

THE CHEMISTRY OF VESUVIANITE

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ABSTRACT

The crystal chemistry and chemical variations in 76 vesuvianite samples from 54 different localities have been examined using electron-microprobe analyses, supplemented by analysis of selected samples for $\text{Fe}^{2+}/\text{Fe}^{3+}$, Li, Be and H_2O . Results of analyses were reduced to formula units on the basis of 50 cations excluding B. A general formula for boron-free vesuvianite can be written as $X_{19}Y_{13}Z_{18}O_{68}W_{10}$, where X are cations occupying [8]-coordinate sites, Y are cations occupying [6]- and [5]-coordinate sites, Z are cations occupying [4]-coordinate sites, and W are monovalent and divalent anions. For 388 boron-free analyses, the mean Si content is 18.0(2) a.p.f.u. (atoms per formula unit), with skew and kurtosis of -0.03 and 0.32, respectively, indicating that only Si occurs at the Z-group sites. The mean (Ca + Na + Ln + Pb + Bi + Th) content is 19.0(3) a.p.f.u., with skew and kurtosis of -0.38 and 0.22, respectively. This indicates that only these cations occupy the X-group sites. The mean (Al + Mg + Fe + Ti + Cr + Mn + Cu + Zn) content is 13.0(2) a.p.f.u., with skew and kurtosis of 0.64 and 0.87, respectively; this indicates that only these cations occupy the Y-group sites. In addition, the individual means for each group of sites support a 50-cation scheme of renormalization. This procedure is recommended for boron-free vesuvianite. The principal cationic substitutions in boron-free vesuvianite occur at the Y-group sites, and involve homovalent (e.g., $\text{Mg} \rightleftharpoons \text{Fe}^{2+}$, $\text{Al} \rightleftharpoons \text{Fe}^{3+}$) and heterovalent (e.g., $\text{Al} \rightleftharpoons \text{Ti}$, $\text{Mg} \rightleftharpoons \text{Al}$) substitutions. For $X = 2+$ and $Z = 4+$, only one heterovalent substitution can solely involve Y-group cations: $(\text{Mg} + \text{Fe}^{2+} + \text{Mn}) + \text{Ti}^{4+} \rightleftharpoons 2(\text{Al} + \text{Fe}^{3+})$. This is a significant substitution in natural vesuvianite. Vesuvianite can contain up to ~4 a.p.f.u. of B (~4 wt. % B_2O_3). The composition of boron-bearing vesuvianite is best renormalized on the basis of 19 X cations p.f.u. Boron is incorporated into vesuvianite primarily by the coupled substitution $\text{B} + \text{Mg} \rightleftharpoons 2\text{H} + \text{Al}$. Boron-bearing vesuvianite has several distinctive features that identify it in the absence of an analysis for boron. It is optically

positive, whereas boron-free vesuvianite is optically negative; the cell dimensions are distinctive, and it is characterized by low Al (+ Fe^{3+}), high Mg (+ Fe^{2+}), and low OH (+ F). The general chemical formula of vesuvianite can be written as $X_{19}Y_{13}Z_{18}T_{0-5}O_{68}W_{10}$, where $X = \text{Ca}, \text{Na}, \text{Ln}^{3+}, \text{Pb}^{2+}, \text{Sb}^{3+}$; $Y = \text{Al}, \text{Mg}, \text{Fe}^{3+}, \text{Fe}^{2+}, \text{Ti}^{4+}, \text{Mn}, \text{Cu}, \text{Zn}$; $Z = \text{Si}$; $T = \text{B}$; $W = (\text{OH}, \text{F}, \text{O})$.

Keywords: vesuvianite, electron-microprobe analyses, boron, chemical formula.

