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THE INCORPORATION OF BORON INTO THE VESUVIANITE STRUCTURE

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ABSTRACT

Vesuvianite can contain significant amounts of boron (up to ~4 wt% B_2O_3). The crystal structures of five boron-bearing vesuvianite crystals have been refined using Mo$K\alpha$ X-ray data. Although the crystals are significantly biaxial ($2V < 20°$), very careful examination of the diffraction data shows no deviation from $4/mmm$ Laue symmetry. All crystals show many reflections apparently violating the extinction criteria for $P4/nnc$ symmetry, but these are due to double diffraction, not true Bragg diffraction; hence the space group $P4/nnc$ was used for all of the refinements. The structure of all specimens of boron-bearing vesuvianite ($\sim$[Ca,Ln^{3+},Na]$_{19}$[Al,Fe^{3+},Mg,Fe^{2+},Mn,Ti]$_{13+x}$[Si]$_{18-y}$O$_{68}$[O,OH,F]$_{10}$, $x > y$, $Z = 2$, $a \approx 15.70$, $c \approx 11.75$ Å, $V \approx 2895$ Å^3) was refined to an R index in the range 3–4%. Two new sites were identified and are common to all the refined structures; these are designated as T sites. T(1) is at the special position $8h$ (~0.05, ~0.05, ¼), and is surrounded by a disordered array of anions that can adopt a tetrahedral configuration around the central position. T(2) is at the special position $2a$ (¼, ¼, ¼) and is surrounded by an array of disordered anions that can adopt a triangular configuration about the central position. The T(1) position is very close to the H(1) position in boron-free vesuvianite, and the T(2) position is very close to the H(2) position in boron-free vesuvianite; hence occupancy of T(1) and T(2) precludes occupancy of two H(1) and the H(2) positions, in agreement with the substitution $B + Mg \rightleftharpoons 2H + Al$ proposed by Groat *et al.* (1992) for boron-bearing vesuvianite.

Keywords: vesuvianite, crystal structure, boron, electron-microprobe analysis.

SOMMAIRE

La vésuvianite peut contenir des quantités importantes de bore, jusqu'à environ 4% de B_2O_3 en poids. On a affiné la structure cristalline de cinq échantillons de vésuvianite borifère, en utilisant des données de diffraction X obtenues avec rayonnement Mo$K\alpha$. Malgré le fait que les cristaux sont définitivement biaxes ($2V < 20°$), un examen minutieux des données de diffraction n'a décelé aucun écart à la symétrie de Laue $4/mmm$. Tous les cristaux révèlent plusieurs réflexions en violation apparente de la symétrie imposée par le groupe spatial $P4/nnc$, mais celles-ci seraient dues au phénomène de diffraction double, et ne seraient donc pas de vraies réflexions de Bragg. Pour cette raison, nous avons adopté le groupe spatial $P4/nnc$ pour tous les affinements. Toutes ces structures ($\sim$[Ca,Ln^{3+},Na]$_{19}$[Al,Fe^{3+},Mg,Fe^{2+},Mn,Ti]$_{13+x}$[Si]$_{18-y}$O$_{68}$[O,OH,F]$_{10}$, $x > y$, $Z = 2$, $a \approx 15.70$, $c \approx 11.75$ Å, $V \approx 2895$ Å^3) ont été affinées jusqu'à un résidu R de 3 à 4%. Nous identifions deux nouveaux sites, que nous désignons T, dans chacune des structures affinées. Le site T(1) occupe la position spéciale $8h$ (~0.05, ~0.05, ¼), et est entouré par des anions dans un agencement désordonné qui peut être tétraédrique autour de la position centrale. Le site T(2) occupe la position spéciale $2a$ (¼, ¼, ¼), et est entouré par des anions dans un agencement désordonné qui peut être triangulaire autour de la position centrale. La position T(1) est en fait très proche de la position H(1) dans la vésuvianite sans bore; de même, le site T(2) est très proche de la position H(2) dans la vésuvianite sans bore. C'est donc dire que si les positions T(1) et T(2) sont occupées, les positions H(1) et H(2) ne pourraient l'être, ce qui concorde avec le schéma de substitution $B + Mg \rightleftharpoons 2H + Al$, qu'avaient proposé Groat *et al.* (1992) pour expliquer la présence du bore dans ce minéral.

(Traduit par la Rédaction)

Mots-clés: vésuvianite, structure cristalline, bore, analyse à la microsonde électronique.

INTRODUCTION

Vesuvianite is a rock-forming or accessory silicate mineral found in skarns, rodingites and altered alkali syenites. It is one of the the least understood of the common minerals, with significant uncertainties concerning its structure, optical properties and chemical composition. The structure of vesuvianite from Wilui, former U.S.S.R., was solved by Warren & Modell (1931); on the basis of their structure, they proposed the formula $Ca_{20}(Mg,Fe)_4Al_8Si_{18}O_{68}(OH)_8$. Various modifications of this formula were proposed in the ensuing forty years. Coda *et al.* (1970) refined the structure of a vesuvianite from Bric Camula, Italy; they confirmed the general validity of the previous structural model, but also discovered an additional anion, an (OH) group in the prominent channels that run through the structure. These details were confirmed in vesuvianite from other localities (Rucklidge *et al.* 1975), and further structural work began to focus on the details of cation ordering in the channels, a feature that is intimately linked to the true symmetry of the material examined. Arem & Burnham (1969) have shown that vesuvianite from some localities have diffractions that violate various glide-plane extinction criteria for the (ideal) space group *P4/nnc*. This problem was addressed by Giuseppetti & Mazzi (1983), who refined the structure of vesuvianite from Val d'Ala, Italy, in the space group *P4/n*. Subsequent refinements of both *P4/nnc* and *P4/n* vesuvianite crystals by Allen (1985), Allen & Burnham (1983a, b), Valley *et al.* (1985), Yoshiasa & Matsumoto (1986), Fitzgerald (1985) and Fitzgerald *et al.* (1986a, b) confirmed these previous models, and provided further details of possible domain models in these structures. Detailed examinations of this specific aspect of vesuvianite are provided by Allen & Burnham (1992) and Groat *et al.* (1993).

In an investigation of vesuvianite from a wide variety of locations around the world (Groat 1988, Groat *et al.* 1992a), we confirmed that boron could be a major constituent in vesuvianite. The detailed chemical results (Groat *et al.* 1992a) indicate that the $[BO_4] \rightleftharpoons [SiO_4]$ isomorphism proposed by Belinskii (1984) is not the principal mechanism of incorporation of boron in vesuvianite. The amounts of boron found are quite large, and must have significant effects on the bulk chemistry and thermal stability of the mineral. In addition, vesuvianite can be a sink for boron in those environments in which it occurs, and hence may play a role in the boron cycle. However, the details of the boron substitution can only be fully understood if complete information on the local mechanism(s) of boron incorporation is known, together with the structural response to local bond-valence requirements. A detailed structural study of crystals of boron-bearing vesuvianite characterized by Groat *et al.* (1992a) was thus undertaken.

PREVIOUS WORK

The topic of boron content of vesuvianite has not been dealt with before in any general way. Hence it seems worthwhile to provide a fairly complete review of previous work, as the fact that vesuvianite can be a potential sink for boron is not generally recognized. Jannasch (1884) analyzed vesuvianite from Wilui, former U.S.S.R., and recorded 2.81 wt% B_2O_3. Rammelsberg (1886) reported 2.54 wt% B_2O_3 in material from Wilui, but no detectable boron in other samples. Widman (1890) reported the composition of two vesuvianite samples from Norway: vesuvianite from Arendal has 1.96 wt% B_2O_3, whereas vesuvianite from Eker has no detectable boron. Thus from the latter two studies, it became apparent that boron is not an essential constituent of vesuvianite. Jannasch & Weingarten (1896) reported compositions for two more vesuvianite samples from Wilui, with 2.84 and 2.39 wt% B_2O_3, respectively. Wherry & Chapin (1908) presented boron determinations for 25 samples of vesuvianite, with up to 4.1 wt% B_2O_3; however, the high value was obtained on Wilui material, for which Jannasch (1884) and Rammelsberg (1886) had previously obtained 2.81 and 2.54 wt% B_2O_3, respectively. Consequently, the results of Wherry & Chapin (1908) should be viewed with caution, particularly as our own results on Wilui material agree closely with the values of Jannasch (1884) and Rammelsberg (1886). Further chemical work (Lacroix & de Gramont 1921, Shannon 1922, Glass *et al.* 1944, Myasnikov 1940, Wickman 1950) show boron to be either a trace or a minor (<1.0 wt% B_2O_3) component in most vesuvianite samples.

Oftedal (1964) reviewed the occurrence of vesuvianite from "contact deposits" in the Oslo region, Norway, showed that B_2O_3 attained 2.5 wt%, and also found that high-boron vesuvianite is slightly biaxial and optically positive. Henriques (1964) recorded minor boron (0.28 wt% B_2O_3) in vesuvianite from a leptite, together with optical properties and unit-cell dimensions. Timofeeva (1962) described optically positive vesuvianite with 2.34 wt% B_2O_3 and some biaxial character. Khotina (1968) reported sector-zoned vesuvianite with 1.22 and 1.10 wt% B_2O_3 in the core and rim zones, respectively, from a skarn associated with the Talnakh intrusion. Serdyuchenko *et al.* (1968) and Mel'nitsky (1966) reported up to ~4.0 wt% B_2O_3 in vesuvianite. Belinskii (1984) reviewed the occurrence of boron in skarn minerals, and proposed that $[BO_4] \rightleftharpoons [SiO_4]$ isomorphism occurs in vesuvianite.

Figure 1 shows a histogram of available data; they fall more or less continuously in the range 0–4.5 wt% B_2O_3, suggesting a continuous solid-solution. However, the boron contents of vesuvianite crystals from a single locality can show considerable variation, and it is possible that samples for bulk-chemical

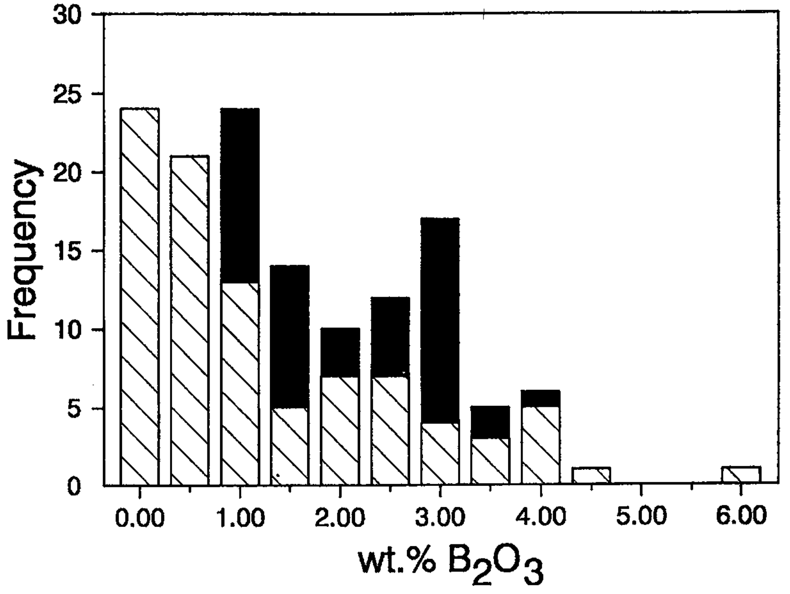

FIG. 1. Histogram of boron content in vesuvianite; literature values (bulk analyses) are cross-hatched, electron-microprobe values (Groat *et al.* 1992a, this study) are shown in black.

analysis included both boron-bearing and boron-free material. Consequently, a wider dispersion of electron-microprobe values is needed before continuous solid-solution can be considered as established.

