578(2)	2.574(1)	2.569(2)
X(3)-OHj		2.498(2)	2.459(2)	2.460(2)	2.469(2)
<X(3)-O> [9]		2.561	2.565	2.563	2.553
<X(3)-O> [8]		2.505	2.508	2.506	2.500
X(4)-O(6)f	×4	2.314(2)	2.279(2)	2.279(2)	2.294(2)
X(4)-O(9)f	×4	2.602(2)	2.669(3)	2.669(2)	2.674(3)
<X(4)-O>		2.458	2.474	2.474	2.484
Y(1A)-O(6)f	×4	2.080(2)	2.077(2)	2.077(2)	2.093(2)
Y(1A)-O(10B)g		2.004(4)	2.166(7)	2.166(8)	2.238(9)
Y(1A)-O(10A)g		-	2.691(7)	2.691(8)	2.598(9)
<Y(1A)-O> [5]		2.065	2.095	2.095	2.122

Y(1B)-O(6)f	×4	-	2.099(2)	2.099(2)	2.101(2)
Y(1B)-O(10B)g		-	1.781(8)	1.781(8)	1.865(9)
Y(1B)-O(10A)g		-	2.306(8)	2.306(8)	2.225(9)
<*Y*(1B)-O>		-	2.035	2.035	2.054
Y(2)-O(4)h	×2	1.948(2)	1.940(2)	1.944(2)	1.941(2)
Y(2)-O(8)	×2	1.871(2)	1.864(2)	1.871(2)	1.864(2)
Y(2)-OH	×2	1.874(1)	1.867(1)	1.873(2)	1.873(2)
<*Y*(2)-O>		1.898	1.890	1.896	1.893
Y(3)-O(1)		1.909(2)	1.919(2)	1.933(2)	1.913(2)
Y(3)-O(2)		1.893(2)	1.898(2)	1.898(2)	1.898(2)
Y(3)-O(3)		1.934(2)	1.951(2)	1.947(2)	1.948(2)
Y(3)-O(4)h		2.058(2)	2.064(2)	2.068(2)	2.063(2)
Y(3)-O(5)		1.973(2)	1.972(2)	1.978(2)	1.965(2)
Y(3)-OH		1.906(2)	1.924(2)	1.899(2)	1.924(2)
<*Y*(3)-O>		1.946	1.955	1.954	1.952
X(4)-*X*(4)d		2.377(4)	2.616(5)	2.604(6)	2.572(6)
X(4)-*Y*(1A)		1.340(2)	0.865(4)	0.813(5)	0.780(6)
X(4)-*Y*(1B)		-	1.250(4)	1.187(4)	1.147(5)
Y(1A)-*Y*(1B)		-	0.385(5)	0.373(5)	0.367(6)
O(10A)-O(10A)r		-	2.076(13)	2.378(16)	2.481(24)
O(10A)-O(10B)		-	0.525(9)	0.360(11)	0.250(17)
O(10A)-O(10B)r		-	2.601(9)	2.738(11)	2.730(17)
O(10A)-*X*(3)f	×4	2.556(1)	2.638(2)	2.607(1)	2.594(2)
O(10A)-*Y*(1A)k		2.004(4)	2.691(8)	2.598(9)	2.587(13)
O(10A)-*Y*(1B)k		-	2.306(8)	2.225(9)	2.220(13)
O(10B)-*X*(3)f	×4	-	2.578(1)	2.574(1)	2.569(1)
O(10B)-*Y*(1A)k		-	2.166(8)	2.238(9)	2.337(13)
O(10B)-*Y*(1B)k		-	1.781(8)	1.865(9)	1.970(13)

Equivalent positions: a: $1+x, y, z$; b: $\bar{y}, \bar{x}, 1/2+z$; c: $1/2+y-1, \bar{x}, 1-z$; d: $y, x, 1/2-z$; e: $1-x, 1/2-y-1, 1/2-z$; f: $1+x, 1+y, z$; g: $x, y, z-1$; h: $\bar{y}, \bar{x}, 1/2+z-1$; i: $1/2-x-1, y, 1/2-z$; j: $\bar{x}, \bar{y}, 1-z$; k: $x, y, 1+z$; l: $1/2-y-1, 1-x, 1+z$; m: $\bar{x}, 1/2+y-1, 1/2+z$; n: $1/2-x, 1/2-y, z$; o: $y, -1+x, 1/2-z$; p: $-1+x, y, 1+z$; q: $-1+x, -1+y, z$; r: $y, x, 1/2-z+1$.

assignment of specific cation-occupancies also requires consideration of the chemical composition.

