The Canadian Mineralogist
Vol. 32, pp. 497-504 (1994)

EXCESS *Y*-GROUP CATIONS IN THE CRYSTAL STRUCTURE OF VESUVIANITE

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ABSTRACT

Some vesuvianite crystals show sums of *Y*-group cations [Al, Mg, Fe^{3+}, Fe^{2+}, Ti^{4+}, Cu^{2+}, Zn, Mn] significantly in excess of 13, the number of sites available to accommodate these cations in the current model of the vesuvianite structure. The structures of four such crystals were refined in the space group *P4/nnc* to *R* indices of 3–4% using single-crystal Mo$K\alpha$ X-ray intensity data. The same crystals were subsequently examined by wavelength-dispersion electron-microprobe analysis; the mean *Y*-group sum is 13.57 apfu. The crystals show an additional site, *T*(1), that is tetrahedrally coordinated by four oxygen atoms. This site is occupied by (Al,Fe), which replaces two H atoms at adjacent H(1) positions. Local bond-valence arguments show that the substitution is accompanied by the incorporation of a vacancy at an adjacent *X*(3) site according to the mechanism $^{T(1)}(Al,Fe^{3+})_2 + {}^{H(1)}\square_4 + {}^{X(3)}\square \rightarrow {}^{T(1)}\square_2 + {}^{H(1)}H_4 + {}^{X(3)}Ca$, or by the substitution $^{T(1)}(Al,Fe^{3+}) + {}^{H(1)}\square_2 + {}^{Y}(Mg,Fe^{2+}) \rightarrow {}^{T(1)}\square + {}^{H(1)}H_2 + {}^{Y}(Al,Fe^{3+})$.

Keywords: vesuvianite, crystal structure, electron-microprobe data, chemical formula, vacancies.

SOMMAIRE

Certains cristaux de vesuvianite font preuve d'un excès de cations dans la position *Y* (Al, Mg, Fe^{3+}, Fe^{2+}, Ti^{4+}, Cu^{2+}, Zn, Mn), en fait plus que 13, le nombre de sites disponibles pour les cations de ce groupe dans le modèle courant de la structure de cette espèce. La structure de quatre cristaux montrant un tel excès a été affinée dans le groupe spatial *P4/nnc* jusqu'à un résidu *R* de 3 à 4% en utilisant des données d'intensités en diffraction X obtenues avec rayonnement Mo$K\alpha$. Les mêmes cristaux ont ensuite été analysés avec une microsonde électronique en dispersion de longueurs d'onde; ces résultats donnent un total de 13.57 atomes par unité formulaire. Les cristaux révèlent un site additionnel, *T*(1), à coordinence tétraédrique avec quatre atomes d'oxygène. Ce site accommode (Al,Fe), qui remplace deux atomes d'hydrogène à des sites H(1) avoisinants. Pour des raisons de satisfaction locale des valences de liaison, la substitution serait accompagnée par la création d'une lacune sur un site *X*(3) adjacent selon le schéma $^{T(1)}(Al,Fe^{3+})_2 + {}^{H(1)}\square_4 + {}^{X(3)}\square \rightarrow {}^{T(1)}\square_2 + {}^{H(1)}H_4 + {}^{X(3)}Ca$, ou bien $^{T(1)}(Al,Fe^{3+}) + {}^{H(1)}\square_2 + {}^{Y}(Mg,Fe^{2+}) \rightarrow {}^{T(1)}\square + {}^{H(1)}H_2 + {}^{Y}(Al,Fe^{3+})$.

(Traduit par la Rédaction)

Mots-clés: vésuvianite, structure cristalline, données de microsonde électronique, formule chimique, lacunes.

INTRODUCTION

Groat *et al.* (1992a) showed that results of chemical analyses of vesuvianite crystals from a wide variety of localities and parageneses can be satisfactorily renormalized to the formula $X_{19}\ Y_{13}\ Z_{18}\ T_5\ O_{68}\ W_{10}$, where X = Ca, Na, *REE*, Pb^{2+}, Sb^{3+}; Y = Al, Mg, Fe^{3+}, Fe^{2+}, Ti^{4+}, Mn, Cu, Zn; Z = Si; T = B, $\square$; W = OH, F, O. If renormalized on the basis of 50 cations, these assignments to *X*, *Y* and *Z* groups (for B-free vesuvianite crystals) agree well with the number of available sites in the ideal structure (Groat *et al.* 1992a, Fitzgerald *et al.* 1992, Hoisch 1985). However, for a small number of crystals, the *Y*-group sums are significantly larger than the ideal value of 13.0 apfu (atoms per formula unit), values reaching up to 13.6 apfu. Re-

analysis showed that these "excess" values are reproducible. Groat *et al.* (1992a) and Allen & Burnham (1992) have drawn attention to the constraints that the close $Y(1)$–$X(4)$ and $X(4)$–$X(4)$ separations down the channels in the vesuvianite structure impose on channel chemistry. The sum of the $Y(1)$ and $X(4)$ cations cannot exceed half the number of $Y(1) + X(4)$ sites, and the $X(4)$ site cannot be more than half occupied. These constraints allow the *Y*-group cation sum to be greater than 13.0 apfu as suggested by the above formula. Hence it is of considerable interest to examine the structure of crystals of vesuvianite showing an excess of *Y* cations to determine where these reside; do they occur at the $Y(1)$ site, the occupancy of which therefore exceeds one-half, or do they occupy another (new) site in the structure?