Most boron-bearing vesuvianite occurs in skarns, although we cannot be definite about the provenance of some of the material for which analytical data are given above. Boron-rich vesuvianite seems to be optically positive, whereas boron-free vesuvianite is optically negative (Deer *et al.* 1982). In a detailed chemical study, Groat *et al.* (1992a) showed that boron is incorporated into the vesuvianite structure primarily *via* the substitution $B + Mg \rightleftharpoons 2H + Al$, with other possible substitutions being of lesser importance. However, the detailed local mechanism needs structural characterization, and this is done here.

EXPERIMENTAL

Chemical analysis

Sample numbers and localities are listed in Table 1. Subsequent to the diffraction experiments, the crystals were detached from their glass fibers, mounted in Crystalbond, ground, polished and carbon-coated. Electron-microprobe analysis was done on a JEOL 733 instrument equipped with an energy-dispersion spectrometer and four automated wavelength-dispersion spectrometers fitted with crystals that allow analysis down to $Z = 5$ (boron). Full details are given in Groat *et al.* (1992a), together with the methods used for Li, Be, Fe^{3+}/Fe^{2+}, H_2O and CO_2 determinations, which were taken from analyses of bulk material by Groat *et al.* (1992a). Results of chemical analyses are given in Table 2.

Optical properties

Oriented sections were cut for optical examination. Values of $2V$ were measured by the method of Tobi (Bloss 1962), and in some cases, checked with spindle-stage measurements reduced with the program EXCALIBR (Bloss 1981); values are less than or equal to 5° in all cases.

X-ray diffraction

For the Wilui vesuvianite, oriented doubly polished sections up to 500 μm thick were examined in plane-polarized and cross-polarized light, and the variation in $2V$ was mapped across the crystals. A section was then fractured "in place", and a fragment of vesu-

TABLE 1. LOCALITIES AND SAMPLE NUMBERS, BORON-BEARING VESUVIANITE

Sample	B (apfu)	Locality (Royal Ontario Museum sample number)
V62	1.24	Tulare Co., California, U.S.A.
V44	1.26	Laguna del Jaco, Chihuahua, Mexico
V38	1.55	Arricia, Italy (M19263)
V75	2.42	Wilui River, Yakutskaya, Russia
V29	2.60	Templeton Twp., Ottawa Co., Quebec (E2207)

TABLE 2. AVERAGE CHEMICAL COMPOSITION OF BORON-BEARING VESUVIANITE CRYSTALS[†]

	V62	V44	V38	V75	V29
SiO_2	35.85	36.38	35.05	36.04	34.83
Al_2O_3	12.64	14.79	11.39	11.74	11.31
TiO_2	0.56	0.78	0.85	0.90	0.94
MgO	4.88	5.10	5.17	6.57	4.74
MnO	0.10	0.03	0.19	0.02	0.25
FeO	1.21	2.09	5.08	1.23	5.32
Fe_2O_3	4.04	–	–	2.32	–
CaO	35.33	35.86	34.26	35.66	33.11
Na_2O	0.10	0.01	0.01	0.00	0.01
Ln_2O_3	0.00	0.25	2.12	0.31	3.16
B_2O_3	1.44	1.47	1.77	2.83	2.90
SO_3	0.00	0.30	0.03	0.16	0.03
F	0.35	0.72	0.67	0.08	0.75
Cl	0.06	0.00	0.00	0.00	0.00
H_2O*	1.41	–	–	0.61	–
H_2O**	1.62	1.36	2.02	1.04	0.50
	97.97	99.14	98.61	98.47	97.86
O=F,Cl	0.16	0.30	0.28	0.03	0.32
TOTAL	97.81	98.84	98.33	98.44	97.54
Si^{4+}	17.90	17.94	17.76	17.87	18.06
Al^{3+}	7.44	8.60	6.80	6.86	6.91
Ti^{4+}	0.21	0.29	0.32	0.34	0.37
Mg^{2+}	3.63	3.75	3.90	4.86	3.66
Mn^{2+}	0.04	0.01	0.08	0.01	0.11
Fe^{2+}	0.51	0.86	2.15	0.51	2.31
Fe^{3+}	1.52	–	–	0.87	–
Ca^{2+}	18.90	18.95	18.60	18.94	18.39
Na^+	0.10	0.01	0.01	0.00	0.01
Ln^{3+}	0.00	0.04	0.39	0.06	0.60
B^{3+}	1.24	1.25	1.55	2.42	2.60
S^{6+}	0.00	0.11	0.01	0.06	0.01
F^-	0.55	1.12	1.07	0.13	1.23
Cl^-	0.05	0.00	0.00	0.00	0.00
OH^-	4.70	4.48	6.82	2.02	1.74
ΣX	19.00	19.00	19.00	19.00	19.00
ΣY	13.35	13.51	13.26	13.45	13.36
ΣZ	17.90	17.94	17.76	17.87	18.06

[†] Analyses are normalized on 19 X cations. * Measured. ** Calculated. Additional components (wt.%): V38: La_2O_3 0.76, Ce_2O_3 1.08, Pr_2O_3 0.09, Nd_2O_3 0.13, Gd_2O_3 0.06.

vianite was removed; in this way, we could ensure that the crystal used for the data collection did not contain included phases or fractures along which alteration could have taken place. In addition, we had a 2*V* measurement at the exact location of the fragment. This fragment was ground to a sphere in a crystal grinder to minimize possible errors due to differential absorption in the absorption correction.

X-ray precession photographs were taken for this crystal with Mo*K*α radiation. A full set of photographs was recorded for two different precession angles (25° and 30°) to identify any double-diffraction (Renninger) effects.

The crystal was then mounted on a Nicolet *R*3*m* automated four-circle diffractometer. A random-orientation photograph was taken, and 25 reflections were selected for centering. The correct unit-cell was chosen from an array of real-space vectors corresponding to potential unit-cell axes, and least-squares refinement produced the cell dimensions given in Table 3, together with the orientation matrix relating the crystal axes to the diffractometer axes.

Intensity data were collected in the θ–2θ scan mode using 96 steps with a scan range from [2θ(Mo$K\alpha_1$) – 1]° – [2θ(Mo$K\alpha_2$) + 1]° and a variable scan-rate between 3.91 and 29.3°/min depending on the intensity of an initial one-second count at the center of the scan range. Backgrounds were measured at the beginning and end of each scan for half the total scan-time. Two standard reflections were monitored every 48 reflections to check for stability and constancy of crystal alignment; no significant fluctuations were noted during data collection. A total of 18 417 reflections were measured over one hemisphere out to a maximum 2θ value of 60°. Ten strong reflections uniformly distributed with regard to 2θ were measured at 10° intervals of psi (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector) from 0 to 355°. These data were used to calculate an empirical absorption correction, modeling the (virtually spherical) crystal as a triaxial ellipsoid; *R*(azimuthal) = 1.2%. This correction was then applied to the whole data-set, which was also corrected for Lorentz, polarization and background effects, and then reduced to structure factors. Miscellaneous details relating to data reduction and refinement are given in Table 3.

As will become apparent in the discussion, the Wilui vesuvianite does not depart significantly from tetragonal symmetry (unlike many samples of boron-free vesuvianite). Preliminary work on crystals of the other samples of boron-bearing vesuvianite indicated that these also adhere closely to tetragonal symmetry, and, except for V44, only an octant of data was collected for the other samples. Otherwise, the experimental techniques were the same as for the Wilui sample; miscellaneous information is listed in Table 3.

TABLE 3. MISCELLANEOUS DATA COLLECTION AND REFINEMENT INFORMATION FOR BORON-BEARING VESUVIANITE CRYSTALS

	V62	V44	V38	V75	V29
B (apfu)	1.24	1.25	1.55	2.42	2.60
a(Å)	15.691(2)	15.656(2)	15.710(1)	15.747(1)	15.745(2)
c(Å)	11.756(3)	11.756(2)	11.719(2)	11.709(2)	11.728(2)
V(Å^3)	2894.6(9)	2881.5(8)	2892.2(6)	2903.5(8)	2907.4(8)
Space group	*P*4/*nnc*	*P*4/*nnc*	*P*4/*nnc*	*P*4/*nnc*	*P*4/*nnc*
Radiation	Mo*K*α	Mo*K*α	Mo*K*α	Mo*K*α	Mo*K*α
Monochromator	Graphite	Graphite	Graphite	Graphite	Graphite
Total no. |*F*|	4951	18461	4729	18417	4763
No. of |*F*| obs	1895	2059	1967	2089	1890
R (anis) %	3.6	3.2	5.7	4.0	3.4
wR (anis) %	3.1	3.1	6.3	2.8	3.4

Structural Symmetry

The crucial aspect of a refinement of vesuvianite is to choose the correct (or, perhaps, most appropriate) space-group. Consequently, this matter was examined in considerable detail, particularly for the Wilui sample. There are two points of importance: (a) is the crystal tetragonal? (b) what is the space group?

Crystal system

Three pieces of information pertain to this problem: (1) Thick polished (001) sections of single crystals are very slightly biaxial, with $2V$ between 0 and 5°. Thus the crystals are not tetragonal. However, the deviation from uniaxial optics is small (particularly compared to what is observed in some crystals of boron-free vesuvianite), suggesting that the structural deviations from tetragonal symmetry are likewise small. (2) Precession photographs were examined closely for deviation from tetragonal Laue symmetry; none was observed. (3) Single-crystal X-ray intensity data were collected from a hemisphere of reciprocal space so that the intensity variation of individual reflections equivalent in the tetragonal system could be examined. No significant variations were detected. In particular, Allen (1985) has reported that a prominently non-tetragonal vesuvianite from Eden Mills, New York, shows unequal intensity for the {346} set of reflections, which are equivalent in the space group *P*4/*nnc*. Table 4 shows intensities for this set of reflections for V75 and for V12, a strongly non-tetragonal boron-free vesuvianite with $2V$ = 68° (Groat *et al.*, in prep.). There is significant variation of intensity for the V12 set of reflections; in particular, reflections related by vertical mirror planes are nonequivalent, whereas reflections related by a mirror plane perpendicular to Z, or by a 90° rotation around Z, have the same intensity. On the other hand, the analogous intensities for V75 are the same (within two standard deviations). Thus the intensity variation of {346} for V75 is conformable with 4/*mmm* Laue symmetry. Similar results were obtained for the other crystals.

