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X-RAY AND NEUTRON CRYSTAL-STRUCTURE REFINEMENTS OF A BORON-BEARING VESUVIANITE

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Abstract

The crystal structure of a sample of B-bearing vesuvianite, $Ca_{19}(Al_{6.20}Fe^{3+}_{1.46}Mg_{3.65}Fe^{2+}_{1.59}Ti_{0.16}Mn_{0.07})(Si_{17.57}Al_{0.43})B_{2.73}O_{68}(\{OH\}_{2.94}F_{0.65}O_{6.41})$, *a* 15.734(1), *c* 11.719(1) Å, *V* 2902.2(5) Å^3, *P4/nnc*, has been refined to an *R* index of 3.8% based on 1709 observed reflections measured at 298 K with Mo*K*α X-radiation, and to an $R(F^2)$ index of 9.4% based on 7482 observed reflections measured at 15 K by TOF (time-of-flight) neutron diffraction. The results of the two refinements confirm the findings of Groat *et al.* (1992, 1994a, b) on the mechanisms of incorporation of B into the vesuvianite structure. Furthermore, the neutron refinement allowed location of the H, which occurs only at the *H*(1) position in the crystal examined here. The absence of H at the *H*(2) channel position, together with the refined scattering at the *T*(2) site and local bond-valence considerations at the O(10) anion, showed that *T*(2) is completely occupied by B. The refined site-populations of the O(10) and O(12) sites are compatible only with 0.15 $^{[2]}$B and 0.85 $^{[3]}$B at the *T*(2) site. Other crystals of B-bearing vesuvianite also contain $^{[3]}$B at *T*(2) (Groat *et al.* 1994b). The incorporation of B at *T*(2) in different coordination environments provides a flexible mechanism that can act in conjunction with other substitutions elsewhere in the structure to satisfy requirements of long-range electroneutrality.

Keywords: vesuvianite, crystal-structure refinement, neutron diffraction, boron, site populations.

Sommaire

Nous avons affiné la structure cristalline d'un échantillon de vésuvianite borifère de composition $Ca_{19}(Al_{6.20}Fe^{3+}_{1.46}Mg_{3.65}Fe^{2+}_{1.59}Ti_{0.16}Mn_{0.07})(Si_{17.57}Al_{0.43})B_{2.73}O_{68}(\{OH\}_{2.94}F_{0.65}O_{6.41})$, *a* 15.734(1), *c* 11.719(1) Å, *V* 2902.2(5) Å^3, *P4/nnc*, jusqu'à un résidu *R* de 3.8% en utilisant 1709 réflexions observées par diffraction X, mesurées à 298 K avec rayonnement Mo*K*α, et jusqu'à un résidu $R(F^2)$ de 9.4% en utilisant 7482 réflexions observées, mesurées à 15 K par diffraction de neutrons (technique de temps de vol). Les résultats des deux affinements confirment les conclusions de Groat *et al.* (1992, 1994a, b) à propos des mécanismes d'incorporation du bore dans la structure de la vésuvianite. De plus, l'affinement par diffraction de neutrons nous permet d'affiner la position de l'atome H, uniquement au site *H*(1) dans le cristal choisi pour notre étude. L'absence de H au site *H*(2), dans les canaux de la structure, de même que l'affinement de la dispersion associée au site *T*(2) et une considération des exigeances de satisfaction locale des valences de liaison sur l'atome O(10), montrent que le bore remplit complètement le site *T*(2). La population affinée des sites O(10) et O(12) est compatible seulement avec une répartition de 0.15 $^{[2]}$B et de 0.85 $^{[3]}$B sur le site *T*(2). Groat *et al.* (1994) ont prouvé la présense de $^{[3]}$B sur *T*(2) dans d'autres échantillons de vésuvianite. L'incorporation de B au site *T*(2) dans des milieux de coordinance divers assure un mécanisme flexible qui peut agir de concert avec les autres substitutions ailleurs dans la structure afin de satisfaire aux exigeances d'électroneutralité à longue échelle dans la structure.

(Traduit par la Rédaction)

Mots-clés: vésuvianite, affinement de la structure cristalline, diffraction de neutrons, bore, occupation des sites.

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INTRODUCTION

Recent work on the structure and chemistry of vesuvianite (Groat *et al.* 1992a, b, 1993, 1994a, b, 1995, Allen & Burnham 1992, Fitzgerald *et al.* 1986a, b, 1992, Hoisch 1985, Yoshiasa & Matsumoto 1986, Ohkawa *et al.* 1992) has greatly improved our understanding of the structural chemistry of this mineral. Of particular crystal-chemical and geochemical interest is the behavior of B in vesuvianite; Groat *et al.* (1992a) emphasized the importance of B and proposed that it is incorporated *via* the substitution B + Mg → 2H + Al. Groat *et al.* (1994b) showed that B directly replaces H in the structure, which gives rise to two new structural positions. This mechanism is consistent with the variation in polarized infrared spectra of vesuvianite as a function of B content (Groat *et al.* 1995). The current combined neutron – X-ray study provides direct evidence of the role of H in the incorporation of B into the vesuvianite structure.

EXPERIMENTAL

The sample used for this work is from the Bill Waley mine, Tulare County, California, and was obtained from the Mineralogical Research Company (San Jose, California). Chemical compositions and cell parameters of this sample, designated V56, are reported by Groat *et al.* (1992a); those data and the values of these parameters determined in the present work are given in Table 1. This sample is unusually rich in B (~2.7 *apfu*; atoms per formula unit) and forms crystals sufficiently large to use for the collection of neutron-diffraction data. For the X-ray work, a small fragment was abraded to a sphere in an air-driven crystal grinder, and mounted on a glass fiber. For the neutron work, an approximately spherical crystal of diameter 3.2 mm was mounted on an aluminum pin with epoxy.

Collection of X-ray-diffraction data

The crystal was mounted on a Nicolet *R*3*m* automated four-circle diffractometer, and the setting angles for 25 automatically aligned reflections were used to refine the cell dimensions (Table 1). Intensity data (4761 reflections) were collected over two asymmetric units (assuming 4/*mmm* Laue symmetry) out to a maximum 2θ value of 60° according to the experimental procedure of Groat *et al.* (1992b). Psi-scan data were collected for an empirical absorption correction assuming an ellipsoidal shape that was refined as part of the absorption-correction procedure. The *R* index for the corrected psi-scan data was 0.8%, and the same correction was applied to the normal intensity data. A reflection was considered as observed if its intensity exceeded that of four times background based on counting statistics.