High *Y*-group sums also are a prominent characteristic of B-bearing vesuvianite crystals, but careful electron-microprobe analysis of the anomalous crystals showed no detectable boron. However, it is notable that both these anomalous crystals *and* the B-bearing crystals show high *Y*-group sums. This suggests that the former could be incorporating other constituents in a manner structurally similar to the mode of incorporation of boron in B-bearing vesuvianite crystals (Groat *et al.* 1994). To resolve this problem, four crystals of B-free vesuvianite with high *Y*-group sums were examined by crystal-structure refinement.

Experimental

Two samples were selected from those described by Groat *et al.* (1992a): V40 and V60, together with two additional samples, N3 and N8. Crystal fragments were ground into spheres and mounted on a Nicolet *R3m* four-circle diffractometer. Unit-cell and intensity data were measured and processed according to the procedure of Groat *et al.* (1992b). Miscellaneous information concerning data collection, data reduction and structure refinement is given in Table 1.

Subsequent to the collection of the intensity data, the crystals used in the data collection were analyzed by electron-microprobe techniques as described by Groat *et al.* (1992a). Ten points were analyzed on each crystal to get a representative composition of the crystal used for the collection of X-ray intensities.

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.

Only a small number of weak reflections violate the criteria for *P4/nnc* symmetry, and this space group was used throughout. The refinements were started with the positional and displacement parameters of a structure of F-free vesuvianite (unpublished), and rapidly converged to *R* indices of 4–6% for an anisotropic displacement model; site-scattering values for $Y(1)$, $Y(2)$ and $Y(3)$ were allowed to vary freely. The $Y(1)$ and O(10) sites showed very anisotropic displacement parameters, with large displacement values along the *c* axis. We interpret these large displacement values as static disorder of the atoms occupying the $Y(1)$ and O(10) sites, and modeled this by splitting the $Y(1)$ and O(10) sites into pairs of half-occupied sites: $Y(1A)$, $Y(1B)$ and O(10A), O(10B). We

TABLE 1. PHYSICAL DATA AND INFORMATION ON REFINEMENT FOR VESUVIANITE CRYSTALS

	N3	N8	V40	V60
Locality	Crestmore, Riverside Co., CA	Culfeightrin, Co. Antrim, Ulster	Monte Somma, Italy	Plumas Co., CA
Sample No.	CMN 36124	CMN 42850	ROM E1541	ROM M28840
a(Å)	15.589(2)	15.571(2)	15.584(1)	15.596(2)
c(Å)	11.885(3)	11.797(4)	11.834(1)	11.843(2)
V(Å^3)	2888.3(9)	2860.3(8)	2874.0(5)	2880.6(7)
Space group	*P4/nnc*	*P4/nnc*	*P4/nnc*	*P4/nnc*
Radiation	Mo*Kα*	Mo*Kα*	Mo*Kα*	Mo*Kα*
Monochromator	Graphite	Graphite	Graphite	Graphite
Total no. $\|F\|$	4688	4255	2118	2122
No. of $\|F\|$ obs	2124	2005	1969	1984
R (observed) %	3.6	3.3	3.1	4.1
wR (observed) %	2.9	2.7	2.7	3.7

have no justification for assuming equal occupancy for each of the sites in a pair; however, we could not adequately refine relative occupancies because of the high correlation resulting from the very small separations of the split-atom sites. Nevertheless, the resulting arrangement gives us a better picture of the local stereochemistry than would a single-site model.

At this stage, difference-Fourier maps showed significant residual density at the following positions, here labeled *T*(1) and *T*(2):

T(1)	0.045	0.045	1/4
T(2)	1/4	1/4	1/4

Electron density at these positions was noted by Allen & Burnham (1983) in a preliminary report of a structure refinement of vesuvianite from Ludwig, Nye County, Nevada. Aluminum was inserted at these positions (with fixed displacement-factors), and the site scattering and allowed positional parameters were considered as variable. Full-matrix least-squares refinement of all variable parameters converged to *R* indices of 3–4%, significant reductions for each crystal. No further peaks were observed in subsequent difference-Fourier maps.