TABLE 4. INTENSITIES (CPS X 10^{-3}) FOR 346 AND EQUIVALENT REFLECTIONS (*P4/nnc*) FOR VESUVIANITE CRYSTALS V75 AND V12

hkl	V75 (core)	*V12 (rim)
$\bar{4}$ 3 $\bar{6}$	215(3)	290(3)
$\bar{4}$ 3 6	217(3)	293(3)
$\bar{3}$ 4 $\bar{6}$	214(3)	263(3)
$\bar{3}$ 4 6	219(3)	257(3)
3 4 $\bar{6}$	211(3)	298(3)
3 4 6	215(3)	299(3)
4 3 $\bar{6}$	216(3)	260(3)
4 3 6	213(3)	264(3)

* Groat (1988)

To summarize, although there is a slight deviation from tetragonal symmetry shown by the optical data, *there is no information in the X-ray intensity data pertaining to any structural deviation from tetragonal symmetry.*

Space group

There are two sets of information that pertain to this question: (1) Precession photographs were examined very carefully for possible Laue-group symmetries. In all cases, the Laue-group symmetry found was 4/*mmm*. The photographs also were examined for reflections that violate the numerous glide planes of the ideal space-group *P*4/*nnc*. Several reflections were found that apparently violate glide planes in this space group. However, on photographs taken with different diffraction conditions (*i.e.*, different precession angles), the "violating" reflections observed on the other photographs are absent, and a new set of "violating" reflections are present. Thus the reflections apparently not conforming to the extinction conditions of *P*4/*nnc* are due to double diffraction, and the precession-camera data are consistent with *P*4/*nnc* space-group symmetry. We should stress that this is the case for boron-bearing vesuvianite; for boron-free vesuvianite, similar experiments show the validity of some of the violating reflections for these crystals. (2) In the X-ray intensity data-set, similar apparently glide-violating reflections were observed. For several of these reflections, psi-scan data were collected. In this mode, the intensity of a specific reflection is measured repeatedly with the crystal rotated around its diffraction vector. For this specific reflection, the conditions for normal Bragg diffraction remain unchanged, and thus a real (Bragg) reflection retains its intensity whatever the value of psi. Conversely, the conditions for double diffraction are altered with rotation around psi, and as the other angles are held constant, a double diffraction cannot retain its intensity at all values of psi. The psi-scan data collected show that all apparent glide-violating reflections are actually double-diffraction effects, except perhaps for the reflection (111), for which $F/\sigma F$ is greater than 4.0. Thus except for this one reflection, the single-crystal intensity data are consistent with the space group *P*4/*nnc*.

The X-ray data seem compatible with the space group *P*4/*nnc*, and this symmetry was adopted for the structure refinements. The optical data do indicate a slight deviation from tetragonal symmetry, but the evidence discussed above indicates that the X-ray intensity data contain no significant information on this departure from tetragonal symmetry.

STRUCTURE REFINEMENT

All calculations were done with the SHELXTL system of programs (Nicolet Corporation 1983). *R* indices are of the usual form, with statistical weights for w*R*. All scattering factors are for ionized atoms with anomalous dispersion corrections. The site nomenclature used is that of Groat *et al.* (1992a), except that their OH site is now designated O(11). The refinement of these structures was quite difficult because of the extensive disorder involving both cations and anions, and took several years to finalize. The steps will be described in some detail here, as the important stereochemical aspects of the problem are contained in the fine detail of the refinements and their interpretation. We will use V75 as the type example.

V75

The input coordinates used were taken from Yoshiasa & Matsumoto (1986), modified as much as was possible for the known differences in composition. Full-matrix least-squares refinement for an isotropic-displacement model converged to an *R* index of 10.4%. At this stage, there were a number of discrepancies between the model and the data, most of which involved the channels in the structure. Figure 2 shows difference-Fourier maps of the channel in boron-free (left) and boron-bearing (right) vesuvianite, in both cases with all of the channel cations removed from the structural models. Several differences are immediately apparent, some of which also gave rise to anomalies in the initial refinement: (1) In boron-bearing vesuvianite, the electron density at the O(10) position is less than that at the same position in boron-free vesuvianite. This is in line with the fact that the displacement factor for O(10) is extremely large (U = 0.19), indicating much less scattering power than formally assigned to this position. To deal with this problem, the displacement factor was fixed at a value approximately equal to the values of the other anions in the structure (U = 0.015), and the occupancy was considered as variable. (2) The difference-Fourier maps showed the presence of significant unassigned density at or near the special position: ¼, ¼, ¼ (position 2*a*). This is absent in the boron-free vesuvianite. This position was assigned to oxygen (as a general scattering species only, without any current chemical

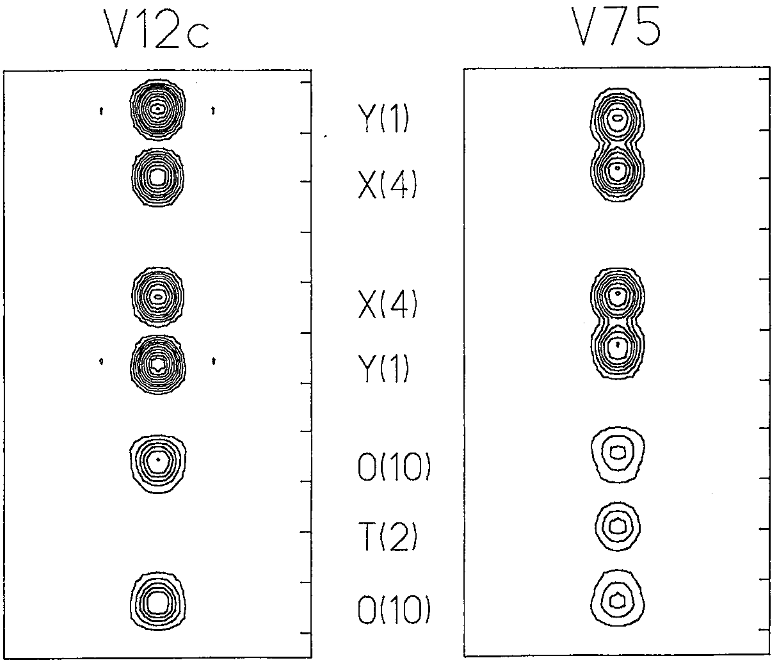

FIG. 2. Difference-Fourier maps of the channel in vesuvianite crystals, omitting the channel atoms from the calculation; *c* axis vertical, *a* axis horizontal: (a) boron-free vesuvianite V12; (b) boron-bearing vesuvianite V75. The letter *c* indicates that the crystal used to collect the X-ray intensity data was taken from the core of a large crystal. Contour intervals are 3 e/Å^3; the vertical scale denotes 1 Å intervals.

significance), the isotropic displacement-factor was fixed at $U = 0.015$, and the occupancy was considered as variable. (3) It is also notable that the *Y*(1) and *X*(4) sites down the channel have moved much closer together.

Other difference-Fourier maps showed more unassigned density at 0.05, 0.05, ¼ (position 8*h*). This was also initially assigned as oxygen with a fixed isotropic displacement-factor and a variable occupancy.

Full-matrix least-squares refinement of this model converged to an *R* index of 6.5%. Conversion of the displacement factors to an anisotropic form followed by least-squares refinement converged at an *R* index of 5.1%. The O(7) anion was extremely anisotropic at this stage, and a more reasonable physical model would involve positional disorder rather than such extreme vibrational displacement. Splitting this site into two half-occupied sites refined to a stable arrangement with a half-atom separation of ~0.5 Å and an *R* index of 5.1%. At this point, difference-Fourier maps showed more unassigned density at 0.18, 0.23, 0.30 (position 16*k*). Again, oxygen was assigned to this site with a fixed isotropic displacement factor and variable occupancy, and full-matrix refinement of all variables led to convergence at an *R* index of 4.4%. At this stage, bond lengths and angles were calculated in order to help in the interpretation of the unassigned scattering power (presently represented by oxygen) in the structural model.

The following points are of significance: (1) The density at the new 16*k* position is at ~2.2 Å from *X*(3); as *X*(3) is completely occupied by large *X*-type cations, the 16*k* position *must* be occupied by an anion; the scattering species was assigned as oxygen, the position was designated as O(12), the isotropic displacement factor was fixed at 0.012, and the occupancy was considered as variable. (2) The new 8*h* position is surrounded by a tetrahedral arrangement of anions; consequently, this must be a cation. The scattering species was assigned as boron, and the position was named *T*(1); the isotropic displacement parameter was fixed at 0.010, and the occupancy was considered as variable. (3) The density at the new 2*a* position is ~1.7 Å from the half-occupied O(10) position and ~1.32 Å from the partly occupied O(12) position. Although it is not definite that the occupancy of the 2*a* position is locally coupled to the occupancies of O(10) and O(12), this was provisionally assumed in the assignment of the scattering species at this stage; the scattering species was set as boron, the isotropic displacement factor was fixed at 0.010, the occupancy was considered as variable, and the site was designated *T*(2). The *Y*(1) and O(10) positions also showed significant displacement anisotropy at this stage, and were split into pairs of sites, *Y*(1*A*), *Y*(1*B*) and O(10*A*), O(10*B*), with equal occupancies for both sites of a pair.

Full-matrix refinement of all variables with anisotropic displacement factors on all positions except *Y*(1*A*), *Y*(1*B*), O(10*A*), O(10*B*), O(12), *T*(1) and *T*(2) (for which the site occupancies were variable) converged to an *R* index of 3.7%. The O(11) position showed significant displacement anisotropy at this stage, and was split into two half-occupied sites, O(11*A*) and O(11*B*), which refined to different positions with a separation of ~0.20 Å. The decision to assign equal occupancies to O(7*A*), O(7*B*), O(11*A*) and O(11*B*) was arbitrary, as there is no need for the split sites to be equally occupied. Consequently, the occupancies of each pair of sites was separately refined with the constraint that the sum of the occupancies of each pair was unity. Both sets of occupancies were equal to 0.5, within rather large standard deviations (0.07); however, this turned out not to be the case for the structures of some of the other crystals of boron-bearing vesuvianite.

For the *T*(1), *T*(2) and O(12) sites, the site occupancies were refined while the isotropic displacement factors were fixed. The rationale behind doing this is to remove correlation between these two parameters during the least-squares process (*i.e.*, if we set the isotropic displacement factor to its correct value, then the site occupancy will refine to its correct value). Normally, such correlations are not a problem. However, for very low occupancies combined with local positional disorder, fixing the displacement factor is in some cases necessary. Of course, one must fix the isotropic displacement factor at the correct value, or error is introduced in the refinement. Refinement of ordered crystal-structures gives us typical displacement factors for specific atoms in a particular coordination number. Thus we do not expect the isotropic displacement factors to be all that different from the values we have used here. To get an idea of the possible errors in site occupancies induced by errors in the displacement factors used, we repeated the refinements using isotropic displacement factors changed by ±0.003 relative to the values used initially. The resultant site-occupancies changed by less than one standard deviation at *T*(2) and O(10), and by less than two standard deviations at *T*(1). These changes are not large enough to materially affect the process of assignment of chemical site-occupancies or discussions of local stereochemistry.

Although the *scattering* model for the refinement was good at this stage, there were problems with the chemical interpretation of the results. We had initially thought that the *T*(1) and *T*(2) positions would contain the boron. This may be the case, but the refined scattering power was approximately twice the scattering power corresponding to the amount of boron indicated by chemical analysis. Consequently, it was apparent that a more complex process was involved, and we examined all the other samples of boron-bearing vesuvianite characterized by Groat *et al.* (1992a).