TABLE 1. MISCELLANEOUS INFORMATION FOR BORON-BEARING VESUVIANITE V56

	Groat* *et al.* (1992)	This work*		Groat *et al.* (1992)	This work		Groat *et al.* (1992)	This work	
								X-ray: 298 K	Neutron: 15 K
SiO_2	34.90	34.32	Si	17.59	17.57	*a* (Å)	15.738(1)	15.736(1)	15.725(2)
Al_2O_3	11.95	11.99				*c*	11.730(2)	11.720(1)	11.716(2)
TiO_2	0.46	0.41	Al	7.10	7.23	*V* (Å^3)	2905.2(6)	2901.9(5)	2897.1(9)
Fe_2O_3	3.83	3.80	Ti	0.17	0.16				
FeO	3.74	3.71	Fe^{3+}	1.45	1.46	Space group	*P4/nnc*		*P4/nnc*
MnO	0.18	0.15	Fe^{2+}	1.58	1.59				
MgO	4.52	4.78	Mn	0.07	0.07			X-ray	Neutron
CaO	35.18	34.64	Mg	3.39	3.65		Radiation	Mo*K*α	TOF
B_2O_3	2.94	3.09	Σ*Y*	13.76	14.16				
F	0.51	0.40					Monochromator	Graphite	
H_2O	0.86	0.86	Ca	19	19				
	99.07	98.15					No. of $\|F_o\|$	1709	7615
O=F	0.21	0.17	B	2.56	2.73				
Sum	98.86	97.98	F	0.40	0.65		*R* (%) / $R(F^2)$	3.8	9.4
			OH	3.16	2.94		*wR* (%) / $wR(F^2)$	3.9	11.2

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$; $wR = [\Sigma w(|F_o|-|F_c|)^2/\Sigma F_o^2]^{1/2}$, $w = 1$

$R(F^2) = \Sigma(F_o^2-F_c^2)/\Sigma F_o^2$; $wR(F^2) = \Sigma w(F_o^2-F_c^2)/\Sigma wF_o^2$, $w = 1/[\sigma_o^2(F_o^2)+0.02F_o^2)^2]^{1/2}$

* Na, Cr, V not detected

Collection of neutron-diffraction data

Low-temperature (15 ± 1 K), single-crystal, time-of-flight neutron-diffraction data were obtained at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory using a diffractometer equipped with an area position-sensitive ^{6}Li-glass scintillation detector (30 × 30 cm) and an Air Products Displex closed-cycle helium refrigerator for cooling. The experiment was done at 15 K to reduce the effects of thermal vibration and to increase the probability of localizing the hydrogen atoms. The instrument and data-collection procedures are described in more detail by Schultz (1993).

A sufficient number of (*hkl*) planes were indexed at low temperature to ensure that *P4/nnc* symmetry was preserved during cooling. Unit-cell parameters [*a* 15.725(2), *c* 11.716(2) Å] were determined at 15 K from least-squares refinement of the centroids of strong reflections (246) well distributed in reciprocal space (Program LATCON). With an area position-sensitive detector and a range of wavelengths determined by the time-of-flight of the neutrons, a solid volume of reciprocal space was sampled with a stationary orientation of the sample and detector. For each setting of the diffractometer angles, data were stored in three-dimensional histogram form with coordinates *x, y, t* corresponding to horizontal and vertical detector positions, and time-of-flight, respectively. A full hemisphere of reciprocal space was covered to sin $\theta/\lambda < 0.767$ Å^{-1} and a partial quadrant in the range $0.767 < \sin\theta/\lambda < 1.205$ Å^{-1}. Integrated intensities (7615) from 31 histograms were converted to structure-factor amplitudes using the expression $I_{hkl} = kT\phi_\gamma\varepsilon_\gamma A_\gamma Y_\gamma |F_{hkl}|^2\gamma^4/\sin^2\theta$, where k is a scale factor, T is the normalized monitor-count, F_{hkl} is the structure factor, and θ is the Bragg angle. The wavelength-dependent terms are the incident flux ϕ_γ, the detector efficiency ε_γ, the absorption correction A_γ, and the extinction correction Y_γ. An absorption correction was applied using a linear absorption coefficient of the form $\mu(\lambda)$ (cm^{-1}) = 0.0646 + 1.4019λ, where the constant and wavelength-dependent terms correspond to the incoherent and absorption cross-sections, respectively, and λ varies from 0.7 to 4.2 Å. Symmetry-related reflections were not averaged because different extinction-factors were applied to reflections measured at different wavelengths.

Structure refinement

The structure of vesuvianite is infamous with regard to the problems of space-group determination; the data bearing on this problem have been reported and reviewed by Groat *et al.* (1992a, 1993) and Allen & Burnham (1992). Groat *et al.* (1994b) have shown that boron-bearing vesuvianite closely obeys *P4/nnc* space-group symmetry, and this symmetry is adopted here.

X-ray data: The model of Groat *et al.* (1994b) was used, except for the *Y*(1) and O(10) sites. In the former work, these sites were modeled as positionally disordered (split); here, we used non-split sites, in order to compare the results with those of the neutron refinement, which was done at low temperature and showed no evidence of splitting. The refinement converged rapidly to an *R* index of 3.8% for this model. Refinement of a split *Y*(1) and O(10) model did not show any improvement in *R* index or give significantly different site-populations.

Neutron data: The refinement was done using a locally modified least-squares program for variable-wavelength data (Program ANVLS). The function minimized was $\Sigma\omega(F^2_{obs} - F^2_{calc})$, where $\omega = 1/\sigma(F^2_{obs})$ and $\sigma(F^2_{obs}) = [\sigma^2 \text{ counting } (F^2_{obs}) + (0.02F^2_{obs})^2]^{1/2}$. Starting positions for the non-hydrogen atoms were taken from the X-ray refinement. Other variables in the refinement model included a scale factor for each of the histograms, and an isotropic (type-1) extinction correction (Zachariasen 1967). Neutron-scattering lengths were obtained from Sears (1986). After convergence with isotropic-displacement factors and full site-occupancies for the non-H atoms, the *H*(1) atom was located by difference-Fourier methods near the position reported by Lager *et al.* (1989). Negative neutron density was not observed along the channel axis near O(10) at the position occupied by *H*(2) in boron-free vesuvianite (Lager *et al.* 1989). The *H*(1)-atom position, site occupancy and isotropic-displacement factor were subsequently refined to convergence. In order to compare X-ray and neutron-diffraction refinements, the occupancies of partly occupied and split-atom sites, as determined by X-ray refinement, were initially varied independently in the neutron refinement without constraints. Constraints consistent with the X-ray model were later applied when it became apparent that constrained and unconstrained occupancies differed by only one standard deviation. In the later cycles of refinement, anisotropic-displacement parameters were refined for all atoms, with the exception of O(7) (split-atom site) and *Y*(1) (non-positive definite tensor). Final agreement (*R*) values for $F^2_{obs} > 3\sigma(F^2_{obs})$ (7482 reflections) were $R(F^2) = 9.4\%$ and $R_w(F^2) = 11.2\%$.