TABLE 2. ATOMIC PARAMETERS FOR VESUVIANITE CRYSTALS

		N3	N8	V40	V60
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
	$*U_{eq}$	61(2)	67(2)	70(2)	68(3)
Z(2)	*x*	−0.18061(4)	−0.18051(4)	−0.18078(4)	−0.18064(4)
	y	0.04122(4)	0.04051(4)	0.04083(4)	0.04141(4)
	z	0.87153(5)	0.87126(5)	0.87155(5)	0.87161(6)
	U_{eq}	67(2)	70(2)	70(2)	68(2)
Z(3)	*x*	−0.08376(4)	−0.08339(5)	−0.08332(4)	−0.08361(5)
	y	−0.15057(4)	−0.15078(4)	−0.15058(4)	−0.15054(4)
	z	0.36432(5)	0.36465(5)	0.36441(5)	0.36438(6)
	U_{eq}	77(2)	81(2)	80(2)	82(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}	82(2)	92(2)	94(2)	95(3)
X(2)	*x*	−0.18928(3)	−0.18914(3)	−0.18907(3)	−0.18925(3)
	y	0.04481(3)	0.04407(3)	0.04442(3)	0.04479(3)
	z	0.37941(4)	0.37957(4)	0.37932(4)	0.37931(4)
	U_{eq}	82(1)	86(1)	87(1)	86(1)
X(3)	*x*	−0.10146(3)	−0.10070(3)	−0.10073(3)	−0.10111(4)
	y	−0.18186(4)	−0.17988(3)	−0.18046(3)	−0.18165(4)
	z	0.89065(5)	0.88689(5)	0.88866(5)	0.89037(6)
	U_{eq}	204(2)	146(1)	178(2)	209(2)
X(4)	*x*	3/4	3/4	3/4	3/4
	y	3/4	3/4	3/4	3/4
	z	0.1502(2)	0.1422(2)	0.1450(2)	0.1487(2)
	U_{eq}	96(5)	123(5)	113(5)	121(5)
Y(1A)	*x*	3/4	3/4	3/4	3/4
	y	3/4	3/4	3/4	3/4
	z	0.0415(5)	0.0560(3)	0.0624(3)	0.0493(4)
	U_{eq}	64(6)	58(7)	73(6)	79(6)
Y(1B)	*x*	3/4	3/4	3/4	3/4
	y	3/4	3/4	3/4	3/4
	z	0.0267(5)	0.0281(3)	0.0304(3)	0.0266(4)
	U_{eq}	64(6)	58(7)	73(6)	79(6)

TABLE 2. continued

		N3	N8	V40	V60
Y(2)	*x*	0	0	0	0
	y	0	0	0	0
	z	0	0	0	0
	U_{eq}	67(3)	55(3)	74(3)	62(3)
Y(3)	*x*	−0.11230(4)	−0.11214(4)	−0.11225(4)	−0.11231(4)
	y	0.12126(4)	0.12098(4)	0.12098(4)	0.12115(4)
	z	0.12588(6)	0.12682(5)	0.12632(5)	0.12588(6)
	U_{eq}	71(2)	75(2)	76(2)	77(2)
O(1)	*x*	−0.2202(1)	−0.2204(1)	−0.2205(1)	−0.2202(1)
	y	0.1727(1)	0.1725(1)	0.1727(1)	0.1729(1)
	z	0.0853(1)	0.0855(1)	0.0857(1)	0.0853(1)
	U_{eq}	88(4)	95(4)	98(4)	95(5)
O(2)	*x*	−0.1175(1)	−0.1176(1)	−0.1173(1)	−0.1176(1)
	y	0.1600(1)	0.1602(1)	0.1602(1)	0.1602(1)
	z	0.2795(1)	0.2797(1)	0.2796(1)	0.2798(2)
	U_{eq}	96(5)	103(5)	99(4)	97(5)
O(3)	*x*	−0.0467(1)	−0.0478(1)	−0.0478(1)	−0.0470(1)
	y	0.2225(1)	0.2223(1)	0.2222(1)	0.2227(1)
	z	0.0756(1)	0.0759(2)	0.0753(1)	0.0753(1)
	U_{eq}	92(4)	93(5)	92(4)	86(5)
O(4)	*x*	−0.0613(1)	−0.0613(1)	−0.0614(1)	−0.0615(1)
	y	0.1057(1)	0.1059(1)	0.1060(1)	0.1059(1)
	z	0.4697(1)	0.4703(1)	0.4696(1)	0.4696(2)
	U_{eq}	90(5)	90(5)	94(4)	91(5)
O(5)	*x*	−0.1709(1)	−0.1706(1)	−0.1706(1)	−0.1710(1)
	y	0.0135(1)	0.0143(1)	0.0141(1)	0.0137(1)
	z	0.1785(2)	0.1792(2)	0.1788(1)	0.1785(2)
	U_{eq}	116(5)	110(5)	111(5)	117(5)
O(6)	*x*	0.8788(1)	0.8810(1)	0.8801(1)	0.8790(1)
	y	−0.2731(1)	−0.2718(1)	−0.2726(1)	−0.2732(1)
	z	0.0587(2)	0.0586(1)	0.0587(2)	0.0586(2)
	U_{eq}	151(5)	154(5)	158(5)	158(5)
O(7)	*x*	0.0555(1)	0.0557(1)	0.0557(1)	0.0550(1)
	y	0.1717(1)	0.1733(1)	0.1730(1)	0.1718(1)
	z	0.3207(2)	0.3211(2)	0.3214(2)	0.3208(2)
	U_{eq}	143(5)	142(5)	136(5)	151(5)
O(8)	*x*	−0.0607(1)	−0.0607(1)	−0.0605(1)	−0.0605(1)
	y	−0.0912(1)	−0.0908(1)	−0.0908(1)	−0.0914(1)
	z	0.0674(2)	0.0665(1)	0.0673(1)	0.0675(2)
	U_{eq}	90(4)	95(5)	100(4)	95(5)
O(9)	*x*	−0.1451(1)	−0.1449(1)	−0.1447(1)	−0.1451(1)
	y	−0.1451(1)	−0.1449(1)	−0.1447(1)	−0.1451(1)
	z	1/4	1/4	1/4	1/4
	U_{eq}	113(5)	119(5)	118(5)	116(5)
O(10A)	*x*	3/4	3/4	3/4	3/4
	y	3/4	3/4	3/4	3/4
	z	0.8569(8)	0.8516(7)	0.8526(9)	0.8550(9)
	U_{eq}	153(12)	153(15)	162(13)	194(15)
O(10B)	*x*	3/4	3/4	3/4	3/4
	y	3/4	3/4	3/4	3/4
	z	0.8767(9)	0.8790(7)	0.8788(7)	0.8768(9)
	U_{eq}	153(12)	153(15)	162(13)	194(15)
O(11)	*x*	−0.0035(1)	−0.0037(1)	−0.0039(1)	−0.0040(1)
	y	0.0609(1)	0.0616(1)	0.0617(1)	0.0612(1)
	z	0.1360(1)	0.1362(1)	0.1355(1)	0.1355(1)
	U_{eq}	103(3)	83(4)	84(4)	100(5)
T(1)	*x*	0.0561(3)	0.052(2)	0.0550(4)	0.0552(3)
	y	0.0561(3)	0.052(2)	0.0550(4)	0.0552(3)
	z	1/4	1/4	1/4	1/4
	$**U_{eq}$	100	100	100	100
T(2)	*x*	1/4	1/4	1/4	1/4
	y	1/4	1/4	1/4	1/4
	z	1/4	1/4	1/4	1/4
	$**U_{eq}$	100	100	100	100