V30, V38, V45, V61

The final model for V75 was used as input to the refinement process of the other samples of boron-bearing vesuvianite. The refinements converged rapidly to *R* indices between 3.5 and 4.0% for an anisotropic displacement model (except for the "split" atoms, for which isotropic displacement factors were used). The "excess occupancy" problem found for V75 persisted in these other crystals, indicating that other species in addition to boron must be involved in the scattering from the *T*(1) and *T*(2) sites. However, resolution of this problem cannot result from site-occupancy refinement alone; a detailed consideration of the chemistry and stereochemistry is necessary. The final parameters for all crystals of boron-bearing vesuvianite are given in Table 5; observed and calculated structure-factors may be obtained from the Depository for Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. Selected interatomic distances are given in Table 6. Refined scattering powers at selected sites are given in Tables 7 and 8. All parameters were calculated from the final chemical models in each case, but do not differ significantly from the initial scattering models from which the chemical models were derived. Bond-

TABLE 5. ATOMIC PARAMETERS FOR BORON-BEARING VESUVIANITE STRUCTURES

		V62	V44	V38	V75	V29
B (apfu)		1.24	1.25	1.55	2.42	2.60
Z(1)	*x*	3/4	3/4	3/4	3/4	3/4
	y	1/4	1/4	1/4	1/4	1/4
	z	0	0	0	0	0
	*U_{eq}	70(3)	76(2)	100(6)	97(3)	105(4)
Z(2)	*x*	−0.18062(5)	−0.17968(3)	−0.1794(1)	−0.17816(5)	−0.17847(6)
	y	0.04141(4)	0.04238(3)	0.0422(1)	0.04379(5)	0.04255(7)
	z	0.87162(6)	0.87159(4)	0.8718(1)	0.87260(7)	0.87180(9)
	U_{eq}	71(2)	91(1)	130(4)	131(2)	122(3)
Z(3)	*x*	−0.08362(5)	−0.08379(3)	−0.0839(1)	−0.08404(5)	−0.08371(6)
	y	−0.15049(5)	−0.15036(4)	−0.1503(1)	−0.15008(5)	−0.15004(6)
	z	0.36441(6)	0.36485(4)	0.3644(1)	0.36489(6)	0.36460(8)
	U_{eq}	83(2)	93(1)	115(4)	104(2)	108(3)
X(1)	*x*	3/4	3/4	3/4	3/4	3/4
	y	1/4	1/4	1/4	1/4	1/4
	z	1/4	1/4	1/4	1/4	1/4
	U_{eq}	96(3)	92(2)	125(6)	114(3)	119(4)
X(2)	*x*	−0.18927(3)	−0.18973(2)	−0.18978(7)	−0.19067(3)	−0.19059(5)
	y	0.04480(3)	0.04522(3)	0.04518(7)	0.04540(3)	0.04500(5)
	z	0.37931(4)	0.37934(3)	0.3794(1)	0.37982(5)	0.37991(6)
	U_{eq}	89(1)	100(1)	131(3)	119(1)	124(2)
X(3)	*x*	−0.10109(4)	−0.10023(3)	−0.10001(6)	−0.10129(4)	−0.10144(5)
	y	−0.18163(4)	−0.17960(3)	−0.17834(6)	−0.17952(4)	−0.17932(5)
	z	0.89038(6)	0.89275(4)	0.89018(9)	0.89717(5)	0.89660(7)
	U_{eq}	211(2)	186(1)	60(3)	180(2)	200(2)
X(4)	*x*	3/4	3/4	3/4	3/4	3/4
	y	3/4	3/4	3/4	3/4	3/4
	z	0.1487(2)	0.1447(1)	0.1421(4)	0.1428(2)	0.1429(3)
	U_{eq}	94(5)	100(3)	117(12)	101(6)	146(8)
Y(1*A*)	*x*	3/4	3/4	3/4	3/4	3/4
	y	3/4	3/4	3/4	3/4	3/4
	z	0.0492(4)	0.0635(3)	0.0680(8)	0.0684(6)	0.0688(6)
	U_{eq}	66(7)	78(6)	101(14)	77(9)	115(8)
Y(1*B*)	*x*	3/4	3/4	3/4	3/4	3/4
	y	3/4	3/4	3/4	3/4	3/4
	z	0.0267(4)	0.0337(2)	0.0417(7)	0.0443(5)	0.0476(6)
	U_{eq}	66(7)	78(6)	101(14)	77(9)	115(8)
Y(2)	*x*	0	0	0	0	0
	y	0	0	0	0	0
	z	0	0	0	0	0
	U_{eq}	72(3)	89(2)	93(6)	92(3)	86(4)
Y(3)	*x*	−0.11230(5)	−0.11217(4)	−0.11188(9)	−0.11142(5)	−0.11146(5)
	y	0.12117(5)	0.12058(4)	0.12043(9)	0.12016(5)	0.12034(5)
	z	0.12587(6)	0.12644(4)	0.1275(1)	0.12809(7)	0.12787(8)
	U_{eq}	65(2)	92(2)	85(4)	89(2)	98(3)
T(1)	*x*	0.0556(3)	0.0545(2)	0.051(1)	0.0538(2)	0.0527(3)
	y	0.0556(3)	0.0545(2)	0.051(1)	0.0538(2)	0.0527(3)
	z	1/4	1/4	1/4	1/4	1/4
	**U_{eq}	100	100	100	100	100
T(2)	*x*	1/4	1/4	1/4	1/4	1/4
	y	1/4	1/4	1/4	1/4	1/4
	z	1/4	1/4	1/4	1/4	1/4
	**U_{eq}	100	100	100	100	100
O(1)	*x*	−0.2205(1)	−0.22023(9)	−0.2209(3)	−0.2198(1)	−0.2199(2)
	y	0.1731(1)	0.17274(9)	0.1727(3)	0.1728(1)	0.1726(2)
	z	0.0853(2)	0.08468(9)	0.0846(3)	0.0844(2)	0.0844(2)
	U_{eq}	95(5)	111(3)	138(11)	125(5)	137(7)
O(2)	*x*	−0.1177(1)	−0.11921(9)	−0.1198(3)	−0.1209(1)	−0.1208(2)
	y	0.1602(1)	0.16018(9)	0.1603(3)	0.1611(1)	0.1607(2)
	z	0.2797(2)	0.2809(1)	0.2815(4)	0.2832(2)	0.2834(2)
	U_{eq}	101(5)	129(4)	170(12)	157(6)	165(8)
O(3)	*x*	−0.0471(1)	−0.04490(9)	−0.0452(3)	−0.0419(1)	−0.0418(2)
	y	0.2228(1)	0.22364(9)	0.2240(3)	0.2256(1)	0.2254(2)
	z	0.0753(2)	0.07690(9)	0.0765(4)	0.0783(2)	0.0776(2)
	U_{eq}	87(5)	125(4)	178(12)	156(6)	162(8)
O(4)	*x*	−0.0614(1)	−0.06134(9)	−0.0612(3)	−0.0615(1)	−0.0618(2)
	y	0.1058(1)	0.10509(9)	0.1055(3)	0.1045(1)	0.1042(2)
	z	0.4696(2)	0.4703(1)	0.4704(4)	0.4713(2)	0.4712(2)
	U_{eq}	93(5)	110(3)	141(12)	131(6)	136(7)
O(5)	*x*	−0.1711(1)	−0.17143(9)	−0.1713(3)	−0.1716(1)	−0.1717(2)
	y	0.0135(1)	0.01262(9)	0.0123(3)	0.0109(1)	0.0113(2)
	z	0.1784(2)	0.1788(1)	0.1797(4)	0.1798(2)	0.1795(2)
	U_{eq}	122(5)	136(4)	175(12)	138(6)	143(7)
O(6)	*x*	0.8793(1)	−0.8784(1)	−0.8788(3)	0.8782(1)	0.8791(2)
	y	−0.2732(1)	−0.2751(1)	−0.2747(3)	−0.2771(1)	−0.2766(2)
	z	0.0586(2)	0.0554(1)	0.0544(4)	0.0526(2)	0.0540(2)
	U_{eq}	159(6)	174(4)	198(13)	166(6)	179(8)
O(7*A*)	*x*	0.0559(3)	0.0555(2)	0.0557(4)	0.0554(4)	0.0559(5)
	y	0.1751(7)	0.1744(2)	0.1754(6)	0.1743(5)	0.1778(7)
	z	0.3216(3)	0.3208(2)	0.3199(6)	0.3180(4)	0.3206(6)
	U_{eq}	113(6)	121(4)	185(13)	163(7)	186(9)
O(7*B*)	*x*	0.052(1)	0.0458(4)	0.044(1)	0.0430(3)	0.0459(4)
	y	0.160(4)	0.1479(5)	0.146(2)	0.1462(4)	0.1485(6)
	z	0.318(2)	0.3070(4)	0.304(2)	0.3072(4)	0.3078(6)
	U_{eq}	113(6)	121(4)	185(13)	163(7)	186(9)
O(8)	*x*	−0.0607(1)	−0.06035(9)	−0.0603(3)	−0.0601(1)	−0.0606(2)
	y	−0.0914(1)	−0.09166(9)	−0.0927(3)	−0.0923(1)	−0.0920(2)
	z	0.0674(2)	0.06689(9)	0.0669(4)	0.0667(2)	0.0673(2)
	U_{eq}	94(5)	110(3)	139(11)	122(5)	129(7)
O(9)	*x*	−0.1450(1)	−0.14560(9)	−0.1455(3)	−0.1466(1)	-0.1462(2)
	y	−0.1450(1)	−0.14560(9)	−0.1455(3)	−0.1466(1)	-0.1462(2)
	z	1/4	1/4	1/4	1/4	1/4
	U_{eq}	120(5)	132(3)	154(11)	145(6)	155(8)
O(10*A*)	*x*	3/4	3/4	3/4	3/4	3/4
	y	3/4	3/4	3/4	3/4	3/4
	z	0.856(1)	0.8564(8)	0.855(4)	0.869(8)	0.865(2)
	U_{eq}	130(16)	147(15)	310(55)	298(35)	625(52)
O(10*B*)	*x*	3/4	3/4	3/4	3/4	3/4
	y	3/4	3/4	3/4	3/4	3/4
	z	0.876(1)	0.8779(8)	0.873(4)	0.865(8)	0.860(2)
	U_{eq}	130(16)	147(15)	310(55)	298(35)	625(52)
O(11*A*)	*x*	−0.0046(3)	−0.0035(2)	−0.0029(5)	−0.0038(4)	−0.0031(6)
	y	0.0636(5)	0.0628(2)	0.0626(5)	0.0619(4)	0.0629(6)
	z	0.1341(4)	0.1338(2)	0.1351(7)	0.1367(6)	0.1360(8)
	U_{eq}	83(5)	94(4)	114(11)	131(6)	149(8)
O(11*B*)	*x*	−0.002(2)	−0.0027(4)	−0.003(1)	−0.0002(4)	−0.0000(6)
	y	0.055(3)	0.0534(4)	0.053(1)	0.0548(4)	0.0536(6)
	z	0.141(2)	0.1512(5)	0.157(2)	0.1557(5)	0.1535(7)
	U_{eq}	83(5)	94(4)	114(11)	131(6)	149(8)
O(12)	*x*	0.19(2)	0.181(1)	0.180(3)	0.1764(8)	0.174(1)
	y	0.28(2)	0.273(1)	0.271(3)	0.2718(8)	0.2749(9)
	z	0.21(2)	0.204(1)	0.206(3)	0.204(1)	0.205(1)
	**U_{eq}	120	120	120	120	120

* $U_{eq} = U_{eq} \times 10^4$ (Å^2)   ** fixed during refinement

TABLE 6. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN BORON-BEARING VESUVIANITE