Electron-microprobe analysis

Subsequent to the diffraction experiments, the crystal used for the collection of the X-ray intensity data was characterized by electron-microprobe analysis according to the method of Groat *et al.* (1992a). Ten points were analyzed and averaged to obtain a representative bulk-composition for the crystal. The ratio Fe^{2+}/Fe^{3+} and H_2O contents were taken from Groat *et al.* (1992a), and represent the mean value for the bulk sample rather than for the crystals used in the X-ray and neutron work.

RESULTS

Structure refinement

Final atomic parameters and displacement-factors are given in Table 2; structure factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2. Selected interatomic distances and angles are given in Table 3, and the site-scattering or site-population values are given in Table 4. The chemical composition of the crystal is given in Table 1; the unit formula was calculated on the basis of 19 Ca (Groat *et al.* 1992a).

CHEMICAL COMPOSITION

Comparison of the compositions of vesuvianite V56 given by Groat *et al.* (1992) and that analyzed here (Table 1) shows that the crystal examined in the present work is slightly more B-rich, and has a slightly

TABLE 2. ATOMIC PARAMETERS FOR BORON-BEARING VESUVIANITE V56

		Neutron	X-ray
Z(1)	*x*	3/4	3/4
	y	1/4	1/4
	z	0	0
	*U_{eq}	51(6)	101(4)
Z(2)	*x*	−0.17861(8)	−0.17845(7)
	y	0.04330(9)	0.04337(7)
	z	0.87219(10)	0.87235(9)
	U_{eq}	86(4)	128(3)
Z(3)	*x*	−0.08392(8)	−0.08377(6)
	y	−0.15005(8)	−0.14983(6)
	z	0.36464(9)	0.36469(9)
	U_{eq}	49(4)	100(3)
X(1)	*x*	3/4	3/4
	y	1/4	1/4
	z	1/4	1/4
	U_{eq}	85(7)	119(4)
X(2)	*x*	−0.19057(7)	−0.19065(4)
	y	0.04537(7)	0.04532(5)
	z	0.38016(9)	0.37977(6)
	U_{eq}	90(3)	117(2)
X(3)	*x*	−0.10175(7)	−0.10155(5)
	y	−0.17934(8)	−0.17959(5)
	z	0.89736(10)	0.89776(7)
	U_{eq}	201(4)	193(2)
X(4)	*x*	3/4	3/4
	y	3/4	3/4
	z	0.1427(4)	0.1440(3)
	U_{eq}	170(14)	148(9)
Y(1)	*x*	3/4	3/4
	y	3/4	3/4
	z	0.0588(2)	0.0595(3)
	U_{eq}	168(9)	181(8)
Y(2)	*x*	0	0
	y	0	0
	z	0	0
	U_{eq}	3(3)	86(4)

TABLE 2. continued

		Neutron	X-ray
Y(3)	*x*	−0.11174(6)	−0.11154(6)
	y	0.12042(6)	0.12045(6)
	z	0.12844(8)	0.12800(8)
	U_{eq}	35(3)	93(3)
T(1)	*x*	0.05207(14)	0.0529(2)
	y	0.05207	0.0529
	z	1/4	1/4
	**U_{eq}	330(10)	100**
T(2)	*x*	1/4	1/4
	y	1/4	1/4
	z	1/4	1/4
	**U_{eq}	170(10)	100**
O(1)	*x*	−0.22023(6)	−0.2199(2)
	y	0.17287(6)	0.1730(2)
	z	0.08453(7)	0.0849(2)
	U_{eq}	87(3)	131(7)
O(2)	*x*	−0.12103(6)	−0.1211(2)
	y	0.16090(6)	0.1608(2)
	z	0.28337(8)	0.2833(2)
	U_{eq}	118(3)	153(8)
O(3)	*x*	−0.04198(6)	−0.0418(2)
	y	0.22508(6)	0.2251(2)
	z	0.07781(8)	0.0775(2)
	U_{eq}	115(3)	153(7)
O(4)	*x*	−0.06153(6)	−0.0617(2)
	y	0.10423(6)	0.1045(2)
	z	0.47154(7)	0.4711(2)
	U_{eq}	86(3)	133(7)
O(5)	*x*	−0.17154(6)	−0.1716(2)
	y	0.01172(6)	0.0112(2)
	z	0.18009(7)	0.1796(2)
	U_{eq}	91(3)	138(8)
O(6)	*x*	−0.12085(6)	−0.1210(2)
	y	−0.27678(6)	−0.2770(2)
	z	0.05290(7)	0.0537(2)
	U_{eq}	113(3)	170(8)

higher Mg content and a lower Al content at the *Y* sites, in accord with the primary mechanism of substitution for the incorporation of B into the vesuvianite structure: B + Mg ⇌ 2H + Al (Groat *et al.* 1992). There is a deficiency of Si at the *Z* sites, and an excess of small divalent and trivalent *Y*-type cations that exceeds 1 *apfu* (Table 1). These values are very sensitive to the method of calculation of the formula unit. For B-bearing vesuvianite V56, the formula was normalized on 19 Ca atoms. The results of the present refinements allow us to assess the accuracy of this method. Calcium occupies the *X*(1), *X*(2), *X*(3) and *X*(4) sites, and the site scattering indicates that the *X*(1), *X*(2) and *X*(3) sites are completely occupied by Ca, in accord with the chemical composition (Table 1) that indicates no detectable Na or *REE* (rare-earth elements) that would occupy these sites. The *X*(4) site is only partly occupied, and the assumption of 19 Ca *apfu* requires that this site is exactly half-occupied by Ca; the occupancy of *X*(4) for the refined X-ray model is 0.516(8) Ca, statistically identical with the ideal value of 0.5 and supporting the 19-Ca renormalization procedure.