$* U_{eq} = U_{eq} \times 10^4$ (Å²) ** Fixed during refinement

TABLE 3. REFINED SITE-SCATTERING* IN VESUVIANITE CRYSTALS

	N3	N8	V40	V60
Y(1)	20.0(2)	23.9(3)	22.2(2)	21.3(2)
Y(3)	109.4(9)	115.1(9)	116.0(3)	105.2(2)
T(1)	10.4(2)	2.5(2)	6.7(1)	9.3(1)
T(2)	0.8(2)	0.9(2)	1.0(1)	1.3(1)

* in epfu (electrons per formula unit)

RESULTS

Structure refinement

Unit-cell data are given in Table 1. Final positional parameters and equivalent isotropic displacement-factors are given in Table 2, and the refined site-scattering values are given in Table 3. Tables of structure factors and anisotropic displacement-parameters 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.

Chemical composition

The chemical composition of each crystal is given in Table 5. The calculation of the unit formulae is not straightforward. Groat *et al.* (1992a) recommended that the composition of B-free vesuvianite be renormalized on the basis of 50 cations pfu, and showed that this is an appropriate procedure for most samples of vesuvianite. However, the crystals chosen for this study were selected because their unit formulae show the maximum deviations from the ideal cation-sums of 19, 13 and 18 apfu for the *X*, *Y* and *Z* groups, respectively. Thus it is not at all apparent that a 50-cation scheme of renormalization is appropriate. As can be seen in Table 4, the <*Z*–O> bond-lengths are reasonably constant in these (and most other) crystals of vesuvianite, suggesting that the *Z* sites are occupied only by Si. Thus, as a first approach to the problem,