		V62	V44	V38	V75	V29
B (apfu)		1.24	1.25	1.55	2.42	2.60
Z(1)–O(1)a	x4	1.636(2)	1.634(1)	1.635(4)	1.638(2)	1.640(3)
<*Z*(1)–O(1)>		1.636	1.634	1.635	1.638	1.640
O(1)a–*Z*(1)–O(1)s	x4	112.1(1)	111.8(1)	111.7(1)	111.4(1)	111.4(1)
O(1)a–*Z*(1)–O(1)n	x2	104.4(1)	105.0(1)	105.0(3)	105.8(1)	105.7(2)
<O–*Z*(1)–O>		109.5	109.5	109.5	109.5	109.5
Z(2)–O(2)b		1.644(2)	1.636(1)	1.644(4)	1.625(2)	1.636(3)
Z(2)–O(3)c		1.642(2)	1.631(1)	1.635(4)	1.621(2)	1.626(3)
Z(2)–O(4)b		1.674(2)	1.673(1)	1.668(4)	1.661(2)	1.678(3)
Z(2)–O(7*A*)b		1.639(4)	1.647(2)	1.655(7)	1.684(6)	1.663(7)
Z(2)–O(7*B*)b		1.631(24)	1.653(6)	1.656(20)	1.645(5)	1.652(7)
<*Z*(2)–O,O(7*A*)>		1.650	1.647	1.651	1.648	1.651
<*Z*(2)–O,O(7*B*)>		1.648	1.648	1.651	1.638	1.648
O(2)b–*Z*(2)–O(3)c		113.0(1)	113.4(1)	112.8(2)	113.3(1)	113.3(1)
O(2)b–*Z*(2)–O(4)b		100.3(1)	101.0(1)	101.0(2)	102.0(1)	100.7(1)
O(2)b–*Z*(2)–O(7*A*)b	x½	115.6(2)	116.0(1)	116.3(3)	116.6(2)	118.2(1)
O(2)b–*Z*(2)–O(7*B*)b	x½	111.3(9)	105.0(2)	103.8(7)	105.7(2)	107.4(3)
O(3)c–*Z*(2)–O(4)b		112.0(1)	112.7(1)	112.5(2)	114.2(1)	113.4(1)
O(3)c–*Z*(2)–O(7*A*)b	x½	103.6(4)	101.8(1)	101.4(4)	98.5(3)	97.7(4)
O(3)c–*Z*(2)–O(7*B*)b	x½	112.4(1.8)	118.1(3)	119.7(9)	115.8(2)	115.3(3)
O(4)b–*Z*(2)–O(7*A*)b	x½	112.6(3)	112.4(1)	113.4(3)	112.9(2)	114.4(3)
O(4)b–*Z*(2)–O(7*B*)b	x½	107.0(1.6)	104.9(2)	105.0(8)	104.5(2)	105.6(3)
<O–*Z*(2)–O>		109.4	109.4	109.4	109.4	109.5
Z(3)–O(5)d		1.637(2)	1.628(2)	1.632(5)	1.620(2)	1.619(3)
Z(3)–O(6)e		1.610(2)	1.610(2)	1.625(5)	1.614(2)	1.609(3)
Z(3)–O(8)d		1.625(2)	1.626(1)	1.634(4)	1.633(2)	1.623(3)
Z(3)–O(9)		1.657(1)	1.663(1)	1.658(3)	1.668(1)	1.667(2)
<*Z*(3)–O>		1.632	1.632	1.637	1.634	1.630
O(5)d–*Z*(3)–O(6)e		109.8(1)	112.2(1)	111.9(2)	112.6(1)	112.0(1)
O(5)d–*Z*(3)–O(8)d		113.1(1)	113.7(1)	114.2(2)	114.4(1)	114.4(1)
O(5)d–*Z*(3)–O(9)		107.6(1)	107.0(1)	106.9(2)	106.9(1)	107.2(1)
O(6)e–*Z*(3)–O(8)d		109.9(1)	108.2(1)	107.8(2)	107.1(1)	107.5(1)
O(6)e–*Z*(3)–O(9)		106.5(1)	107.0(1)	107.5(3)	106.8(1)	106.9(2)
O(8)d–*Z*(3)–O(9)		108.2(1)	108.5(1)	108.2(2)	108.7(1)	108.5(1)
<O–*Z*(3)–O>		109.2	109.4	109.4	109.4	109.4
Y(1*A*)–O(6)q	x4	2.063(2)	2.051(2)	2.067(4)	2.071(2)	2.083(3)
Y(1*A*)–O(10*A*)g		2.272(12)	2.435(10)	2.519(50)	2.341(91)	2.389(26)
Y(1*A*)–O(10*B*)g		2.033(12)	2.182(10)	2.304(49)	2.381(91)	2.448(28)
<*Y*(1*A*)–O(6),O(10*A*)		2.105	2.128	2.157	2.125	2.144
<*Y*(1*A*)–O(6),O(10*B*)		2.057	2.077	2.114	2.133	2.156
Y(1*B*)–O(6)q	x4	2.094(2)	2.064(2)	2.065(2)	2.065(2)	2.077(3)
Y(1*B*)–O(10*A*)g		2.008(12)	2.085(10)	2.198(49)	2.059(91)	2.139(26)
Y(1*B*)–O(10*B*)g		1.768(12)	1.831(10)	1.983(49)	2.099(90)	2.199(28)
<*Y*(1*B*)–O(6),O(10*A*)		2.077	2.068	2.092	2.064	2.089
<*Y*(1*B*)–O(6),O(10*B*)		2.029	2.017	2.049	2.072	2.101
Y(2)–O(4)d	x2	1.953(2)	1.937(1)	1.946(4)	1.939(2)	1.937(3)
Y(2)–O(8)	x2	1.895(2)	1.890(1)	1.907(4)	1.902(2)	1.906(2)
Y(2)–O(11*A*)	x2	1.867(6)	1.855(3)	1.868(8)	1.876(7)	1.878(9)
Y(2)–O(11*B*)	x2	1.866(29)	1.965(6)	2.033(23)	2.017(6)	1.988(9)
<*Y*(2)–O,O(11*A*)>		1.905	1.894	1.907	1.906	1.907
<*Y*(2)–O,O(11*B*)>		1.905	1.931	1.962	1.953	1.944
Y(3)–O(1)		1.942(2)	1.942(2)	1.964(4)	1.965(2)	1.963(3)
Y(3)–O(2)		1.912(2)	1.922(1)	1.921(4)	1.933(2)	1.936(3)
Y(3)–O(3)		1.986(2)	2.013(2)	2.025(4)	2.073(2)	2.069(3)
Y(3)–O(4)h		2.065(2)	2.060(1)	2.071(4)	2.058(2)	2.060(3)
Y(3)–O(5)		2.021(2)	2.024(2)	2.032(4)	2.055(2)	2.053(3)
Y(3)–O(11*A*)		1.918(6)	1.928(3)	1.940(8)	1.930(7)	1.933(9)
Y(3)–O(11*B*)		2.033(31)	2.032(6)	2.039(21)	2.057(6)	2.067(9)
<*Y*(3)–O,O(11*A*)>		1.974	1.982	1.992	2.002	2.002
<*Y*(3)–O,O(11*B*)>		1.993	1.999	2.009	2.024	2.025
X(1)–O(1)a	x4	2.328(2)	2.336(1)	2.339(4)	2.338(2)	2.341(3)
X(1)–O(2)a	x4	2.534(2)	2.510(1)	2.510(4)	2.498(2)	2.502(3)
<*X*(1)–O>		2.431	2.423	2.425	2.418	2.422

TABLE 6. continued

X(2)–O(1)i		2.497(2)	2.480(1)	2.482(4)	2.487(2)	2.489(3)
X(2)–O(2)		2.431(2)	2.408(1)	2.409(4)	2.410(2)	2.409(3)
X(2)–O(3)b		2.363(2)	2.382(1)	2.380(4)	2.389(2)	2.383(3)
X(2)–O(4)		2.464(2)	2.462(1)	2.473(4)	2.480(2)	2.475(3)
X(2)–O(5)		2.429(2)	2.429(1)	2.422(4)	2.423(2)	2.428(3)
X(2)–O(5)i		2.346(2)	2.335(1)	2.346(4)	2.342(2)	2.339(3)
X(2)–O(8)d		2.344(2)	2.343(1)	2.338(4)	2.356(2)	2.358(3)
<*X*(2)–O>		2.411	2.406	2.407	2.412	2.412
X(3)–O(3)j		2.447(2)	2.401(2)	2.421(4)	2.385(2)	2.390(3)
X(3)–O(6)p		2.464(2)	2.450(1)	2.476(4)	2.403(2)	2.418(3)
X(3)–O(6)l		2.952(2)	2.879(2)	2.900(4)	2.794(2)	2.818(3)
X(3)–O(7*A*)j	x½	2.593(4)	2.608(2)	2.568(7)	2.634(5)	2.647(7)
X(3)–O(7*B*)j	x½	2.592(23)	2.546(5)	2.503(19)	2.616(5)	2.597(7)
X(3)–O(7*A*)m	x½	2.492(10)	2.537(3)	2.538(9)	2.580(7)	2.527(10)
X(3)–O(7*B*)m	x½	2.740(51)	3.006(7)	3.067(25)	3.080(7)	3.033(9)
X(3)–O(7*A*)b	x½	2.428(6)	2.416(3)	2.408(8)	2.446(6)	2.451(8)
X(3)–O(7*B*)b	x½	2.386(28)	2.441(6)	2.446(20)	2.497(5)	2.459(7)
X(3)–O(8)k		2.596(2)	2.545(2)	2.553(4)	2.499(2)	2.513(3)
X(3)–O(10*A*)n	x½	2.603(2)	2.626(2)	2.643(8)	2.613(13)	2.616(4)
X(3)–O(10*B*)n	x½	2.576(1)	2.597(1)	2.618(4)	2.619(14)	2.625(5)
X(3)–O(11*A*)j	x½	2.504(7)	2.466(3)	2.450(8)	2.515(7)	2.493(9)
X(3)–O(11*B*)j	x½	2.589(37)	2.601(6)	2.603(21)	2.607(6)	2.610(9)
X(3)–O(12)j		2.415(243)	2.242(16)	2.228(39)	2.215(13)	2.236(14)
X(3)–O(12)c		2.278(260)	2.295(16)	2.317(39)	2.324(13)	2.285(14)
X(3)–O(12)m		2.629(258)	2.658(14)	2.628(40)	2.666(12)	2.622(14)
X(4)–O(6)q	x4	2.317(2)	2.302(2)	2.303(5)	2.318(2)	2.323(3)
X(4)–O(9)f	x4	2.616(3)	2.622(2)	2.646(5)	2.623(3)	2.631(4)
<*X*(4)–O>		2.467	2.462	2.475	2.471	2.477
T(1)–O(7*A*)	x2	2.056(11)	2.053(4)	2.128(20)	2.063(8)	2.134(11)
T(1)–O(11*A*)	x2	1.663(5)	1.646(3)	1.602(11)	1.612(7)	1.608(9)
T(1)–O(7*B*)	x2	1.820(50)	1.614(8)	1.630(30)	1.611(7)	1.657(10)
T(1)–O(11*B*)	x2	1.565(24)	1.467(6)	1.376(25)	1.394(6)	1.404(9)
T(2)–O(10*A*)r		1.246(12)	1.251(10)	1.233(49)	1.348(90)	1.351(25)
T(2)–O(10*B*)r		1.485(11)	1.504(10)	1.448(48)	1.338(91)	1.291(27)
T(2)–O(12)	x2	1.065(266)	1.256(17)	1.263(40)	1.325(13)	1.361(15)

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

valence tables for structures of boron-free and boron-bearing vesuvianite (V12 and V75, respectively) are given in Table 9; these will be used extensively in the following discussion.

RESULTS

Unit formulae

Following Groat *et al.* (1992a), the unit formulae of these boron-bearing vesuvianite crystals were initially calculated on the basis of 19 *X* cations. However, from the *X*-, *Y*- and *Z*-group sums of Table 2, it is not clear whether or not this is the optimum basis for normalization for boron-bearing vesuvianite. The *Y*-group sums vary in the range 13.0–13.5 apfu (atoms per formula unit), and these sums show no relation to the amount of boron in the unit formula. Groat *et al.* (1992a) showed that the *X*-, *Y*- and *Z*-group stoichiometry is different in boron-free and boron-bearing vesuvianite, and this is in line with analysis of other samples of boron-bearing vesuvianite (Table 2, also Groat *et al.* 1994). The processes of renormalization recommended by Groat *et al.* (1992a) are different with and without the presence of boron. However, the resulting differences in stoichiometry between boron-free and boron-bearing vesuvianite do not seem to be related to the amount of boron present. Thus the unit formulae of Table 2 are to be regarded as preliminary values, and subject to re-evaluation in light of the crystal-chemical results.