TABLE 2. continued

		Neutron	X-ray
O(7A)	*x*	0.05546(16)	0.0561(4)
	y	0.17608(18)	0.1746(4)
	z	0.31925(20)	0.3201(5)
	U_{eq}	71(7)	170(9)
O(7B)	*x*	0.04553(14)	0.0438(4)
	y	0.14752(17)	0.1472(4)
	z	0.30690(18)	0.3072(5)
	U_{eq}	132(4)	170(9)
O(8)	*x*	−0.06027(6)	−0.0606(2)
	y	−0.09210(6)	−0.0918(2)
	z	0.06682(7)	0.0674(2)
	U_{eq}	77(3)	111(7)
O(9)	*x*	−0.14627(6)	−0.1460(2)
	y	−0.14627(6)	−0.1460(2)
	z	1/4	1/4
	U_{eq}	87(3)	138(7)
O(10)	*x*	3/4	3/4
	y	3/4	3/4
	z	0.86801(34)	0.8647(9)
	U_{eq}	220(10)	580(35)
O(11)	*x*	−0.00124(7)	−0.0014(2)
	y	0.05765(8)	0.0580(2)
	z	0.14630(11)	0.1451(2)
	U_{eq}	213(4)	193(8)
O(12)	*x*	0.17532(52)	0.1780(8)
	y	0.22656(37)	0.2735(8)
	z	0.29539(51)	0.2040(11)
	$**U_{eq}$	590(3)	120**
H(1)	*x*	0.4603(9)	–
	y	0.4873(12)	–
	z	0.3032(11)	–
	U_{eq}	650(70)	–

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

Site-Scattering Refinement

The X and Y sites

For the cation sites, the results of site-scattering refinement are expressed in terms of *epfu* (electrons per formula unit; Hawthorne *et al.* 1995) and scattering length; significant additional information is required to derive the corresponding site-populations.

Y(1) site: This site is normally half-occupied, and is usually dominated by transition metals, particularly Fe^{2+}. We tested for the presence of Ti^{4+} at *Y*(1) in the neutron structure-refinement, as Ti has a negative scattering-length. Thus structure refinement using neutron data is ideal for locating Ti in a structure. However, the results were rather inconclusive. A neutron-diffraction study of a more Ti-rich vesuvianite is currently under way in order to resolve the behavior of Ti in vesuvianite.

Y(2) site: Site-scattering refinement converged to 52 *epfu*, and this value was fixed in the final stages of refinement; this result is in accord with the results of Groat *et al.* (1994b) on other crystals of B-bearing vesuvianite. The <*Y*(2)–O> distance indicates that this site is occupied predominantly by Al, possibly with a small amount of Mg present, as is the case for almost all other crystals of vesuvianite analyzed.

Y(3) site: The formula unit (Table 1) indicates that the *Y*(3) site must be dominated by Al, Mg and Fe. The refined site-scattering value of 121.7(8) *epfu* may be compared with the value of 104 *epfu* for complete occupancy by Al; this comparison indicates significant occupancy of *Y*(3) by Fe, and the <*Y*(3)–O> value of 2.103 Å is in accord with this conclusion. Site populations were calculated directly from the refined site-scattering value and are given in Table 5.

X(4) site: The refined site-scattering at this site is 20.8(3) *epfu*. This value is statistically identical to the ideal value of 20 *epfu* for exact half-occupancy of *X*(4) by Ca, the usual situation for vesuvianite (Groat *et al.*

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN BORON-BEARING VESUVIANITE V56

B (apfu)		Neutron	X-ray
Z(1)–O(1)a	x4	1.6343(9)	1.638(3)
<*Z*(1)–O(1)>		1.6343	1.638
O(1)a–*Z*(1)–O(1)s	x4	111.54(3)	111.5(1)
O(1)a–*Z*(1)–O(1)n	x2	105.40(6)	105.1(2)
<O–*Z*(1)–O>		109.49	109.4
Z(2)–O(2)b		1.629(2)	1.632(3)
Z(2)–O(3)c		1.624(2)	1.627(3)
Z(2)–O(4)b		1.675(3)	1.667(3)
Z(2)–O(7*A*)b		1.673(3)	1.681(6)
Z(2)–O(7*B*)b		1.666(2)	1.645(6)
<*Z*(2)–O,O(7*A*)>		1.650	1.652
<*Z*(2)–O,O(7*B*)>		1.649	1.643
O(2)b–*Z*(2)–O(3)c		113.54(6)	113.7(1)
O(2)b–*Z*(2)–O(4)b		101.31(8)	101.3(1)
O(2)b–*Z*(2)–O(7*A*)b	x½	117.1(1)	117.3(2)
O(2)b–*Z*(2)–O(7*B*)b	x½	106.6(1)	106.1(2)
O(3)c–*Z*(2)–O(4)b		113.75(9)	113.8(1)
O(3)c–*Z*(2)–O(7*A*)b	x½	98.3(1)	98.7(2)
O(3)c–*Z*(2)–O(7*B*)b	x½	115.4(1)	115.7(2)
O(4)b–*Z*(2)–O(7*A*)b	x½	113.58(1)	112.9(2)
O(4)b–*Z*(2)–O(7*B*)b	x½	104.9(1)	104.9(2)
<O–*Z*(2)–O>		109.4	109.4
Z(3)–O(5)d		1.628(2)	1.619(3)
Z(3)–O(6)e		1.611(2)	1.607(3)
Z(3)–O(8)d		1.629(2)	1.619(3)
Z(3)–O(9)		1.664(1)	1.664(2)
<*Z*(3)–O>		1.633	1.627
O(5)d–*Z*(3)–O(6)e		112.20(9)	112.0(1)
O(5)d–*Z*(3)–O(8)d		114.29(9)	114.4(1)
O(5)d–*Z*(3)–O(9)		106.97(7)	107.0(1)
O(6)e–*Z*(3)–O(8)d		107.16(8)	107.5(1)
O(6)e–*Z*(3)–O(9)		107.29(8)	107.0(2)
O(8)d–*Z*(3)–O(9)		108.68(8)	108.6(1)
<O–*Z*(3)–O>		109.43	109.4
Y(1)–O(6)q	x4	2.075(1)	2.076(3)
Y(1)–O(10)g		2.235(5)	2.283(11)
<*Y*(1)–O>		2.107	2.117
Y(2)–O(8)	x2	1.8996(9)	1.902(2)
Y(2)–O(11)	x2	1.939(1)	1.929(3)
Y(2)–O(4)d	x2	1.932(10)	1.939(2)
<*Y*(2)–O>		1.924	1.923
Y(3)–O(1)		1.964(1)	1.962(3)
Y(3)–O(2)		1.929(1)	1.933(3)
Y(3)–O(3)		2.065(1)	2.066(3)