Chemical composition

The results of chemical analysis of the crystals are given in Table 6. Unit formulae were recalculated on the basis of 50 cations and were assigned to specific groups of positions as recommended by Groat *et al.* (1992).

TABLE 5. REFINED SITE-OCCUPANCIES* IN F-BEARING VESUVIANITE

	V27	V4	V33
Y(1)	11.43	11.97	12.64
Y(3)	14.34	14.33	14.38

*Occupancies given in terms of M.A.N. (Mean Atomic Number - no. of electrons at site).

TABLE 6. AVERAGE COMPOSITION OF VESUVIANITE SAMPLES

	V12	V27	V4	V33
SiO_2 wt.%	36.27	37.05	36.52	37.54
Al_2O_3	18.31	16.21	16.87	17.33
TiO_2	0.76	2.83	0.80	0.66
MgO	1.46	1.72	1.65	1.75
MnO	0.08	0.01	0.34	0.73
FeO	1.31	2.68	2.96	3.16
Fe_2O_3	1.76	-	1.22	0.37
CaO	36.49	34.79	35.13	35.42
Na_2O	0.00	0.21	0.04	0.10
Ln_2O_3	0.00	0.00	0.00	-
B_2O_3	0.00	-	0.00	0.00
SO_3	0.00	0.21	0.01	0.00
F	0.00	1.30	2.48	3.10
Cl	0.01	0.17	0.08	0.00
H_2O†	-	-	1.70	1.63
H_2O‡	2.67	1.57	1.57	1.30
	99.12	98.75	99.81	101.79
O=F,Cl	-	0.59	1.06	1.31
TOTAL	99.12	98.16	98.75	100.48
Si^{4+}	17.75	18.38	18.10	18.27
Al^{3+}	10.56	9.48	9.86	9.94
Ti^{4+}	0.28	1.06	0.30	0.24
Mg^{2+}	1.07	1.27	1.22	1.27
Mn^{2+}	0.03	0.00	0.14	0.30
Fe^{2+}	0.54	1.11	1.23	1.29
Fe^{3+}	0.65	-	0.46	0.14
Ca^{2+}	19.13	18.49	18.66	18.47
Na^+	0.00	0.20	0.04	0.09
Ln^{3+}	0.00	0.00	0.00	-
B^{3+}	0.00	-	0.00	0.00
S^{6+}	0.00	0.08	0.00	0.00
F^-	0.00	2.04	3.89	4.77
Cl^-	0.01	0.14	0.07	0.00
OH^-	8.73	5.20	5.62	5.29
ΣX	19.13	18.70	18.70	18.56
ΣY	13.12	12.92	13.20	13.17
ΣZ	17.75	18.38	18.10	18.27

†Measured. ‡Calculated for charge balance.

V33 includes 0.15 wt.% BeO. The number of analyses used in the averaging are (in brackets) V12 (6), V28 (5), V4 (8), V33 (2).

DISCUSSION

In the structure of vesuvianite, the hydroxyl groups are generally involved in fairly strong hydrogen bonding. As a consequence, the substitution of F^- for $(OH)^-$ must involve significant local changes in stereochemistry in order to satisfy the bond-valence requirements of those anions that acted as hydrogen-bond acceptors in F-free vesuvianite.