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

	N3	N8	V40	V60
Z(1)–O(1)a x4	1.640(2)	1.638(2)	1.641(2)	1.638(2)
<*Z*(1)–O>	1.640	1.638	1.641	1.638
Z(2)–O(2)b	1.645(2)	1.645(2)	1.645(2)	1.642(2)
Z(2)–O(3)c	1.638(2)	1.641(2)	1.641(2)	1.636(2)
Z(2)–O(4)b	1.678(2)	1.679(2)	1.676(2)	1.674(2)
Z(2)–O(7)b	1.629(2)	1.615(2)	1.621(2)	1.625(2)
<*Z*(2)–O>	1.648	1.645	1.646	1.644
Z(3)–O(5)d	1.631(2)	1.637(2)	1.632(2)	1.632(2)
Z(3)–O(6)e	1.609(2)	1.607(2)	1.608(2)	1.608(2)
Z(3)–O(8)d	1.623(2)	1.624(2)	1.624(2)	1.624(2)
Z(3)–O(9)	1.661(1)	1.660(1)	1.660(1)	1.662(1)
<*Z*(3)–O>	1.631	1.632	1.631	1.632
X(1)–O(1)a x4	2.341(2)	2.331(2)	2.334(2)	2.338(2)
X(1)–O(2)a x4	2.522(2)	2.516(2)	2.522(2)	2.519(2)
<*X*(1)–O>	2.432	2.424	2.428	2.429
X(2)–O(1)l	2.479(2)	2.481(2)	2.480(2)	2.482(2)
X(2)–O(2)	2.424(2)	2.429(2)	2.428(2)	2.424(2)
X(2)–O(3)b	2.383(2)	2.374(2)	2.377(2)	2.380(2)
X(2)–O(4)	2.455(2)	2.457(2)	2.455(2)	2.453(2)
X(2)–O(5)	2.448(2)	2.426(2)	2.436(2)	2.444(2)
X(2)–O(5)l	2.337(2)	2.337(2)	2.340(2)	2.335(2)
X(2)–O(6)o	2.991(2)	2.939(2)	2.964(2)	2.990(2)
X(2)–O(8)d	2.332(2)	2.326(2)	2.327(2)	2.329(2)
<*X*(2)–O> [8]	2.481	2.471	2.476	2.480
<*X*(2)–O> [7]	2.408	2.404	2.406	2.407
X(3)–O(3)l	2.428(2)	2.444(2)	2.442(2)	2.432(2)
X(3)–O(6)p	2.467(2)	2.496(2)	2.490(2)	2.471(2)
X(3)–O(6)l	2.947(2)	2.991(2)	2.973(2)	2.951(2)
X(3)–O(7)j	2.611(2)	2.554(2)	2.586(2)	2.607(2)
X(3)–O(7)m	2.532(2)	2.513(2)	2.518(2)	2.533(2)
X(3)–O(7)b	2.402(2)	2.371(2)	2.384(2)	2.408(2)
X(3)–O(8)k	2.606(2)	2.608(2)	2.611(2)	2.605(2)
X(3)–O(10A)n x½	2.579(2)	2.602(1)	2.601(2)	2.589(2)
X(3)–O(10B)n x½	2.553(1)	2.570(1)	2.569(1)	2.560(1)
X(3)–O(11)j	2.517(2)	2.471(2)	2.438(2)	2.512(2)
<*X*(3)–O> [9]	2.564	2.559	2.559	2.566
<*X*(3)–O> [8]	2.516	2.505	2.507	2.518
X(4)–O(6)q x4	2.310(2)	2.305(2)	2.298(2)	2.305(2)
X(4)–O(6)f x4	2.597(2)	2.642(2)	2.633(2)	2.607(2)
<*X*(4)–O>	2.454	2.474	2.466	2.456

TABLE 4. continued

	N3	N8	V40	V60
Y(1A)–O(6)q x4	2.050(2)	2.067(2)	2.059(2)	2.047(2)
Y(1A)–O(10A)g	2.187(12)	2.411(9)	2.482(9)	2.301(12)
Y(1A)–O(10B)g	1.953(12)	2.088(9)	2.172(9)	2.043(11)
Y(1B)–O(6)q x4	2.075(2)	2.098(2)	2.085(2)	2.078(2)
Y(1B)–O(10A)g	2.013(12)	2.083(9)	2.104(9)	2.033(12)
Y(1B)–O(10B)g	1.778(12)	1.759(9)	1.794(9)	1.775(11)
Y(2)–O(4)d x2	1.938(2)	1.937(2)	1.942(2)	1.944(2)
Y(2)–O(8) x2	1.885(2)	1.873(2)	1.878(2)	1.886(2)
Y(2)–O(11) x2	1.871(2)	1.873(2)	1.870(2)	1.867(2)
<*Y*(2)–O>	1.898	1.894	1.897	1.899
Y(3)–O(1)	1.924(2)	1.929(2)	1.930(2)	1.927(2)
Y(3)–O(2)	1.920(2)	1.906(2)	1.916(2)	1.924(2)
Y(3)–O(3)	1.973(2)	1.963(2)	1.965(2)	1.975(2)
Y(3)–O(4)h	2.077(2)	2.070(2)	2.076(2)	2.074(2)
Y(3)–O(5)	2.011(2)	1.992(2)	1.997(2)	2.009(2)
Y(3)–O(11)	1.944(2)	1.929(2)	1.929(2)	1.935(2)
<*Y*(3)–O>	1.975	1.965	1.969	1.974
X(4)–*X*(4)d	2.366(4)	2.543(4)	2.486(4)	2.400(4)
X(4)–*Y*(1A)	1.289(6)	1.017(4)	0.978(4)	1.177(5)
X(4)–*Y*(1B)	1.464(6)	1.348(4)	1.366(4)	1.445(5)
Y(1A)–*Y*(1B)	0.175(9)	0.329(5)	0.378(5)	0.268(6)
O(10A)–*X*(3)f x4	2.579(2)	2.602(1)	2.601(2)	2.589(2)
O(10A)–*Y*(1A)k	2.187(12)	2.411(9)	2.482(9)	2.301(12)
O(10A)–*Y*(1B)k	2.013(12)	2.083(9)	2.104(9)	2.033(12)
O(10B)–*X*(3)f x4	2.553(1)	2.570(1)	2.569(1)	2.560(1)
O(10B)–*Y*(1A)k	1.953(12)	2.088(9)	2.172(9)	2.043(11)
O(10B)–*Y*(1B)k	1.778(12)	1.759(9)	1.794(9)	1.775(11)
T(1)–O(7) x2	1.987(5)	2.064(23)	2.024(5)	2.003(5)
T(1)–O(11) x2	1.642(3)	1.607(11)	1.639(3)	1.643(3)
T(2)–O(10A)r x2	1.268(10)	1.198(8)	1.214(8)	1.243(11)
T(2)–O(10B)r	1.502(10)	1.522(8)	1.524(8)	1.502(11)

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: $x, 1+y, z$; r: $-x+1, -y+1, -z+1$.