TABLE 7. SITE-SCATTERING REFINEMENT RESULTS FOR SELECTED CATION SITES* IN BORON-BEARING VESUVIANITE STRUCTURES

	V62	V44	V38	V75	V29
T(1)	12.9(2)	16.2(2)	16.0(4)	18.7(2)	15.4(3)
T(2)	1.8(1)	4.3(1)	3.9(2)	5.3(1)	4.5(2)
Y(1)	21.4(2)	17.9(2)	22.4(3)	16.9(2)	24.8(3)
Y(2)	52	52	52	52	52
Y(3)	107.6(7)	107.2(7)	117.6(8)	109.4(6)	126.9(9)
**E1^{B}	6.2	6.3	7.8	12.1	13.0

* Expressed in terms of equivalent electrons per formula unit.

** Number of electrons per formula unit due to boron, calculated from the boron values of Table 2.

TABLE 8. SITE-SCATTERING REFINEMENT RESULTS FOR SELECTED ANION SITES* IN BORON-BEARING VESUVIANITE STRUCTURES

	V62	V44	V38	V75	V29
O(7A)–O(11*A*)	0.67(1)	0.69(1)	0.74(2)	0.47(1)	0.49(1)
O(7B)–O(11*B*)	0.33(1)	0.31(1)	0.26(2)	0.53(1)	0.51(1)
O(10)	1.80(3)	1.39(3)	1.44(6)	1.08(2)	1.35(3)
O(12)	0.07(3)	0.63(2)	0.83(6)	1.16(3)	1.33(4)

* Values for the O(7) and O(11) sites are expressed as site occupancy of oxygen (vs. vacancy); values for O(10) and O(12) are expressed as atoms (of oxygen) per formula unit.

TABLE 9. BOND-VALENCE* TABLES FOR BORON-FREE (V12) AND BORON-BEARING (V75) VESUVIANITE STRUCTURES, CALCULATED WITH THE CURVES OF BROWN (1981)

V12	*Z*(1)	*Z*(2)	*Z*(3)	*X*(1)	*X*(2)	*X*(3)	*X*(4)	*Y*(1)	*Y*(2)	*Y*(3)	Σ	H(1)	Σ
O(1)	0.954$^{\times4}$↓			0.339$^{\times4}$↓	0.239					0.498	2.030		
O(2)		0.939		0.227$^{\times4}$↓	0.270					0.515	1.951		
O(3)		0.949			0.308	0.258				0.470	1.985		
O(4)		0.869			0.265				0.454$^{\times2}$↓	0.361	1.949		
O(5)			0.969		0.266					0.432	2.008		
					0.341								
O(6)			1.049		0.102	0.240	[0.354]$^{\times4}$↓	[0.397]$^{\times4}$↓			1.852		
						(0.086)							
O(7)		1.013				0.202					1.764	0.292	2.056
						0.239							
						0.310							
O(8)			1.005		0.351	0.184			0.542$^{\times2}$↓		2.082		
O(9)			0.905$^{\times2}$→				[0.188]$^{\times2\rightarrow}_{\times4\downarrow}$				1.998		
O(10)						0.208$^{\times4}$→		[0.495]			1.327		
O(11)						0.236			0.548$^{\times2}$↓	0.508	1.292	0.708	2.000
Σ	3.815	3.770	3.928	2.264	2.142	1.963	[2.168]	[2.083]	3.088	2.784			

V75	*Z*(1)	*Z*(2)	*Z*(3)	*X*(1)	*X*(2)	*X*(3)	*X*(4)	*Y*(1)	*Y*(2)	*Y*(3)	Σ	*T*(1)	Σ
O(1)	0.966$^{\times4}$↓			0.335$^{\times4}$↓	0.240					0.447	1.988		
O(2)		0.979		0.237$^{\times4}$↓	0.288					0.479	1.983		
O(3)		0.997			0.300	0.303				0.355	1.955		
O(4)		0.896			0.244				0.463$^{\times2}$↓	0.370	1.973		
O(5)			1.005		0.274					0.369	1.983		
					0.335								
O(6)			1.021		0.078	0.289	[0.346]$^{\times4}$↓	[0.408]$^{\times4}$↓			1.893		
						0.128							
O(7*A*)		0.873				0.176					1.493		
						0.181							
						0.263							
O(7*B*)		0.924				0.184					1.414	0.560$^{\times2}$↓	1.974
						0.073							
						0.233							
O(8)			0.979		0.319	0.234			0.505$^{\times2}$↓		2.037		
O(9)			0.889$^{\times2}$→				[0.180]$^{\times2\rightarrow}_{\times4\downarrow}$				1.958		
O(10)						0.182$^{\times4}$→		[0.275]			1.003		
O(11)						0.204			0.456$^{\times2}$↓	0.415	1.075	0.724$^{\times2}$↓	1.799
Σ	3.864	3.771	3.894	2.288	2.078	1.895	[2.104]	[2.732]	2.848	2.435		2.568	

TABLE 10. REFINED Y-SITE POPULATIONS IN BORON-BEARING VESUVIANITE CRYSTALS

		V62	V44	V38	V75	V29
Y(1)	Ti*	0.21	0.29	0.32	0.34	0.37
	Fe*	0.52	0.21	0.51	0.11	0.63
	Mg*	0.27	0.50	0.17	0.55	-
Y(2)	Al*	4.00	4.00	4.00	4.00	4.00
Y(3)	Fe*	0.28	0.25	1.05	0.42	1.76
	Al*	7.72	7.75	6.95	7.58	6.24

* Site-populations are expressed in terms of atoms per formula unit (apfu): Fe* = Fe^{2+} + Fe^{3+}; Mg* = Mg + Al; Al* = Al + Mg

Results of cation site-scattering refinements

The results of the cation site-scattering refinements are given in Table 7. They are expressed in terms of equivalent electrons per formula unit (epfu), as these are the direct result of the refinement procedure, whereas their expression as site occupancies requires additional chemical and stereochemical interpretation.

Y(2) site: All site-scattering refinements converged to 52 epfu for this site, and hence this value was fixed in the final stages of refinement. The <Y(2)–O> bond-lengths (Table 6) are remarkably constant at 1.895 Å, with a spread of ±0.004 Å (except for V75). The sum of the empirical radii (Shannon 1976) for $^{[6]}$Al and (O^{2-},OH) is 0.535 + 1.36 = 1.895 Å, equal to the grand <Y(2)–O> distance, and consistent with the complete occupancy of Y(2) by Al. The <Y(2)–O> value of 1.908 Å for V75 and V29 is significantly larger, and indicates the incorporation of some magnesium at this site.

Y(3) site: The compositions of boron-bearing vesuvianite (Table 2) indicate that the occupancy of this site must be dominated by aluminum and magnesium, but the site-scattering results (Table 7) indicate the presence of significant amounts of transition metals. Groat *et al.* (unpublished) show that Ti^{4+} orders at the Y(1) site, and hence the transition metal(s) at the Y(3) site in these crystals is Fe. The amounts may be calculated directly from the site-scattering results, and are given in Table 10, expressed as Al* (= Al + Mg) and Fe* (= Fe^{2+} + Fe^{3+}).

Y(1) site: It is normally considered that the Y(1) site is half occupied, dominantly by transition metals. The site-scattering results of Table 7 indicate that *if* the Y(1) site is half occupied, then it must contain significant amounts of scattering species of lower atomic number than the transition metals. This is particularly notable for crystals V44 and V75 (Table 7), in which Y(1) occupancy by (Al, Mg) must occur if Y(1) is to be half occupied. Possible site-populations of Y(1) are shown in Table 10; these were calculated from the site-scattering results assuming that all Ti orders at Y(1).

Details concerning the local coordination are shown in Table 9. The O(6) site is always occupied, and supplies a total of ~1.7 v.u. (4 × 0.408 v.u.) to the Y(1) cation. Thus Y(1) must bond to an O(10) anion to bring its incident bond-valence to the minimum required value of 2 v.u. If Y(1) is half-occupied and must bond to O(10), the anion occupancy of O(10) cannot fall below 1 apfu, and this is in accord with the site-scattering results of Table 8.

The T sites: The refined site-scattering at the T(1) and T(2) sites cannot be due solely to boron at these sites, as the refined scattering is greatly in excess of that possible from the amount of boron derived by chemical analysis (Fig. 3). There are two possible explanations for this: (1) our boron values are systematically too low; (2) other species, in addition to boron, occupy the T(1) and T(2) sites.

Let us first consider possibility (1). This is unlikely to be a significant factor here, as most of the available evidence suggests that our data are reasonably accurate.

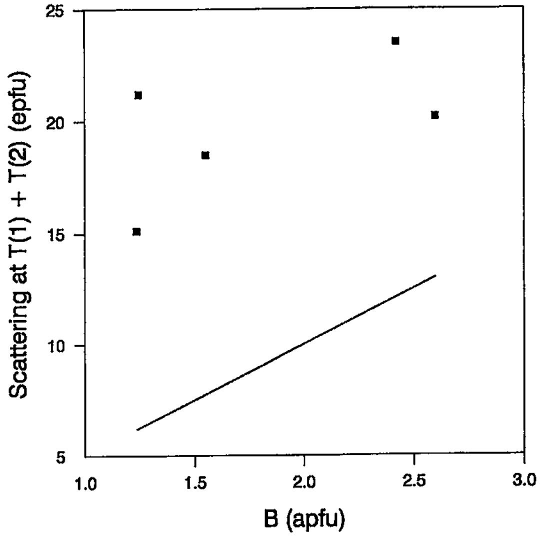

FIG. 3. Refined site-scattering at the T(1) and T(2) sites (squares) as a function of the amount of boron in vesuvianite derived by chemical analysis; the full line denotes the effective scattering corresponding to the analyzed boron content of the vesuvianite crystals.

Firstly, analytical boron contents reported here agree well with previous measurements on vesuvianite from the same localities (*e.g.*, Jannasch 1884, Rammelsberg 1886, Jannasch & Weingarten 1896). Secondly, if the scattering at *T*(1) and *T*(2) were due solely to boron, this would indicate ~5 apfu of boron in vesuvianite crystals V75 and V30; there is no way in which such large amounts of positive charge (15+ pfu) can be compensated, given the results of chemical analysis and the diffraction characteristics of these crystals (Tables 2, 7). *Thus we conclude that additional scatterers must be present at the T(1) or T(2) sites (or both).*

Groat *et al.* (1994) have shown that in boron-free vesuvianite, (Al, Fe) may occur at the *T*(1) site, entering into the structure *via* the substitutions

$$^{T(1)}(\mathrm{Al,Fe^{3+}})_2 + {}^{\mathrm{H}(1)}\square_4 + {}^{X(3)}\square \rightarrow$$
$$^{T(1)}\square_2 + {}^{\mathrm{H}(1)}\mathrm{H}_4 + {}^{X(3)}\mathrm{Ca}$$

$$^{T(1)}(\mathrm{Al,Fe^{3+}}) + {}^{Y}(\mathrm{Mg,Fe^{2+}}) + {}^{\mathrm{H}(1)}\square_2 \rightarrow$$
$$^{T(1)}\square + {}^{Y}\mathrm{Al} + {}^{\mathrm{H}(1)}\mathrm{H}_2$$

The fact that the total scattering from the *T* sites exceeds the amount of boron present in these crystals of boron-bearing vesuvianite suggests that (Al, Fe) also occupies the *T* sites, and the fact that the sum of the *Y*-group cations exceeds the number of *Y* sites (Table 2) is conformable with this suggestion.