The OH environment in F-free vesuvianite

In the vesuvianite structure, there are two anion sites that can be occupied by $(OH)^-$ and F^-, the OH site and the O(10) site. For the convenience of this discussion,

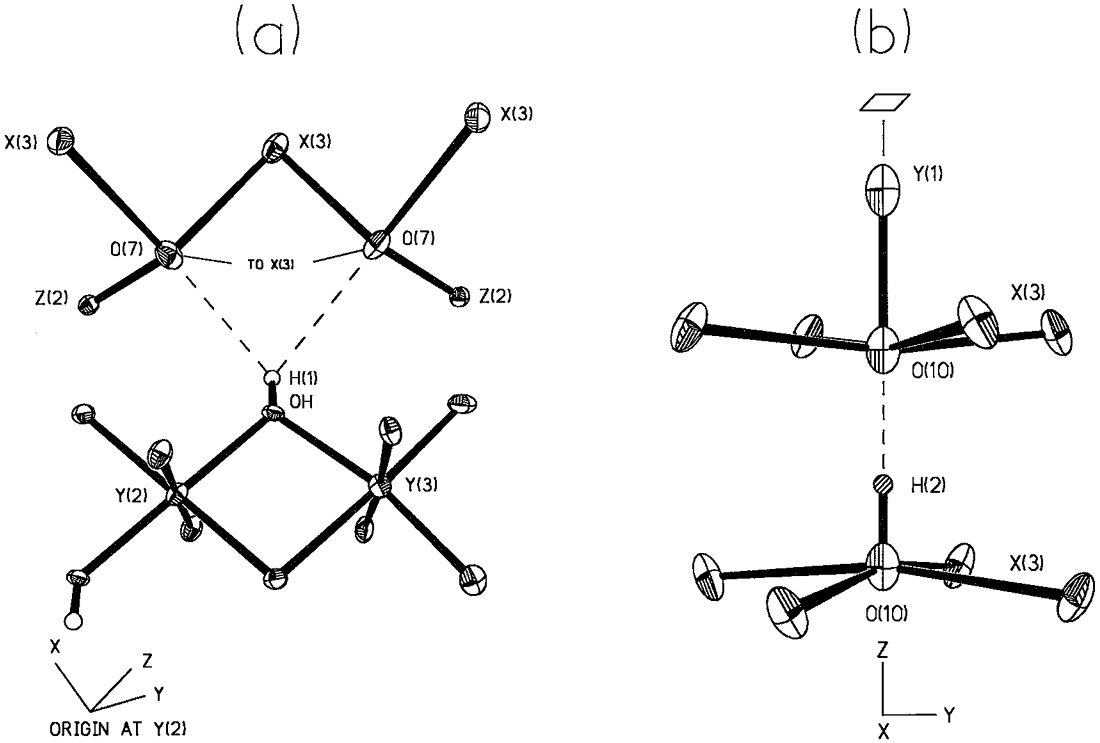

FIG. 1. The anion sites that can be occupied by OH^- or F^- in the vesuvianite structure, together with the neighboring structure: (a) the OH site; (b) the O(10) site; hydrogen bonds are shown by dashed lines.

the local environment of these sites is illustrated in Figure 1.

Each OH site is coordinated to cations at the *X*(3), *Y*(2) and *Y*(3) sites; these three sites form the apices of a triangle subparallel to (001), with the OH site occupying a "pyramidal" position above. Where the OH site is occupied by $(OH)^-$, the H(1) atom lies above the donor oxygen such that the O(donor) – H bond is at an angle of ~30° to the *c* axis. Bond-valence arguments (Yoshiasa & Matsumoto 1986, Groat 1988) show that there is a strong hydrogen bond between H(1) and O(7); the *Z*(2) and *X*(3) cations that coordinate O(7) contribute only ~1.7 v.u. in F-free vesuvianite, and the hydrogen bond from H(1) is necessary for bond-valence satisfaction at the O(7) anion.

The O(10) anion lies on the four-fold axis that passes down the channel(s) through the structure (Fig. 1b), and is coordinated by one *Y*(1) and four *X*(3) cations in a square pyramidal arrangement. Exclusive of F, O(10) must be occupied by some OH, and it is generally considered that both OH^- and O^{2-} occupy this site (see summary of current and previous views in Groat *et al.* 1992). The neutron-diffraction structure refinement of Lager *et al.* (1989) located the H(2) site; it is asymetrically positioned between two O(10) sites on the 4-fold axis. In the crystal they examined, the H(2) position is only partly (0.85) occupied and is assumed to be locally disordered about the center of symmetry at (1/4, 1/4, 1/4). Presumably when H(1) is close (~1 Å) to one O(10) oxygen, it forms a strong hydrogen bond to the neighboring O(10) approximately 1.8 Å away.