TABLE 5. AVERAGE COMPOSITION OF VESUVIANITE CRYSTALS*

	N3	N8	V40	V60
SiO_2	36.75	36.15	36.51	37.02
Al_2O_3	17.19	14.57	15.95	16.39
TiO_2	0.14	1.00	0.92	0.22
MgO	3.80	3.17	3.00	3.47
MnO	0.00	0.49	0.29	0.00
FeO	2.87	4.44	4.15	0.63
Fe_2O_3	–	–	–	3.06
CaO	35.90	34.92	35.33	35.62
Na_2O	0.00	0.02	0.08	0.00
$^{+}Ln_2O_3$	0.00	0.21	0.00	0.00
SO_3	0.00	0.00	0.00	0.15
F	0.10	1.18	1.43	0.00
Cl	0.04	0.06	0.07	0.00
H_2O**	2.12	1.39	2.52	2.77
	98.91	97.59	100.17	99.33
O=F,Cl	0.05	0.51	0.60	0.00
TOTAL	98.86	97.08	99.57	99.33
Si	18.00	18.00	18.00	18.00
Al	9.93	8.55	9.26	9.39
Ti^{4+}	0.05	0.37	0.34	0.08
Mg	2.78	2.35	2.21	2.52
Mn^{2+}	0.00	0.21	0.12	0.00
Fe^{2+}	1.18	1.85	1.71	0.26
Fe^{3+}	–	–	–	1.12
Ca	18.84	18.63	18.66	18.55
Na	0.00	0.02	0.07	0.00
$^{+}Ln^{3+}$	0.00	0.04	0.03	0.00
S	0.00	0.00	0.00	0.04
F	0.16	1.86	2.22	0.00
Cl	0.03	0.04	0.06	0.01
OH	7.00	4.70	8.29	8.98
ΣX	18.84	18.69	18.76	18.55
ΣY	13.93	13.34	13.65	13.34
ΣZ	18.00	18.00	18.00	18.00

* Analyses are normalized on 18 Si.
** Calculated for charge balance.
$^{+}$Ln = total REE

we renormalized the compositions on the basis of 18 Si apfu; this does not make allowance for the possibility of Si being in excess of 18 apfu, with Si occupying another site. Table 5 shows the unit formulae renormalized on this basis.

Site-Scattering Considerations

All structures show significant scattering at the *T*(1) and *T*(2) positions. However, the assignment of this electron density is not straightforward, as determination of the local stereochemistry is complicated by extensive positional disorder and partly occupied sites.

T(1) site

The O(7) and O(11) anions form a tetrahedron around the *T*(1) site, with *T*(1)–O(7) and *T*(1)–O(11) distances of ~2.02 and 1.64 Å, respectively. The tetrahedral coordination and mean bond-lengths suggest that *T*(1) is occupied by Al or Fe^{3+}. This is in accord with the observation that the *Y*-group cation sum is generally in excess of 13 apfu.

T(2) site

In all crystals, the refined site-scattering at *T*(2) is ~1 e, and the O(10) position is fully occupied. This is compatible with half-occupancy of the H(2) position (Groat *et al.* 1992a) by H, the positional disorder of the half-occupied site (Lager *et al.* 1989) giving rise to electron density at the *T*(2) position. Hence the local composition and stereochemistry are similar to those observed in normal stoichiometric vesuvianite.

Chemical Composition

Inspection of Table 5 shows that the crystals have *Y*-group sums significantly in excess of the ideal value of 13 apfu. As discussed above (Fig. 1), the incorporation of (Al,Fe^{3+}) at *T*(1) is accompanied by the introduction of vacancies at the adjacent H(1) positions. This substitution results in an excess positive charge, and hence must be coupled to a complementary charge-balancing substitution. Some possible substitutions are listed in Table 6. Inspection of Table 5 allows us to dismiss some of these possible substitutions immediately. The crystals examined here contain negligible Na, and thus substitution (1) can be discounted. If substitution (6) is significant, the amount of excess *Y*-cations should correlate with increasing <<*Z*–O>> distance as Al replaces Si. Examination of Table 4 shows that <*Z*(2)–O> and <*Z*(3)–O> are constant in these vesuvianite crystals, and fall within the ranges observed in refined structures of vesuvianite (Groat *et al.* 1992a, Fig. 6a). Observed <*Z*(1)–O> values are similar to those observed in most other vesuvianite crystals (including boron-bearing vesuvianite; Groat *et al.* 1994). This indicates