Results of the anion site-scattering refinements

The results of the anion site-scattering refinements are given in Table 8, expressed in terms of oxygen atoms pfu.

The O(7) site: The O(7) site was split, and the occupancies of the resultant pair of sites [the O(7*A*) and O(7*B*) sites] were constrained to be equal to the occupancies of the split O(11) sites [the O(11*A*) and O(11*B*) sites]; in addition, the sum of the O(7*A*) and O(7*B*) occupancies were constrained to unity. The relative occupancies of the O(7*A*) site vary between ~0.7 (for crystal V44) and ~½ (for crystals V38, V75 and V29), and correlate crudely with the amount of boron in the crystal.

The O(10) site: The refined site-scattering indicates that O(10) varies between complete occupancy for the low-boron (and boron-absent) crystals and ~½ occupancy for the boron-rich crystals. However, as with the O(7*A*) occupancy, there is only a low correlation with boron content.

The O(12) site: This (new) site varies between zero occupancy in boron-free crystals to ~½ occupancy [1.15(3) apfu compared with 2 sites pfu] in boron-rich crystals. With regard to overall stoichiometry, note that the sum of the O(10) and O(12) oxygen atoms varies in the range 2.11–2.90 apfu, compared with the O(10) value of 2 apfu in boron-free vesuvianite.

The Incorporation of Boron into the Vesuvianite Structure

The extensive positional disorder and chemical complexity observed in boron-bearing vesuvianite do not allow facile interpretation of the occupancy and stereochemical details of the mechanism of boron incorporation; the arguments that follow are involved but essential. Groat *et al.* (1992a) showed that vesuvianite incorporates boron *primarily* via the substitution

$$\mathrm{B + Mg(+Fe^{2+}) \rightleftharpoons 2H + Al(+Fe^{3+})}$$

As shown by Groat *et al.* (1992b), the replacement of hydroxyl by fluorine occurs at both the O(11) and O(10) sites, and produces considerable positional disorder within the structure. If the incorporation of boron into the structure is always connected with local replacement of hydrogen, the local occurrence of $\mathrm{F^-}$ instead of $\mathrm{OH^-}$ will presumably prevent *local* incorporation of boron. Furthermore, the long-range structure model derived from crystal-structure refinement will incorporate disorder due to boron incorporation *and* disorder due to $\mathrm{F^- \rightleftharpoons OH^-}$ substitution. Both of these factors need to be borne in mind when considering the stereochemistry of boron-bearing vesuvianite.

There are two possibilities as to the incorporation of boron into the vesuvianite structure: (1) it occupies the additional *T*(1) and *T*(2) sites observed in boron-bearing vesuvianite; (2) it occupies "conventional" sites in vesuvianite; in this case, the additional electron-density at *T*(1) and *T*(2) must come either from "displaced" species or from other species involved in a polyvalent substitution.

Although (1) seems more reasonable, the observed scattering at the *T* sites is much greater than that indicated by the boron contents derived from chemical analysis; hence the complexity of the problem demands that we formally consider all possibilities, particularly as direct B-for-Si substitution has previously been proposed as the mechanism of incorporation (Belinskii 1984). Boron usually has coordination numbers [3] and [4] where coordinated to oxygen; coordination numbers [2] and [5] have been recorded, but are extremely rare. Consequently, the possible sites available to boron in the structure of "normal" vesuvianite are *Y*(1), *Z*(1), *Z*(2) and *Z*(3).

Substitution at the Z sites

Results of chemical analyses show that boron does not extensively replace silicon in vesuvianite.

Although boron-bearing vesuvianite may be slightly silicon-deficient compared to boron-free vesuvianite, the amount of the deficiency is of the order of 0.20 apfu, whereas the amount of boron can be greater than 2.5 apfu; consequently, direct substitution of silicon by boron can be discounted as the *primary* mechanism of boron incorporation. The other possibility is that boron displaces silicon at one or more of the *Z* sites, with the displaced silicon occupying one or more of the new sites in the boron-bearing structure. However, both the observed scattering at the *Z* sites and the <*Z*–O> values show that there is not significant substitution of Si by B at the *Z* sites.

Substitution at Y(1)

The refined scattering at *Y*(1) in many of the crystals of boron-bearing vesuvianite is approximately compatible with half occupancy of this site dominantly by Fe and Ti. If significant amounts of boron were incorporated at *Y*(1), then the site occupancy would need to considerably exceed one half in order to obtain the *Y*(1) site-scatterings actually observed (Table 7). The scattering at *X*(4) is always consistent with half-occupancy of this site (by Ca); as the close approaches of the *Y*(1) and *X*(4) sites constrain their mean occupancy never to exceed one-half, then the occupancy of *Y*(1) cannot exceed one-half. Hence *Y*(1) does not contain significant boron.

Substitution at the T sites

We have argued that boron does not occupy any of the usual sites in the vesuvianite structure, and hence are left with the "Ockham's razor" solution (Ockham 1330) that boron must occupy one or more of the new positions found in boron-bearing vesuvianite. As the refined scattering powers at these sites do not agree with the analyzed amounts of boron in the crystals used for data collection, additional scattering species must occur at the *T* sites.

THE *T*(1) SITE: SCATTERING AND STEREOCHEMICAL CONSIDERATIONS

Next we will consider the *T*(1) site and its neighboring positions; local coordination details for V75 are given in Table 9 and Figure 4.

The T(1) site

In boron-free vesuvianite, the local configuration (Fig. 4a) involves a pseudotetrahedral arrangement of O(7) and O(11) anions, with O(11)...O(7) hydrogen bonds defining two edges of the tetrahedron. In boron-bearing vesuvianite (Fig. 4b), the *T*(1) site occurs at the center of this [O(11)$_2$O(7)$_2$] tetrahedron. If *T*(1) is occupied, the H positions associated with the two O(11) sites must be vacant because of the very close H–*T*(1) approach. If the H(1) positions are vacant, O(7) is no longer the acceptor of a hydrogen bond (Table 9), and needs an additional bond-valence contribution to satisfy its bond-valence requirements; this comes from the *T*(1) cation, to which it is directly bonded (Table 9).

There are four problems associated with the refined site-scattering at the *T*(1) site and the boron content derived from chemical analysis: (1) the refinement

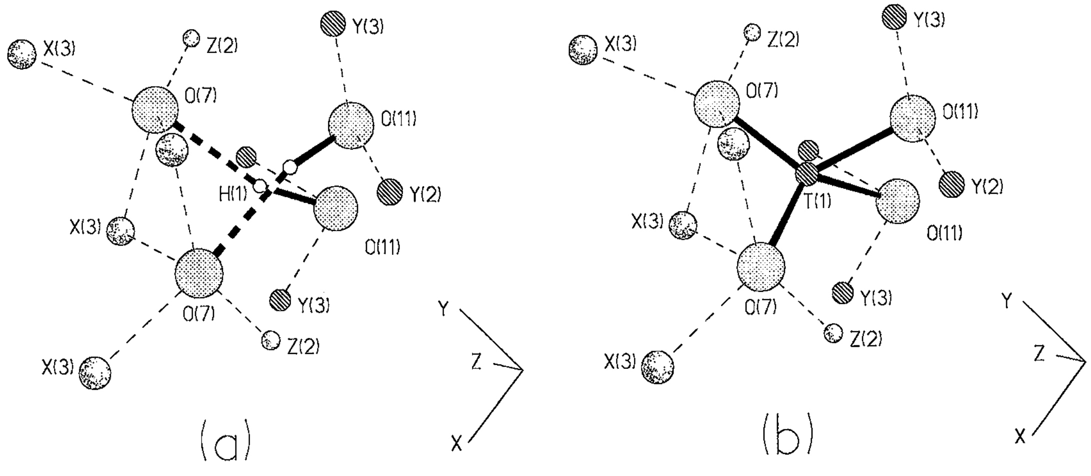

FIG. 4. The local environment of the *T*(1) position in (a) boron-free vesuvianite; (b) boron-bearing vesuvianite.

indicates sufficient scattering to more-or-less fill the *T*(1) site with boron in most of these crystals of boron-bearing vesuvianite, whereas the analytical results indicate that only about half of this amount of boron is present; (2) if the *T*(1) site were fully occupied (by boron), there would seem no need for the O(7) anion to positionally disorder; (3) if the *T*(1) and *T*(2) sites were fully occupied by boron, the structure could not achieve electroneutrality; (4) if *T*(2) and *T*(1) were full of boron, there would be no satisfactory site to put the "excess" *Y*-group cations (Groat *et al.* 1994) that characterize the formula unit of boron-bearing vesuvianite. *Thus we must conclude that the T(1) site is occupied by B, (Al,Fe) and □ (vacancy).*

The O(7) sites

Presumably the splitting of the O(7) and O(11) anions into O(7*A*)–O(11*A*) and O(7*B*)–O(11*B*) pairs is related to the occupancy of the *T*(1) site. Inspection of Table 6 shows that the O(7*B*)–O(11*B*) configuration forms a reasonable tetrahedron around *T*(1), with *T*(1)–O(7*B*) and *T*(1)–O(11*B*) distances of ~1.64 and ~1.44 Å, respectively, whereas O(7*A*) and O(11*A*) do not occur at reasonable bonding distances from *T*(1). The extensive disorder in this part of the structure suggests that the *T*(1)–O distances may not be very accurate, but the observed geometry is reasonable for tetrahedral coordination of mixed B and (Al,Fe). This *model* therefore gives us the aggregate occupancy of the *T*(1) site, which must equal the occupancy of the O(7*B*) and O(11*B*) sites.

TABLE 11. OCCUPANCY DETAILS FOR THE *T*(1) AND *T*(2) SITES IN BORON-BEARING VESUVIANITE CRYSTALS

	V62	V44	V38	V75	V29
Occupancy *T*(1)	0.33	0.31	0.26	0.53	0.51
T(1) scattering (epfu)	12.9	16.2	16.0	18.7	15.4
$B^{T(1)}$ (apfu)*	1.02	0.76	0.53	1.73	1.79
$Fe^{T(1)}$ (apfu)	0.30	0.48	0.51	0.39	0.25
$B^{T(1)}$ (apfu)**	0.53	0.00	0.00	1.11	1.39
$Al^{T(1)}$ (apfu)	0.79	1.24	1.23	1.01	0.65
Occupancy *T*(2)	0.20	0.61	0.56	0.92	0.65
T(2) scattering (epfu)	1.8	4.3	3.9	5.3	4.5
$B^{T(2)}$ (apfu)	0.16	0.55	0.51	0.89	0.59
$Fe^{T(2)}$ (apfu)	0.04	0.06	0.05	0.03	0.06
$\Sigma Fe^{T(1)+T(2)}$ (apfu)	0.34	0.55	0.56	0.42	0.31
ΔY (apfu)	0.35	0.51	0.26	0.45	0.36
$B^{T(1)+T(2)}$ (apfu)	1.18	1.31	1.04	2.62	2.38
B^{EMP} (apfu)	1.24	1.25	1.55	2.42	2.60

* $B^{T(1)}$ value for (B + Fe) occupancy;
** $B^{T(1)}$ value for (B + Al) occupancy.