TABLE 3. continued

		Neutron	X-ray
Y(3)–O(4)h		2.062(1)	2.062(3)
Y(3)–O(5)		2.043(1)	2.053(3)
Y(3)–O(11)		2.009(2)	2.002(3)
<*Y*(3)–O>		2.012	2.013
X(1)–O(1)a	x4	2.3342(9)	2.331(3)
X(1)–O(2)a	x4	2.4957(10)	2.498(3)
<*X*(1)–O>		2.4150	2.415
X(2)–O(1)i		2.482(2)	2.488(3)
X(2)–O(2)		2.405(2)	2.403(3)
X(2)–O(3)b		2.379(2)	2.383(3)
X(2)–O(4)		2.474(2)	2.476(3)
X(2)–O(5)		2.422(2)	2.425(3)
X(2)–O(5)i		2.341(2)	2.339(3)
X(2)–O(8)d		2.354(2)	2.362(2)
<*X*(2)–O>		2.408	2.411
X(3)–O(3)j		2.390(2)	2.384(3)
X(3)–O(6)p		2.400(2)	2.404(3)
X(3)–O(6)l		2.797(2)	2.801(3)
X(3)–O(7*A*)j	x½	2.641(3)	2.653(6)
X(3)–O(7*B*)j	x½	2.601(3)	2.618(6)
X(3)–O(7*A*)m	x½	2.558(3)	2.570(6)
X(3)–O(7*B*)m	x½	3.054(3)	3.064(6)
X(3)–O(7*A*)b	x½	2.450(3)	2.435(6)
X(3)–O(7*B*)b	x½	2.465(3)	2.492(6)
X(3)–O(8)k		2.500(2)	2.505(3)
X(3)–O(10)n	x½	2.607(2)	2.614(2)
X(3)–O(11)j	x½	2.560(2)	2.558(3)
X(3)–O(12)j		2.226(8)	2.247(13)
X(3)–O(12)c		2.301(8)	2.300(13)
X(3)–O(12)m		2.646(8)	2.674(13)
X(4)–O(6)q	x4	2.326(2)	2.329(3)
X(4)–O(9)f	x4	2.629(2)	2.628(3)
<*X*(4)–O>		2.478	2.479
T(1)–O(7*A*)	x2	2.113(3)	2.084(7)
T(1)–O(11)	x2	1.479(2)	1.500(3)
T(1)–O(7*B*)	x2	1.646(3)	1.634(7)
<*T*(1)–O>		1.562	1.567
T(2)–O(10)r		1.383(4)	1.345(11)
T(2)–O(12)	x2	1.341(7)	1.309(13)

Equivalent positions: a: 1+*x*, *y*, *z*; b: ½+*y*, $\bar{x}$, $\bar{z}$; c: 1/2–*x*, ½–*y*, *z*; d: $\bar{y}$, $\bar{x}$, 1/2+*z*; e: –1+*x*, 1/2–*y*–1, 1/2–*z*; f: *y*, *x*, ½–*z*; g: *x*, ½–*y*–1, ½–*z*; h: ½–*x*–1, *y*, 1/2–*z*; i: 1+*x*, 1+*y*, *z*; j: *x*, *y*, *z*–1; k: $\bar{y}$, $\bar{x}$, ½+*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: ½–*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*.

1992). The site population was thus assigned as 1.0 Ca *apfu*.

The T sites

As found by Groat *et al.* (1994b), the total refined X-ray scattering from the *T* sites (Fig. 1) significantly exceeds that possible from the B content of the crystal, and hence the *T* sites must contain other cations in addition to B. The total refined X-ray scattering at *T*(1) and *T*(2) is 24.6(2) *epfu*, whereas the effective X-ray scattering from the analyzed B content of the crystal determined by chemical analysis is 13.7 *epfu*. The refined X-ray scattering at the *T*(1) and *T*(2) sites is equal to the X-ray scattering that would occur if these sites were completely occupied by B. It would be very easy to conclude that the *T*(1) and *T*(2) sites are completely occupied by B if only the X-ray site-

TABLE 4. REFINED SITE-SCATTERING AND SITE OCCUPANCIES IN BORON-BEARING VESUVIANITE V56

	X-ray Site-Scattering*	Neutron Scattering-Length
T(1)	19.9(2)	0.362(8)
T(2)	4.7(1)	0.112
Y(1)	25.5(1)	–
Y(2)	52	–
Y(3)	121.7(8)	–
X(4)	20.8(3)	–
	X-ray Site-Occupancy	**Neutron Site-Occupancy**
O(7*A*)	0.47(2)	0.43(1)
O(7*B*)	0.53	0.57
	X-ray Site-Population⁺	**Neutron Site-Population⁺**
O(10)	1.20(4)	1.10(2)
O(12)	1.58(4)	1.80(2)

* values given in *epfu* (electrons per formula unit);
⁺ values given in *apfu* (atoms per formula unit)

TABLE 5. ASSIGNED CATION SITE-POPULATIONS IN BORON-BEARING VESUVIANITE

Site	Site population (*apfu*)
Y(1)	1.00 Fe*
Y(2)	4.00 Al*
Y(3)	6.31 Al* + 1.69 Fe*
T(1)	1.73 B + 0.73 Al
T(2)	1.00 B

*Fe = Fe^{2+} + Fe^{3+} + Mn + Ti; Al = Al + Mg

scattering results were taken into account. However, the following points show that this conclusion must be wrong: (1) the results of the neutron site-scattering refinement are not compatible with complete occupancy of *T*(1) and *T*(2) by B; (2) the B content of the crystal resulting from complete occupancy of *T*(1) and *T*(2) by B (= 5 B *apfu*) is not in agreement with the analytically determined B value; (3) the vesuvianite structure cannot accommodate 15+ additional charges that a B content of 5 *apfu* would require; (4) the local stereochemistry around both the *T*(1) and *T*(2) sites is incompatible with complete occupancy of these