TABLE 6. POSSIBLE SUBSTITUTIONS INVOLVING THE INCORPORATION OF (Al,Fe^{3+}) AT THE *T*(1) SITE IN VESUVIANITE

Substitutions involving X-group cations

(1) $^{T(1)}[Al,Fe^{3+}] + {}^{X}Na \rightarrow {}^{H(1)}H_2 + {}^{X}Ca$

(2) $^{T(1)}[Al,Fe^{3+}]_2 + {}^{X}\square \rightarrow {}^{H(1)}H_4 + {}^{X}Ca$

Substitutions involving Y-group cations

(3) $^{T(1)}[Al,Fe^{3+}] + {}^{Y}(Mg,Fe^{2+}) \rightarrow {}^{H(1)}H_2 + {}^{Y}Al$

(4) $^{T(1)}[Al,Fe^{3+}]_2 + {}^{Y}\square \rightarrow {}^{H(1)}H_4 + {}^{Y}Mg$

(5) $^{T(1)}[Al,Fe^{3+}]_3 + {}^{Y}\square \rightarrow {}^{H(1)}H_6 + {}^{Y}Al$

Substitutions involving Z-group cations

(6) $^{T(1)}[Al,Fe^{3+}] + {}^{Z}Al \rightarrow {}^{H(1)}H_2 + {}^{Z}Si$

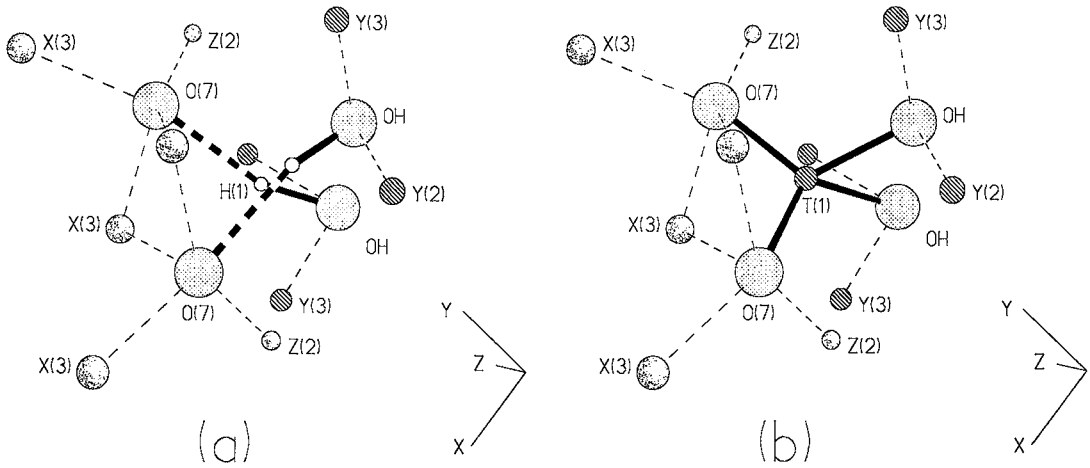

FIG. 1. The proposed local arrangements around the $T(1)$ site. (a) $T(1)$ vacant; note that the H(1) positions are occupied. (b) $T(1)$ occupied by Al, and $H(1)$ positions vacant. To avoid complications in the figure, bond valences are not shown, but may be read directly from Table 7.

that there is little Al occurring at $Z(1)$, certainly insufficient for substitution (6) to be the primary mechanism for incorporation of excess Y-group cations; substitution of 0.57 Al at $Z(1)$ would increase <$Z(1)$–O> by ~0.037 Å over that value corresponding to full Si occupancy, whereas the observed differences are less than or equal to 0.005 Å. Hence we discount substitution (6) as an important mechanism in this context. Substitutions (4) and (5) also can be discounted, as the observed scattering values at the Y-sites and at $T(1)$ are not compatible with these mechanisms. This leaves substitutions (2) and (3) to be considered.

Groat *et al.* (1992a, 1994) have shown that boron is incorporated into the vesuvianite structure primarily by substitution (3). In addition, the fact that $\Sigma(X\text{–}19)$ is greater than $\Sigma(Z\text{–}18)$ in boron-bearing vesuvianite suggests that substitution (2) is not important in boron-bearing vesuvianite (which invariably has Y-cation sums significantly larger than 13 apfu). The situation is less clear in the vesuvianite crystals examined here. Firstly, the amount of substitution at the $T(1)$ site is far less in boron-free vesuvianite than in boron-bearing vesuvianite, and hence the mechanism is less clear. Secondly, unlike boron-bearing vesuvianite, $\Sigma(X\text{–}19)$ is *less* than $\Sigma(Z\text{–}18)$ in Y-cation-excess vesuvianite,

TABLE 7. LOCAL BOND-VALENCE ARRANGEMENTS AROUND THE $T(1)$ POSITION IN VESUVIANITE

				$T(1)$ vacant			
	$Z(2)$	$X(3)$	$Y(2)$	$Y(3)$	Σ	H(1)	Σ
O(7)	1.013	0.202			1.764	0.29	2.054
		0.239					
		0.310					
O(11)		0.236	0.548	0.508	1.292	0.71	2.002
				$T(1)$ occupied*			
	$Z(2)$	$X(3)$	$Y(2)$	$Y(3)$	Σ	$T(1)$	Σ
O(7)	1.00	0.20			1.76	0.75	1.95
		0.27 **					
		0.29					
O(11)		0.24	0.55	0.51	1.30	0.75	2.05