Occupancy of T(1)

The site populations for the *T*(1) site may be calculated from the occupancy (Table 11) and the refined site-scattering, assuming occupancy by (1) B + Al, and (2) B + Fe; the results for these two models are shown in Table 11. For *T*(1) occupancy by B + Al, the amounts of Al are much larger than the "excess" *Y*-group cations, as indicated by the formula-unit calculation (Table 2). For *T*(1) occupancy by B + Fe, the amounts of Fe are similar to the amounts of "excess" *Y*-group cations (Table 2), suggesting strongly that *T*(1) is occupied by B + Fe. This type of site occupancy is also indicated by the assigned site-populations of the *Y*(1) and *Y*(3) sites (Table 10), which indicate that not all the Fe in the formula unit occurs at *Y*(1) and *Y*(3).

THE *T*(1) SITE: CONSEQUENCES OF ITS OCCUPANCY

Chemical composition

We have concluded that the *T*(1) site is occupied by B and (Al,Fe^{3+}), and shown that occupancy of *T*(1) must be accompanied by vacancies at the two adjacent H(1) positions. As this involves introduction of an additional positive charge, there must be an accompanying substitution to compensate for this. Some substitutions are shown in Table 12; not all possible substitutions are shown, as we have omitted those we regard as unlikely (*e.g.*, ${}^{T(1)}B \rightarrow {}^{H(1)}H_3$). Groat *et al.* (1992a) have shown that substitution (3) is the princi-

TABLE 12. POSSIBLE SUBSTITUTIONS INVOLVING A TRIVALENT CATION AT THE *T*(1) SITE IN VESUVIANITE

Substitutions involving X-group cations

(1) ${}^{T(1)}M^{3+} + {}^{X}Na \rightarrow {}^{H(1)}H_2 + {}^{X}Ca$

(2) ${}^{T(1)}M^{3+}_2 + {}^{X}\square \rightarrow {}^{H(1)}H_4 + {}^{X}Ca$

Substitutions involving Y-group cations

(3) ${}^{T(1)}M^{3+} + {}^{Y}Mg \rightarrow {}^{H(1)}H_2 + {}^{Y}Al$

(4) ${}^{T(1)}M^{3+}_2 + {}^{Y}\square \rightarrow {}^{H(1)}H_4 + {}^{Y}Mg$

(5) ${}^{T(1)}M^{3+}_3 + {}^{Y}\square \rightarrow {}^{H(1)}H_6 + {}^{Y}Al$

Substitutions involving Z-group cations

(6) ${}^{T(1)}M^{3+} + {}^{Z}Al \rightarrow {}^{H(1)}H_2 + {}^{Z}Si$

pal way of incorporating B into the vesuvianite structure. However, B is not the only cation to occur at the *T*(1) site, and the question arises as to whether other substitutions occur for B, and whether the substitutions leading to (Al,Fe^{3+}) at *T*(1) are the same as for the incorporation of B at *T*(1). Groat *et al.* (1994) have shown that substitutions of the type (2) and (3) (Table 12) are probably both involved in the occurrence of (Al,Fe^{3+}) at the *T*(1) site, and discussed the mechanism for local bond-valence compensation resulting from substitution (2). Groat *et al.* (1992a) proposed that boron is incorporated into the vesuvianite structure *via* the substitution B + Mg $\rightleftharpoons$ 2H + Al; this has the same stoichiometry as substitution (3) (Table 12), which accounts for the incorporation of perhaps 60–70% of the boron in these vesuvianite crystals.

Local bond-valence considerations

Incorporation of a trivalent cation at a normally empty site obviously requires significant rearrangement of the neighboring atoms, particularly with regard to local bond-valence requirements. Groat *et al.* (1994) have discussed the local re-arrangements associated with substitution (2) (Table 12). Here we examine the local consequences of substitution (3).

The *T*(1) site is coordinated to two O(7) and two O(11) anions in a tetrahedral arrangement. Where *T*(1) is vacant, the two adjacent H(1) positions are occupied. The H(1) atoms provide 0.71 v.u. to O(11) and 0.29 v.u. to O(7), to bring the bond-valence sums around O(7) and O(11) to their ideal values of 2.0 v.u. (Table 9, V12). Where *T*(1) is occupied, the two adjacent H(1) positions are vacant, and both O(7) and O(11) need additional incident bond-valence to compensate for the loss of bond valence from the H(1) atoms. This bond valence is provided by the *T*(1) cation that bonds both to O(7) and O(11) (Table 9, V75). It is here that we see the reason for the splitting of the O(7) and O(11) anions: to achieve tetrahedral coordination about the *T*(1) cation and adequate local bond-valence satisfaction of the anion.

THE *T*(2) SITE: SCATTERING AND STEREOCHEMICAL CONSIDERATIONS

We will consider the *T*(2) and neighboring positions; information on coordination is given in Table 9 and Figure 5.

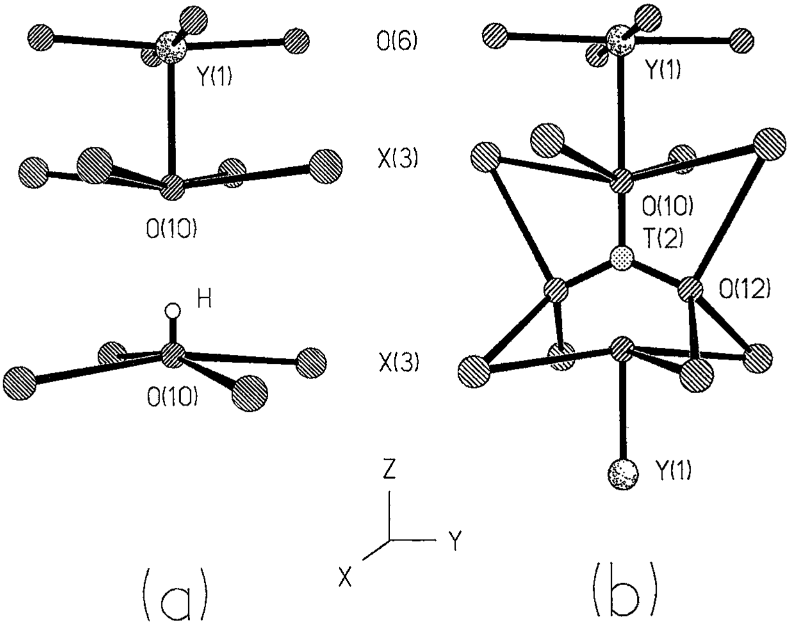

FIG. 5. The suggested local environment of the T(2) position in (a) boron-free vesuvianite; (b) boron-bearing vesuvianite.

The O(10) site

Although O(10) is not always occupied in boron-bearing vesuvianite, $X(3)$ is filled with Ca, and so the O(10) atoms are always coordinated to $X(3)$. Hence O(10) is always occupied by an anion (or a vacancy) and receives ~0.75 v.u. from the coordinating $X(3)$ cations (Table 9). A bond-valence contribution of ~0.60 v.u. from $Y(1)$ brings the bond-valence sum to ~1.35 v.u. [excluding contributions from H(2) or $T(2)$ and assuming that O(10) is occupied by oxygen]. The O(10) occupancy varies between 2 apfu [1.79(3) apfu for V62] and ~1 apfu [1.18(3) apfu for V75, Table 2]. Note that if the $Y(1)$ occupancy is 0.5 (*i.e.*, 1 apfu) and always bonds to O(10), then the O(10) occupancy cannot fall below 0.5 (*i.e.*, 1 apfu); as seen in Table 8, this is the case in the boron-bearing vesuvianite crystals examined here.

The situation is further complicated by the fact that the O(10) site also shows positional disorder. This was modeled in the refinement process by two split sites [O(10*A*) and O(10*B*)], the occupancies of which are variable but constrained to be equal. This model is almost certainly unrealistic, but all attempts to refine the occupancies of O(10*A*) and O(10*B*) independently were unsuccessful. Thus the resulting stereochemistry is not accurate, and only gives a qualitative indication of the possible local configurations.

The T(2) site

The suggested local configurations around the $T(2)$ site in boron-free and boron-bearing vesuvianite are shown in Figure 5. If $T(2)$ is occupied, one of the two adjacent O(10) sites must be vacant [unless the cation at $T(2)$ adopts a linear [2]-coordination]. If occupancy of $T(2)$ is locally associated with a vacancy at one of the adjacent O(10) sites, the occupancies (in unspecified atoms pfu) will be related by the following expression: occupancy of $T(2)$ = 2 – occupancy of O(10). From this occupancy, the mean atomic number of the cations occupying the $T(2)$ site can be calculated from the refined site-scattering values of Table 7, allowing for a contribution to $T(2)$ from H where adjacent O(10) sites are occupied; the resultant values are shown in Table 11. Crystals V38, V75 and V29 have $T(2)$ completely occupied by B ($Z = 5$); note that this conclusion is in line with the polarized infrared spectra of the vesuvianite crystals in the principal O(11)-stretching region (Groat *et al.* 1995). Crystals V44 and V62 have $^{T(2)}\langle Z \rangle$ values too large for $T(2)$ to be occupied only by B. For V62 and V44, the occupancy and scattering indicate a combination of B and Fe; although the anion disorder prevents resolution of the local coordination around Fe at the $T(2)$ position, local steric factors suggest that it is probably square pyramidal. As with $T(1)$, Fe seems the dominant Y-cation, and the calculated values [allowing for some contribution to the $T(2)$ scattering by hydrogen] are given in Table 11. In a study of vesuvianite crystals with Y-cation sums much larger than 13 apfu, Groat *et al.* (1994) found that the excess Y-cations occur solely at the $T(1)$ site; this is also the case for boron-bearing vesuvianite crystals V38, V75 and V29. However, V62 and V44 have small amounts of Fe assigned to the $T(2)$ site; we are not convinced that this difference in behavior is real, given the many problems associated with local disorder and the recalculation of the unit formulae. However, the agreement between the sum of the $T(1)$ and $T(2)$ site-populations (derived solely from site-scattering refinement) is in good agreement with the boron content determined by analysis *and* the "excess" Y-cations in the unit formulae (Table 11).

SUMMARY

The extensive local disorder that accompanies the incorporation of boron into the vesuvianite structure, coupled with the variable hydrogen content, give significant problems in the interpretation of the chemical composition of boron-bearing vesuvianite. However, the crystal-structure refinements presented here do provide important information on the mechanism of boron incorporation in vesuvianite:

(1) Boron is not incorporated into the vesuvianite structure by simple Si $\rightleftharpoons$ B substitution, as has been suggested previously.

(2) Boron is incorporated into vesuvianite primarily *via* the substitution 2H + Al $\rightleftharpoons$ B + Mg.

(3) The structure of boron-bearing vesuvianite has two sites, $T(1)$ and $T(2)$, that are occupied by B, Al and Fe.

(4) Boron at $T(1)$ replaces two hydrogen atoms at adjacent O(11) anions, assuming tetrahedral coordination by two O(7) and two O(11) [where O^{2-} occurs at the O(11) positions]; Fe and Al also occur at the $T(1)$ site.

(5) The $T(1)$ site is only partly occupied, and there is extensive positional disorder of the anions coordinating this site.

(6) Boron replaces hydrogen attached to O(11) anions at the O(10) position, forming the $T(2)$ site that can also be occupied by Fe or Al in square-pyramidal coordination.

(7) Boron-bearing vesuvianite usually has "excess" Y-group cations that occur at the $T(1)$ and $T(2)$ sites (in addition to boron).

(8) Vesuvianite can incorporate boron in the (observed) range 0–4 wt% B_2O_3 (Groat *et al.* 1992a, this work).

(9) Vesuvianite may be an important "sink" for boron in some environments (particularly skarns).

(10) The current work illustrates the importance of

looking at a wide range of compositions and structures when trying to unravel a complicated problem. It would have been relatively simple to derive a model to explain just *one* structure refinement; however, such solutions commonly are nonunique, and it is only by examining the range of known compositions that adequate models can be derived.

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