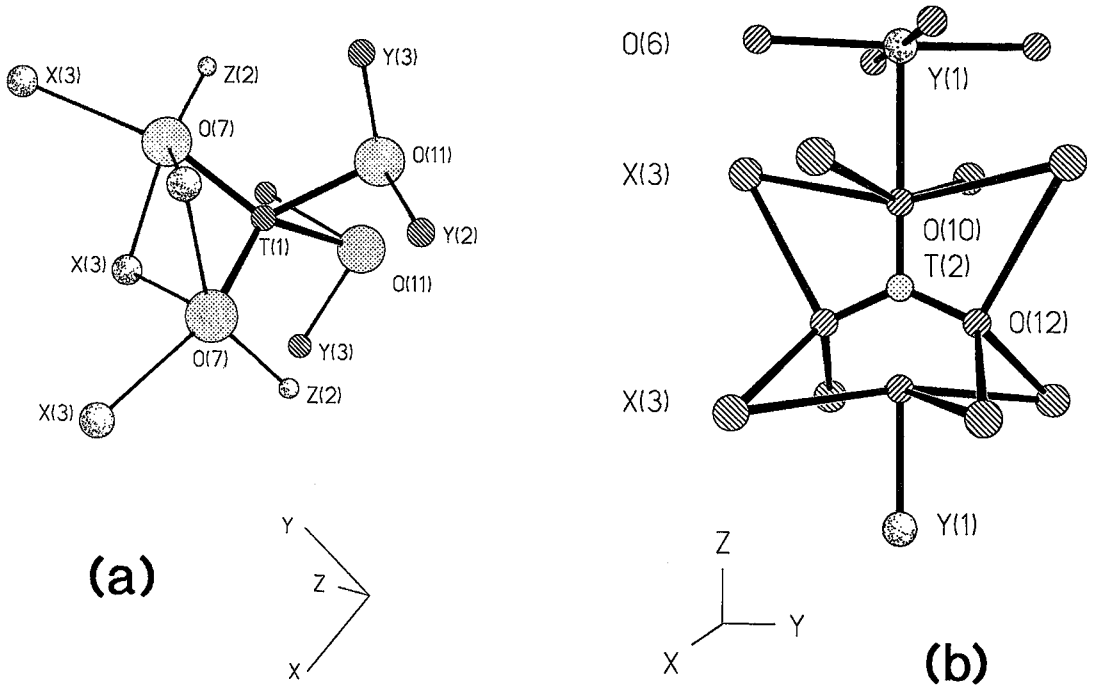

FIG. 1. The local environments of the occupied *T*(1) and *T*(2) sites in B-bearing vesuvianite: (a) *T*(1); (b) *T*(2).

two sites by B. *This emphasizes the importance of combining the results of chemical and crystal-chemical analysis with the results of crystal-structure refinement* in trying to characterize the structural chemistry of complex minerals.

Groat *et al.* (1994a) have shown that the *T*(1) site (Fig. 1a) can be occupied by Al and Fe^{3+} in both B-free and B-bearing vesuvianite crystals. The sum of the *Y*-type cations is 14.16 *apfu*; *as there are only 13 Y sites pfu, this leaves an excess of 1.16 apfu* to be accommodated elsewhere in the structure. The Si content of this crystal is 17.57 *apfu*, leaving 0.43 *Z* sites *pfu* to be filled by Al. This leaves an excess of 1.16 – 0.43 = 0.73 *Y*-type cations to be accommodated elsewhere in the structure; as the *T*(1) and *T*(2) sites are the only other possible occupied sites, the excess *Y*-type cations (Al and Fe^{3+}) *must* be accommodated at these sites. Is the observed scattering in accord with this occupancy? If the 0.73 *Y*-type cations are assigned as Al, this produces a total X-ray scattering at the *T* sites of 0.73 ± 13 (= Al) + 2.73 ± 5 (= B) = 23.2 *epfu*, in reasonable accord with the observed X-ray *and* neutron *T*-site scattering (Table 4). Thus the refined scattering at the *T* sites is in accord with both the analyzed B content of the crystal and the amount of excess *Y*-type cations indicated by the chemical analysis (Table 1).

The O sites

These sites are occupied only by O or F, and hence the occupancies can be directly expressed in terms of O (≡ O + F) as site populations in *apfu* (Table 4).

O(7) sites: Site-scattering refinement converged to the following occupancies for the O(7A) and O(7B) sites: X-ray: 0.47(2) and 0.53 O; neutron: 0.43(1) and 0.57 O, respectively. These results are in accord with the results of Groat *et al.* (1994b) on vesuvianite crystals of comparable B content.

O(10) and O(12) sites: Site-scattering refinement converged to the values of Table 4. The total anion content of the O(10) and O(12) sites is 2.78 *apfu* from the X-ray refinement and 2.90 *apfu* from the neutron refinement, for an average value of 2.84 *apfu*. In B-free vesuvianite, the O(10) site is complete occupied (= 2 *apfu*) and the O(12) site is vacant for a sum of 2 O atoms *pfu*. Note that the additional 0.84 anions *pfu* in vesuvianite V56 have two functions: (1) they help compensate for the additional positive charge in the structure due to the *T* cations, and (2) they coordinate cations at the *T*(2) site.

Stereochemical Relations: The T(2) Site

The *T*(2) site is adjacent to the O(10) and O(12) sites (Fig. 1b), and the refined populations of the O(10) and O(12) sites, together with their geometrical relations, provide constraints on the possible coordination of the *T*(2) cations.

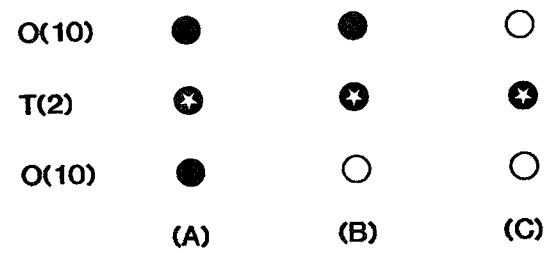

FIG. 2. Possible short-range configurations about the *T*(2) site (circled star) in boron-bearing vesuvianite: (A) both adjacent O(10) sites occupied by O (black circles); (B) one adjacent O(10) site occupied by O, the other is vacant (hollow circle); (C) both adjacent O(10) sites vacant.

The O(10) site

There are two O(10) sites locally associated within the channel (Fig. 1b), and this pair of sites can have three short-range configurations: (A) both sites are occupied, (B) one site is occupied, and (C) neither site is occupied (Fig. 2). The sum of the short-range configurations within the crystal gives the long-range site-occupancy, which is 1.15 O + 0.85 □ for this crystal. As the O(10) site-population exceeds 1.0 O *apfu*, there *must* be arrangements of type (A) present, and hence we can identify two end-member situations: (1) 0.58 (A) + 0.42 (C); (2) 0.15 (A) + 0.85 (B). This means that between 0.15 and 0.58 of the *T*(2) site must be [2]-coordinated by O(10).

The O(12) site

The O(10) and O(12) sites are separated by 1.44(1) Å when they are at the same level in the channel, and hence O(10) and O(12) sites locally associated at the same level *cannot* be simultaneously occupied. This means that we may calculate the number, N, of occupied O(12) sites for the two end-member situations (1) and (2), using the refined site-population for O(12). For situation (1), there are 0.42 configurations of type C, and hence 0.42 ± *N* = 1.69, giving *N* = 4(4.0); for (2), there are 0.85 configurations of type B, and hence 0.85 ± *N* = 1.69, giving *N* = 2(2.0). Thus situation (1) would give rise to 0.58 *T*(2) coordinated by two O(10) anions and 0.42 *T*(2) coordinated by four O(12) anions; situation (2) would give rise to 0.15 *T*(2)

coordinated by two O(10) anions and 0.85 *T*(2) coordinated by one O(10) and two O(12)anions. The observed *T*(2)–O distances (Table 3) are not compatible with tetrahedral coordination, and hence we can discount any significant component of situation (1) in this crystal (as this requires [4]-coordination for 0.42 of the *T*(2) cations). *The refined site-populations (and mean T(2)–O bond lengths) of O(10) and O(12) are only compatible with 0.15 [2]-coordination [by 2 ± O(10)]+ 0.85 [3]-coordination [by O(10) and 2 ± O(12)] for the* *T*(2) site.