The F^--for-$(OH)^-$ substitution at OH

Inspection of Tables 2 and 3 shows that the replacement of $(OH)^-$ by F^- across this series does not involve any discernable positional disorder about OH or O(7). The isotropic displacement factors at both these positions do not show any significant increase with increasing F content of the crystals. Similarly, there is no increase in the anisotropy of the displacement factors across the series. Hence any local adjustments that occur as a result of the F^--for-$(OH)^-$ substitution must take place at the cations coordinating OH or O(7) (or both). Inspection of Table 4 allows us to identify those features that are specifically related to the F^--for-$(OH)^-$ substitution. Comparison of the *Z* sites (occupied only by Si) across the series shows that their coordination geometry is virtually unaffected, despite the fact that H(1) strongly hydrogen-bonds to O(7) and that replacement of $(OH)^-$ by F^- must disturb this arrangement. Similarly, there is no change in the anisotropic displacement parameters of *Z*(3) with changing F content. This indicates that the bond-valence deficiency at O(7), caused by removal of the hydrogen-bond contribution, must be compensated by an increase in incident bond-valence from one or more of the other coordinating cations. The O(7) anion is bonded to *Z*(2) and three *X*(3) cations. Inspection of Table 4 shows that there is significant variation in the O(7)–*X*(3) bond lengths across the series (Fig. 2), an aggregate shortening correlated with increased F^--for-OH^- substitution.

Channel configurations in vesuvianite

First let us examine the possible channel arrangements in fluorine-free vesuvianite (Fig. 3). Important constraints on the possible arrangements are the *experimental* observations that the *Y*(1) and *X*(4) sites always seem to be half-occupied, whereas the O(10) site is fully occupied. This gives two possibilities: (i) there are two distinct local arrangements [labeled (1) and (2) in Fig. 3] that occur in equal amounts; (ii) there is one local arrangement [labeled (3) in Fig. 3] that is polar and can occur in two different orientations. It is perhaps of significance that there is no obvious reason why arrangements (1) and (2) *should* occur in equal proportions [thus giving rise to half-occupied *Y*(1) and *Y*(4) sites], whereas arrangement (3) constrains *Y*(1) and *X*(4) each to be half-occupied. The bond-valence structures of these three arrangements are shown in Figure 4. We focus specifically on the aggregate bond-valence incident to *both* O(10) anions; numerical values are calculated from the observed distances and site-occupancies for V12 (core) using the bond-valence curves of Brown (1981), whereas fractional values are calculated by Pauling's second rule (Pauling 1960). The bond-valences incident to both O(10) sites in the three arrangements should be equal to the sum of the formal valences of the simple anions at the two O(10) positions; if these simple anions are oxygen [*i.e.*, both O(10) positions are occupied by OH^- or O^{2-}], the sum of the incident bond-valences (including those from the H) should be 4 v.u. The calculations for the three arrangements are shown in Figure 4. Each O(10) oxygen (labeled O in the figure) is bonded to four equivalent *X*(3) cations (primarily Ca), and receives an incident bond-valence of 0.17 × 4 v.u. from these cations (and a Pauling bond strength of 2/8). The O(10) anion can also be bonded to the *Y*(1) cation, with an average bond-valence contribution of 0.51 v.u. [and a Pauling bond strength of 2/5 for divalent occupancy of *Y*(1)]. The H atom at H(1) forms two bonds with an aggregate bond-valence of 1.0 v.u. The aggregate bond-valence incident to both O(10) anions for the three arrangements (Fig. 4) are 3.70, 2.68 and 3.19 v.u., respectively. There is a problem here: the incident bond-valences are far too low for both O(10) positions to be occupied by oxygen (for which the incident bond-valence should be 4.0 v.u.). *In a fluorine-free vesuvianite, there seems to be no way around this*