* these values are only approximate as the observed bond-lengths are for a combination of $T(1)$-vacant and $T(1)$-occupied configurations;
** for satisfaction of the O(7) bond-valence requirements, one or two of these bonds must be absent (i.e., there must be local vacancies at the $X(3)$ position).

suggesting that substitution (2) is significant. Thirdly, the lack of knowledge of Fe^{2+} and Fe^{3+} contents in these boron-free vesuvianite crystals prevents quantitative evaluation of the importance of substitution (3). At the moment, we must be content with accepting both substitutions (2) and (3) (Table 6) as being involved with the occurrence of (Al,Fe^{3+}) at the *T*(1) site in boron-free vesuvianite. In this regard, it is notable that detailed consideration of the *X*-, *Y*- and *Z*-group cation-sums (Groat *et al.* 1992a) shows negligible skew for the *Z* group, a positive skew for the *Y* group and a negative skew for the *X* group, in line with the substitutions (2) and (3) deduced to be of importance here.

Local stereochemistry and (Al,Fe) incorporation at the T(1) site

If the *T*(1) site is locally occupied by (Al,Fe), the two neighboring H(1) positions must be vacant. Figure 1 shows the local arrangements with *T*(1) vacant and occupied, and Table 7 shows the local bond-valence arrangements. If *T*(1) is vacant and H(1) is fully occupied, H(1) provides 0.71 v.u. to O(11) and 0.29 v.u. to O(7). If H(1) is vacant and *T*(1) is occupied by (Al,Fe), the *T*(1) cation provides ~0.75 v.u. to O(11) (where this site is now occupied by O^{2-}) and ~0.75 v.u. to O(7); this arrangement results in excess incident bond-valence at O(7) (Table 7). As discussed above, the occurrence of (Al,Fe^{3+}) may occur *via* substitutions (2) and (3) (Table 6). Groat *et al.* (1994) deal with the local details of substitution (3) in regard to the incorporation of boron at *T*(1). Here, we will consider the stereochemical details of substitution (2). The bond-valence excess at O(7) caused by occupancy of the *T*(1) site may be compensated by a vacancy or vacancies at one or more of the three *X*(3) positions that coordinate O(7), reducing the bond-valence incident at O(7) to ~2.0 v.u. This suggests that the occurrence of (Al,Fe) at *T*(1) should be accompanied by the occurrence of vacancies at the *X*(3) site. This mechanism accounts for the lower-than-ideal *X*-group cation sums in these vesuvianite crystals (Table 5).

The proposed substitution may be written as

$$^{T(1)}(Al,Fe)_2 + {}^{H(1)}\square_4 + {}^{X(3)}\square \rightarrow {}^{T(1)}\square_2 + {}^{H(1)}H_4 + {}^{X(3)}Ca \quad (1)$$

where the → indicates that the constituents on the left are replacing the constituents on the right. This is the simplest form of this substitution, but more complex formulations are possible. The vacant *X*(3) site can potentially be associated with three different *T*(1) sites, and the electroneutrality constraint would also require an additional heterovalent substitution, possibly involving substitution (3) (Table 6). Hence a simple relation between $^{T(1)}$(Al,Fe) and the *X*-group sum is not expected. However, the fact that $\sum X$ is less than 19 apfu in all of these crystals is compatible with the above substitution. This result requires a modification to the site-group contents of the general formula proposed by Groat *et al.* (1992a). The formula itself remains the same, $X_{19}\ Y_{13}\ Z_{18}\ T_5\ O_{68}\ W_{10}$, but the *T* constituents must be modified to include Al and Fe [*T* = B, Al, Fe, □], and the *X* constituents must be modified to include □.

Conclusions

1. Some vesuvianite crystals may have an excess of *Y*-group constituents; in such crystals, (Al,Fe) in excess of 13.0 apfu occupies the *T*(1) site, a tetrahedrally coordinated site linked to anions occupying the O(7) and O(11) sites.
2. Excess (Al,Fe) is incorporated into the vesuvianite structure *via* the substitutions

$$^{T(1)}(Al,Fe)^{+} + {}^{H(1)}\square_4 + {}^{X(3)}\square \rightarrow {}^{T(1)}\square_2 + {}^{H(1)}H_4 + {}^{X(3)}Ca$$

$$^{T(1)}(Al,Fe^{3+}) + {}^{H(1)}\square_2 + {}^{Y}(Mg,Fe^{2+}) \rightarrow {}^{T(1)}\square + {}^{H(1)}H_2 + {}^{Y}(Al,Fe^{3+}).$$

Acknowledgements

We thank the Mistress of Minerals, Department of Mineralogy, Royal Ontario Museum, for some of the samples used in this work, F.M. Allen and P.B. Leavens for comments on the manuscript, and the Natural Sciences and Engineering Research Council of Canada for Operating and Equipment Grants to LAG and FCH.

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Received April 28, 1993, revised manuscript accepted November 30, 1993.