Occupancy of the T(2) site

The refined X-ray site-scattering at the *T*(2) site is 4.7(1) *epfu* (Table 4), a value compatible with complete occupancy of the *T*(2) site by B. A key result of the current neutron refinement is that there is no H at the *H*(2) site, between the two O(10) sites. Hence in *every* local configuration in the channel, the bond-valence requirements of the O(10) anion must be satisfied by the incident bond-valence from four Ca atoms at *X*(3), the *Y*-group cation at *Y*(1), and the cation at the *T*(2) site. Groat *et al.* (1994b) showed that the *X*(3) and *Y*(1) cations contribute between 1.00 and 1.33 *vu* (valence units) to the O(10) anion, and this is also the case for the crystal examined here. As there is no H associated with O(10) in this crystal, the O(10) anion can be F^- or O^{2-}. If there is F at an O(10) site, there *must* be a vacancy at the adjacent *T*(2) site, and hence F at the other O(10) site in that local configuration. As the F content of the crystal is 0.65 *apfu*, this would give 0.33 [F–$T(2)$□–F] configurations and 0.67 [O–*T*(2)–O] configurations; to produce the refined site-scattering at *T*(2), this would require 0.50B +0.17Al at *T*(2). The <*T*(2)–O> distances do not seem compatible with occupancy of *T*(2) by Al, and there is no correspondence between the coordination numbers around *T*(2) and those expected for Al; hence we discount this possibility.

The alternative situation is that O(10) is occupied only by O^{2-} and □, and the bond-valence requirements of O(10) thus constrain the *T*(2) site to be completely occupied by B; note that this is in accord with the refined site-scattering the *T*(2) site. Thus the *T*(2) site consists of 0.15 $^{[2]}$B and 0.85 $^{[3]}$B. Groat *et al.* (1994b) suggested that the *T*(2) site is triangularly coordinated if occupied by B. We note that this is almost the case for the vesuvianite crystal examined here, as complete occupancy of *T*(2) by triangularly coordinated B would give the site populations O(10) = 1.0 *apfu* and O(12) = 2.0 *apfu*, in fairly close agreement with the refined site-populations (particularly considering the uncertainty in the site-scattering values (Table 4).

We may represent the general situation for coordination of *T*(2) by O(10) and O(12) as shown in Figure 3. Triangular coordination around *T*(2) requires O(10) + O(12) = 3 *apfu*, whereas [2]-coordination

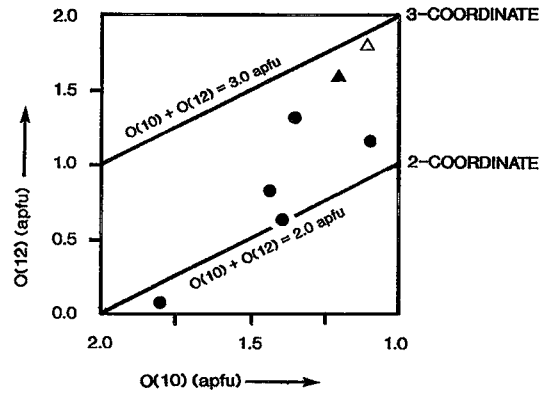

FIG. 3. Variation in O(10) and O(12) site-populations in vesuvianite crystals from Groat *et al.* (1994) (black circles) and for V56 (X-ray value: solid triangle; neutron value: hollow triangle). At O(10) = 2, O(12) = 0 *apfu*, the *T*(2) site has linear [2]-coordination; at O(10) = 1 *apfu*, the *T*(2) site has the following coordinations: O(12) = 1 *apfu*: bent [2]-coordination; O(12) = 2 *apfu*: triangular coordination; O(12) = 3 *apfu*: tetrahedral coordination. The observed site-populations for all B-bearing vesuvianite crystals are compatible with [2]- and [3]-coordination at the *T*(2) site.

requires O(10) + O(12) = 2 *apfu*. Note that we can read the coordinations of the *T*(2) site directly from this graph. For example, V56 lies just below the O(10) + O(12) = 3 curve; hence, a small proportion of the *T*(2) sites is [2]-coordinated, and most sites have triangular coordination. The refined O(10) and O(12) site-populations for B-bearing vesuvianite crystals show a range of distribution, indicating that B is incorporated at the *T*(2) site in a variety of coordinations.

Comparison of X-ray and neutron-refinement models

The structural details from the X-ray refinement and the neutron refinement are very similar, except for the environment of the *T*(2) site. As the X-ray data were collected at room temperature and the neutron data were collected at 15 K, the differences in the two models represent the effect of variable temperature on the structure. Some of the differences are undoubtedly due to the difficulty of fitting the rather complex distribution of channel density to a structure model involving disordered and partly occupied sites with small interatomic separations (in an averaged unit-cell). Nevertheless, some of the differences (and similarities) do seem significant. The neutron refinement indicates an ordered occupancy of *T*(2) by B, with only isotropic displacements. Although the

displacement model for $T(2)$ in the X-ray refinement was fixed (at a somewhat arbitrary value), the refined occupancy is again consistent with complete occupancy of $T(2)$ by B.

The O(12) sites have significantly different coordinates in the two models, and it is notable that the O(10) site has a much longer and more anisotropic displacement in the X-ray model. Presumably this denotes increased disorder in the room-temperature (X-ray) structure, resulting from larger thermal displacements. However, despite the differences in the two models in the vicinity of the $T(2)$ site, the general crystal-chemical interpretation is unaffected.

Stereochemical Relations: The T(1) Site

The $T(1)$ site is tetrahedrally coordinated by anions at the O(7B) and O(11) site (Fig. 1a). When the occupancies of the O(7A) and O(7B) sites were varied during refinement of the X-ray and neutron data, the occupancies converged to 0.47(2) and 0.53, and 0.43(1) and 0.57, respectively. For the purposes of stereochemical argument, we will use the values from the neutron refinement, as they are more precise (although statistically equivalent to the corresponding X-ray values). From the observed $T(1)$–O(7*A*) and $T(1)$–O(7*B*) distances (Table 3), we may conclude that O(7*A*) is associated with a vacancy at $T(1)$, and O(7*B*) is associated with an occupied $T(1)$ site. Hence the refined O(7*B*) occupancy also indicates the fractional occupancy of the $T(1)$ site by atoms.