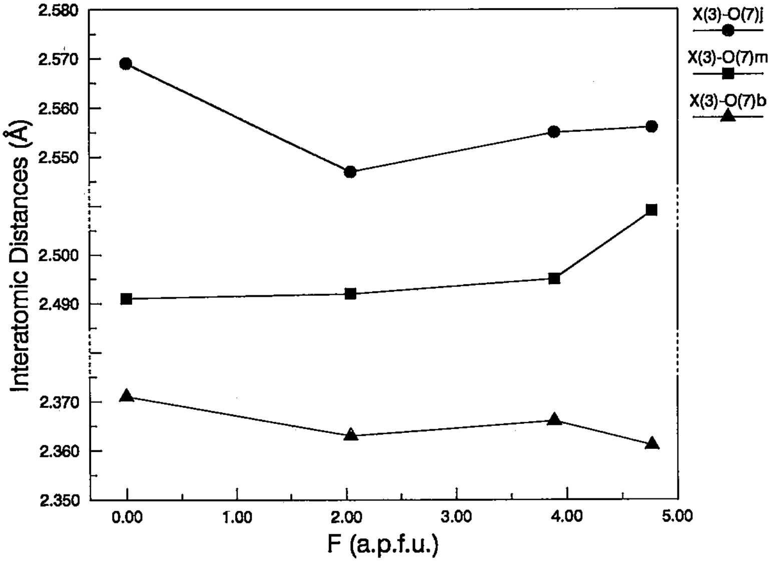

FIG. 2. Variation in O(7)–*X*(3) bond lengths as a function of F content in vesuvianite.

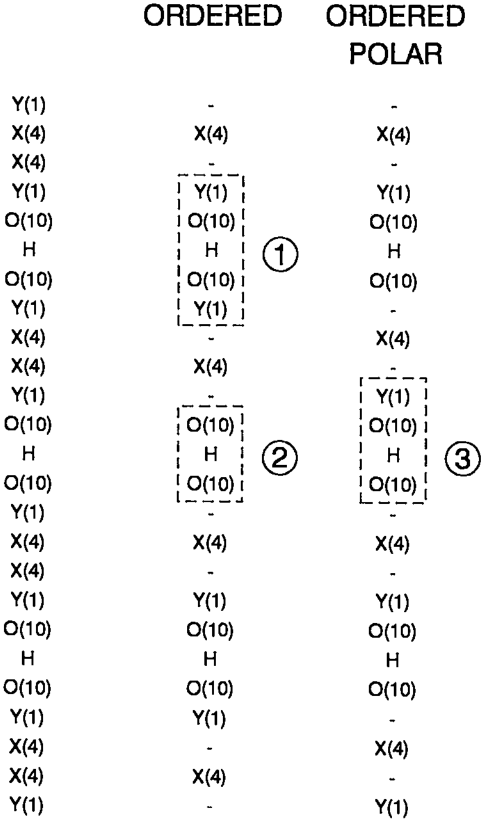

FIG. 3. Possible arrangements in the channel in fluorine-free vesuvianite. There are two distinct arrangements, labeled "ordered" and "ordered polar". In the ordered configuration, there are two local arrangements, labeled 1 and 2; in the ordered polar arrangement, there is one local arrangement, labeled 3, that may point along ±*c*. The four *X*(3) cations bonded to each O(10) anion are omitted for clarity; their positions may be seen in Figure 4.