The local stereochemistry around the $T(2)$ site is incompatible with occupancy of $T(2)$ by Al or Fe, and hence all of the "excess" *Y*-type cations (Groat *et al.* 1994a) must be accommodated at the *Z* sites (0.43 *apfu*) and at the $T(1)$ site (0.73 *apfu*). This means that we must assign the following cations to the $T(1)$ site: 0.73 Al *apfu*; 1.73 B *apfu* (*i.e.*, total B – $^{T(2)}$B). These site populations give an effective scattering value at $T(1)$ of 0.73 ± 13 + 1.73 ± 5 = 18.1 *epfu*. The refined scattering at the $T(1)$ site is 19.9 *epfu*, to be compared with 18.1 *epfu* from the excess *Y*-type cations and the B not resident at $T(2)$. This value of 18.1 *epfu* can be increased to 19.9 *epfu* by assigning 0.11 Fe to the excess *Y*-type cations. The assigned occupancy of the $T(1)$ site is (0.73 + 1.73)/4 = 0.61, to be compared with 0.57(1) at the coordinating O(7B) site. We regard this as adequate agreement for the proposed short-range-order configuration, considering the amount of positional and chemical disorder in the structure. The assigned $T(1)$ and $T(2)$ site-populations are given in Table 5. The <$T(1)$–O> distance should be compatible with the site population given in Table 5. Assuming ideal <$^{[4]}$B–O>, <$^{[4]}$Al–O> and <$^{[4]}$Fe^{3+}–O> distances of 1.47, 1.76 and 1.86 Å, respectively, the assigned site-populations predict a <$T(1)$–O> distance of (1.73 ± 1.47 + 0.62 ± 1.76 + 0.11 ± 1.86)/(1.73 + 0.62 + 0.11) = 1.56 Å, in agreement with the values of 1.56 and 1.57 Å derived from structure refinement (Table 3).

A $T(1)$ occupancy of 0.61 atoms (*versus* 0.39 □) requires an O(7*B*) occupancy of 0.61 atoms, in agreement with the refined occupancy of 0.57(1) O atoms. In turn, the O(7*A*) occupancy of 0.39 O atoms implies an $H(1)$ occupancy of 0.39 H atoms in order to maintain the usual H-bond interaction between the OH and O(7) atoms that is operative in the absence of $T(1)$ cations (Yoshiasa & Matsumoto 1986, Groat *et al.* 1992a, b). The analyzed H content of sample V56 is ~3 H *apfu* (Table 1), which gives an $H(1)$ occupancy of 0.38 H atoms [given that the neutron refinement shows the $H(2)$ site to be unoccupied in this crystal], in close agreement with the above reasoning. The refined $H(1)$ occupancy of 0.25(2) H atoms is somewhat less than the analytical value of 0.38 H atoms. The H atom is very well-behaved in the neutron structure-refinement (*i.e.*, the displacement parameter is quite isotropic), and the refined occupancy should be accurate. Possibly the discrepancy (which is small compared with the total range of H content observed in vesuvianite: Groat *et al.* 1992) results from inhomogeneity of the sample used. However, despite this discrepancy in the two H contents, their values are in reasonable accord with the occupancy model for the $T(1)$ site developed here.

The Y(1) Site

When the $T(2)$ site is unoccupied, the incident bond-valence at O(10) is 1.33 *vu* + the contribution from $H(1)$ (Groat *et al.* 1994b); thus occurrence of B in tetrahedral coordination at $T(2)$ brings the bond-valence incident at O(10) to 1.33 + 0.75 = 2.08 *vu*. Where B is linearly coordinated at $T(2)$, it *must* contribute 1.5 *vu* to each of the coordinating O(10) anions. Each O(10) anion is also coordinated to four $X(3)$ Ca cations with a total incident bond-valence of 0.159 ± 4 = 0.63 *vu*. Thus each O(10) in this configuration receives 0.63 + 1.50 = 2.13 *vu* from the coordinating $X(3)$ and $T(2)$ cations, and *hence cannot have a significant* bonding interaction with the adjacent $Y(1)$ cation. Examination of the anisotropic-displacement parameters (Table 2) for $Y(1)$ shows very anisotropic displacement, with the large amplitude in the [001] direction, and a similar elongation of electron density is apparent at the O(10) site. Refinement of a split-site model for the X-ray data resulted in $Y(1)$–O(10) distances of 2.24 and 2.61 Å, respectively; it is stereochemically reasonable to associate the former with [4]-coordinated B at $T(2)$, and the latter is associated with [2]-coordinated B at $T(2)$. Note that the latter configuration also requires square-planar coordination of the $Y(1)$ cation (which site-scattering refinement shows to be Fe); a Mössbauer study is planned to test this point.

The Substitution of B at the T(2) Site

We may write a different substitution reaction for each coordination number of B at the *T*(2) site:

[2] $^{T(2)}B \rightarrow {}^{H(2)}H$ charge increase: 2^+

[3] $^{T(2)}B + {}^{O(10)}\square + {}^{O(12)}O_2 \rightarrow {}^{H(2)}H + {}^{O(10)}O + {}^{O(12)}\square_2$ charge increase: 0

This provides the structure with a very flexible mechanism for satisfying long-range electroneutrality that can act in conjunction with the mechanism proposed by Groat *et al.* (1992, 1994b): B + Mg → 2H + Al.

Summary

The results of this work generally confirm those of Groat *et al.* (1992, 1994b) on the mechanisms of incorporation of B into the vesuvianite structure. In addition, we have clarified the stereochemical details of B at the *T*(2) site in the channel region of the structure.

(1) The neutron structure refinement shows that there is no H at the *H*(2) channel site.

(2) As there is no H at *H*(2), the *T*(2) site must be completely occupied to satisfy the local bond-valence requirements at the O(10) anion.

(3) The refined site-scattering at *T*(2) indicates that this site can only be completely occupied by B.

(4) The refined site-populations of O(10) and O(12) are only compatible with 0.15 [2]-coordination and 0.85 [3]-coordination of the *T*(2) site. Thus there is both linear [2]-coordinated B and triangularly coordinated B at the *T*(2) site.

(5) The flexibility in coordination number of B at the *T*(2) site provides a mechanism for charge compensation for other substitutions elsewhere in the structure of vesuvianite.

Acknowledgements

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