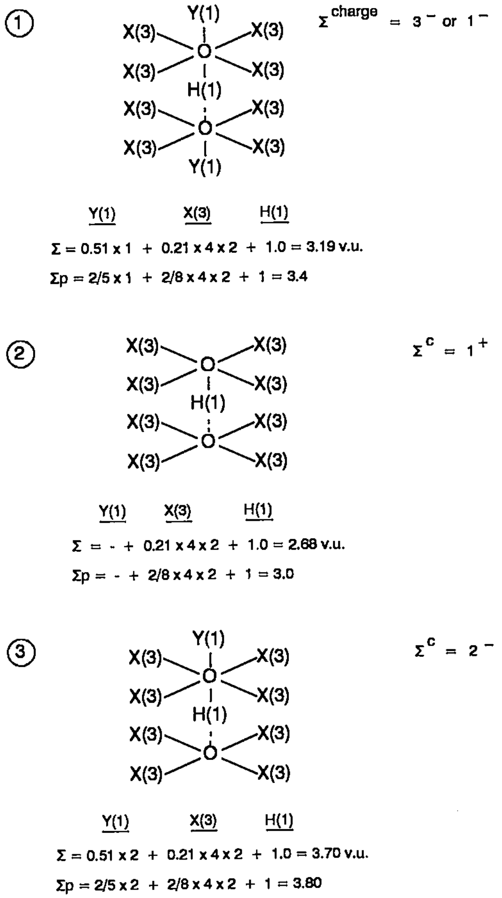

FIG. 4. Bond-valence structures in the three possible channel arrangements of Figure 3. The bond-valence (and Pauling bond-strength) sums are the aggregate bond-valences incident to *both* O(10) anions in each arrangement.

problem. We emphasize this very strongly because it is one of the major stumbling blocks in understanding the vesuvianite structure. Previous investigators (Coda *et al.* 1970, Allen 1985) have discussed the OH occupancy of O(10), but did so only on a qualitative level, where this problem is not apparent.

This situation is greatly relieved in fluorine-bearing vesuvianite. Replacement of the (hydrogen-bond) acceptor anion by F^- removes this charge problem in arrangements (2) and (3) (Fig. 4), but still gives somewhat of a problem with arrangement (1). It is perhaps significant that arrangement (3) also has good bond-valence arrangements around each O(10) position, in view of the following points:

(i) Arrangement (3) *requires* equal occupancy of the *Y*(1) and *X*(4) positions, whereas the combination of arrangements (1) and (2) does not.

(ii) Arrangement (3) can give complete order within a specific channel, and polar disorder between (or within) channels will lead to *P4/nnc* symmetry; it is notable that the structures of fluorine-bearing vesuvianite refine well in that space group.

(iii) Most samples of vesuvianite have minor to significant fluorine, suggesting that the vesuvianite structure has an affinity for fluorine.

These points suggest that arrangement (3) will be preferred in fluorine-bearing vesuvianite. However, we are still left with the problem of local charge-balance in fluorine-free vesuvianite.

The F^--for-$(OH)^-$ substitution at O(10)

Now let us examine the bond-valence constraints on the possible local configurations involving this substitu-

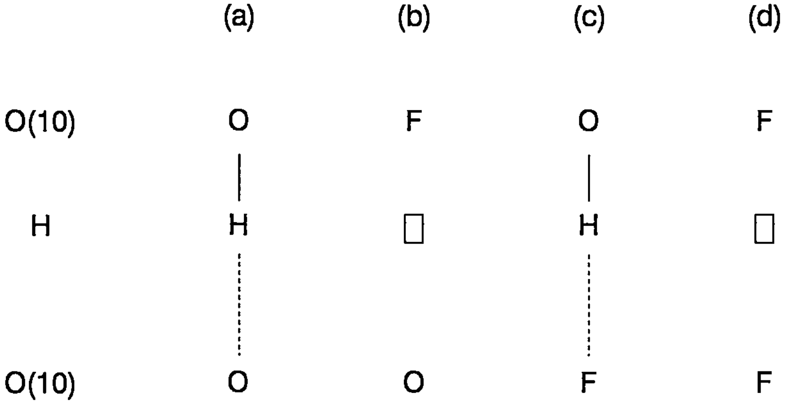

FIG. 5. Possible local configurations of the channel involving the replacement of OH$^-$ by F$^-$ at O(10).

tion. Firstly, Table 4 shows two distinct *X*(3)–O(10) distances. It seems reasonable to assign the shorter length (2.57 Å) to a Ca–F bond and the longer length (2.62 Å) to a Ca–O bond, with the resulting bond-valences of 0.158 and 0.181 v.u., respectively; thus F$^-$ at O(10) receives 0.158 × 4 = 0.63 v.u., and O^{2-} at O(10) receives 0.181× 4 = 0.72 v.u. from the coordinating *X*(3) cations.

The possible combinations of O^{2-} and F$^-$ surrounding a single H(1) position are shown in Figure 5; (a) is the standard arrangement with no F, (b), (c) and (d) have compositions OF, OHF and F_2, respectively. For configuration (b), the aggregate bond-valence sums incident to F$^-$ and O^{2-} are [0.158×4 + 0.5 = 1.13 v.u.) and [0.181× 4 + 0.5 = 1.22 v.u.], respectively, assuming that both associated *Y*(1) sites are occupied. The sum at the O^{2-} anion is far too small, and hence configuration (b) cannot occur. For configuration (c), the analogous bond-valence sums for F$^-$ and O^{2-} are [0.158× 4 + 0.5 + 0.3 = 1.43 or 0.93 v.u. if the *Y*(1) site adjacent to the F$^-$ is vacant] and [0.181 × 4 + 0.7 + 0.5 = 1.92 v.u.], respectively. This arrangement only has acceptable bond-valence sums around F$^-$ and O^{2-} if one of the two associated *Y*(1) sites is vacant; this is only compatible with the ordered polar channel configuration (Fig. 3). For configuration (d) (Fig. 5), the bond-valence sum around each F$^-$ is [0.158 × 4 + 0.5 = 1.13 v.u.]; as both associated *Y*(1) sites must be occupied for this (acceptable) bond-valence arrangement, configuration (d) can only fit into configuration 1 (Fig. 3) of the ordered channel arrangement.

Constraints on O(10) site-occupancies

These arrangements have implications concerning the bulk chemistry of the O(10) site. If configuration (c) (Fig. 5) occurs, O(10) cannot be more than half occupied by F$^-$. If configuration (d) occurs, again O(10) cannot be more than half occupied by F$^-$ because this configuration is only compatible with channel arrangement (1) (Fig. 4), which must combine in a 1:1 ratio with channel arrangement (2) in order to satisfy the observed chemistry of the *Y*(1) and *X*(4) sites. As channel arrangements (1) and (3) cannot occur together [the observed *Y*(1) and *X*(4) occupancies are not compatible with this], the F$^-$ occupancy of the O(10) position can never exceed one-half; thus a maximum of 1 F$^-$ a.p.f.u. can occur at the O(10) site in vesuvianite. Note that this is in direct contradiction to the proposal of Ohkawa *et al.* (1992) that the O(10) site in two samples of vesuvianite refined by them is completely occupied by F.

Configuration (c) does not change the OH$^-$ occupancy of the O(10) site (which remains at 0.5), whereas configuration (d) reduces it to 0.25.

Disorder at the channel positions

Unlike the OH position, there is strong variation in the magnitude of the equivalent isotropic displacement factor at O(10) with increasing F content of the crystals. This variation is positively correlated with an increase in anisotropy of displacement, indicating that the F$^-$-for-(OH)$^-$ substitution produces significant disorder at O(10). The O(10) anion is bonded to one *Y*(1) and four *X*(3) cations. The anisotropic displacement coefficients of the initial refinements indicate that the anions at O(10) are positionally disordered along the $\bar{4}$ axis of the channel in the vesuvianite structure. The O(10) displacements are parallel to the O(10)–*Y*(1) bond, and this will significantly affect the details of this interaction. Inspection of Table 2 shows that the isotropic displacement factor at the *Y*(1) position significantly increases with increasing F content of the crystal. Accompanying this change is a very strong increase in the degree of anisotropy of this displacement. The direction of the maximum displacement at the *Y*(1) position is parallel to the maximum displacement of the anion at the O(10) position; this suggests that these displacements are locally coupled and relate to the variation in local bond-valence requirements with the progressive loss of hydrogen-bonding that accompanies the F^--for-$(OH)^-$ substitution. The final split-site models are an effort to get some indication of the geometry of the local configurations. However, it should be emphasized that we do not have sufficient resolution to derive accurate occupancies for the split sites; as a consequence of this, the local bond-lengths derived are probably less accurate than their precision would suggest.

There are two O(10) anions fairly close together (2.4–2.8 Å) along the four-fold axis, resulting in three different types of substitution that could occur (Fig. 5). F^- could replace an $(OH)^-$ group (Fig. 5b), with the adjacent O(10) remaining as an O^{2-} anion. Fluorine also could replace an O^{2-} anion that was the acceptor of the hydrogen bond (Fig. 5c); in this case, the F^- also would be the acceptor of the hydrogen bond unless there also is a rearrangement of the H atom. In addition, both substitutions could occur simultaneously at the local scale (Fig. 5d).

The split-site refinements produce several disordered positions in the channel, and it is now necessary to try and derive the most reasonable local atomic arrangements. First let us consider the local coordination of the *Y*(1A) and *Y*(1B) sites. As indicated in Table 4, there are four calculated *Y*(1A,B)–O(10A,B) approaches, only two of which are possible. These alternative possibilities are listed in Table 7, together with the local bond-valence arrangements in each case. The values are only very approximate here as the site occupancies were assumed to be 0.5, and the bond-valence curves used are valid for Fe^{2+}–O only. Nevertheless, arrangement (1) is much more reasonable than arrangement (2) for both V27 and V33, both with regards to observed stereochemistry and the calculated bond-valences. Thus we may conclude that *Y*(1A) bonds to O(10B) and *Y*(1B) bonds to O(10A).

TABLE 7. POSSIBLE LOCAL COORDINATIONS AND BOND-VALENCES* AROUND THE *Y*(1) SITES IN SOME F-BEARING VESUVIANITE SAMPLES

		V27		V33	
		Arrangement (1)			
Y(1A)-O(6)	×4	2.077 Å	0.407 v.u.	2.093 Å	0.390 v.u.
Y(1A)-O(10B)		2.166	0.323	2.238	0.270
<*Y*(1A)-O>		2.095	1.951	2.122	1.830
Y(1B)-O(6)	×4	2.099	0.384	2.101	0.382
Y(1B)-O(10A)		2.306	0.229	2.225	0.279
<*Y*(1B)-O>		2.140	1.765	2.126	1.807
		Arrangement (2)			
Y(1A)-O(6)	×4	2.077	0.407	2.093	0.390
Y(1A)-O(10B)		2.691	0.098	2.598	0.119
<*Y*(1A)-O>		2.200	1.726	2.194	1.679
Y(1B)-O(6)	×4	2.099	0.384	2.101	0.382
Y(1B)-O(10A)		1.781	0.949	1.865	0.736
<*Y*(1B)-O>		2.035	2.485	2.054	2.264

*Calculated with M-O bond-valence curves of Brown (1981).

TABLE 8. BOND LENGTHS (Å) AND BOND-VALENCES* ABOUT THE O(10A) AND O(10B) POSITIONS IN SELECTED STRUCTURES OF VESUVIANITE

		V12		V27		V33	
O(10A)-*X*(3)	×4	2.556	0.207	2.638	0.174	2.594	0.191
O(10A)-*Y*(1B)		2.004	0.496	2.306	0.229	2.225	0.279
Sum			1.324		0.925		1.043
O(10B)-*X*(3)	×4	2.556	0.207	2.578	0.197	2.569	0.201
O(10B)-*Y*(1A)		2.004	0.496	2.166	0.323	2.238	0.270
Sum			1.324		1.111		1.074

*Calculated with M-O bond-valence curves of Brown (1981).

Next, we will examine the bond-valence structure around both of the O(10) positions (Table 8). In fluorine-free V12, the bond-valence sum to O(10) from the bonded cations is 1.324 v.u.; this leaves 0.676 v.u. to be supplied by the associated hydrogen atom, which then hydrogen-bonds to the adjacent O(10) anion. In both crystals of F-bearing vesuvianite, the bond-valence sums to O(10A) and O(10B) are ~1.0 v.u. when calculated for O^{2-} at both O(10) positions. Whatever the constituent anions, this indicates much weaker hydrogen bonding than in F-free vesuvianite; this finding is consistent with the loss of a low-frequency (~3200 cm^{-1}) band in the infrared absorption spectra of F-bearing vesuvianite (Groat, Hawthorne, Rossman and Ercit, in prep.)

Fluorine avoidance by Fe^{2+}

It should be noted that incorporation of F at the O(10) site *via* channel arrangement (3) (Fig. 4) means that Fe^{2+} at the *Y*(3) site should never bond to F^-, only to OH^-. Although this seems to be dictated by the satisfaction of local bond-valences that specifically involve the presence or absence of hydrogen bonding, the observation is in line with the well-known "fluorine-avoidance" rule (Rosenberg & Foit 1977).

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