SOMMAIRE

La chimie cristalline et les variations en composition de 76 échantillons de vésuvianite de 54 localités ont fait l'objet d'une étude par microsonde électronique. Quelques-uns des échantillons ont été analysés pour $\text{Fe}^{2+}/\text{Fe}^{3+}$, Li, Be et H_2O . Les résultats d'analyses sont exprimés sous forme d'unité formulaire sur une base de 50 cations, en excluant le B. Une formule générale de la vésuvianite sans bore serait $X_{19}Y_{13}Z_{18}O_{68}W_{10}$, dans laquelle les cations X ont une coordination de 8, les cations Y occupent des sites à coordination 6 ou 5, les cations Z ont une coordination de 4, et les anions W sont monovalents ou bivalents. A la lumière de 388 compositions exprimées sans bore, la teneur moyenne en Si est 18.0(2) a.p.u.f. (atomes par unité formulaire), avec coefficients d'asymétrie et d'aplatissement de -0.03 et de 0.32, respectivement. Ce résultat montre que seul le Si occupe la position Z. La teneur moyenne en (Ca + Na + Ln + Pb + Bi + Th) est de 19.0(3) a.p.u.f., avec coefficients d'asymétrie et d'aplatissement de -0.38 et 0.22, respectivement. Ce résultat fait penser que seuls ces éléments occupent la position X. La teneur moyenne en (Al + Mg + Fe + Ti + Cr + Mn + Cu + Zn) est 13.0(2) a.p.u.f., avec coefficients d'asymétrie et d'aplatissement de 0.64 et 0.87, respectivement. Ce résultat mène à l'hypothèse que seuls ces cations occupent la position Y. De plus, les moyennes individuelles pour chaque position appuient le schéma de normalisation fondé sur 50 cations; c'est cette normalisation que nous recommandons pour toute vésuvianite sans bore. Les substitutions cationiques importantes dans la vésuvianite sans bore impliquent la position Y, et peuvent être homovalentes (e.g., $\text{Mg} \rightleftharpoons \text{Fe}^{2+}$, $\text{Al} \rightleftharpoons \text{Fe}^{3+}$), ou hétérovalentes (e.g., $\text{Al} \rightleftharpoons \text{Ti}$, $\text{Mg} \rightleftharpoons \text{Al}$). Dans le cas où X a une charge 2+, et

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INTRODUCTION

Z, 4+, une seule substitution hétérovalente peut impliquer uniquement les cations du groupe Y: $(Mg + Fe^{2+} + Mn) + Ti^{4+} \approx 2(Al + Fe^{3+})$. Cette substitution est importante dans la vésuvianite naturelle. Ce minéral peut aussi contenir jusqu'à 4 a.p.u.f. de B (environ 4% de B_2O_3 par poids). Pour la vésuvianite borifère, la normalisation se fait sur la base de 19 cations du groupe X. Le bore participe à une substitution couplée: $B + Mg \approx 2H + Al$. La vésuvianite borifère possède plusieurs traits distinctifs qui permettent de l'identifier même en l'absence d'une détermination de sa teneur en bore. Elle est optiquement positive, tandis que la vésuvianite sans bore est négative. Les dimensions de la maille sont distinctes, et elle possède des faibles teneurs en Al (et Fe^{3+}) et OH (et F), et des teneurs élevées en Mg (et Fe^{2+}). La formule chimique générale de la vésuvianite serait $X_{19}Y_{13}Z_{18}T_{0-5}O_{68}W_{10}$, dans laquelle X correspond à Ca, Na, Ln^{3+} , Pb^{2+} et Sb^{3+} , Y, à Al, Mg, Fe^{3+} , Fe^{2+} , Ti^{4+} , Mn, Cu, et Zn, Z, à Si, T, à B, et W, à (OH, F et O).

(Traduit par la Rédaction)

Mots-clés: vésuvianite, données à la microsonde électronique, bore, formule chimique.

Vesuvianite ("idocrase") is a rock-forming or accessory silicate mineral found in skarns, rodingites, and altered alkali syenites. It has long been the least understood of all the rock-forming minerals. The true symmetry is unclear, and some details of the crystal structure are unresolved. Numerous chemical formulae have been proposed, but none has yet been shown to be of general applicability. These uncertainties are complicated by the diverse range of conditions under which vesuvianite forms in nature, with consequent variations in habit, chemistry and paragenesis. Although there has been considerable progress on many of these points over the last 10 years, significant uncertainties still remain, and an extensive examination of vesuvianite from a large number of localities seems justified.

There have been a number of different schemes of nomenclature proposed for the atomic positions

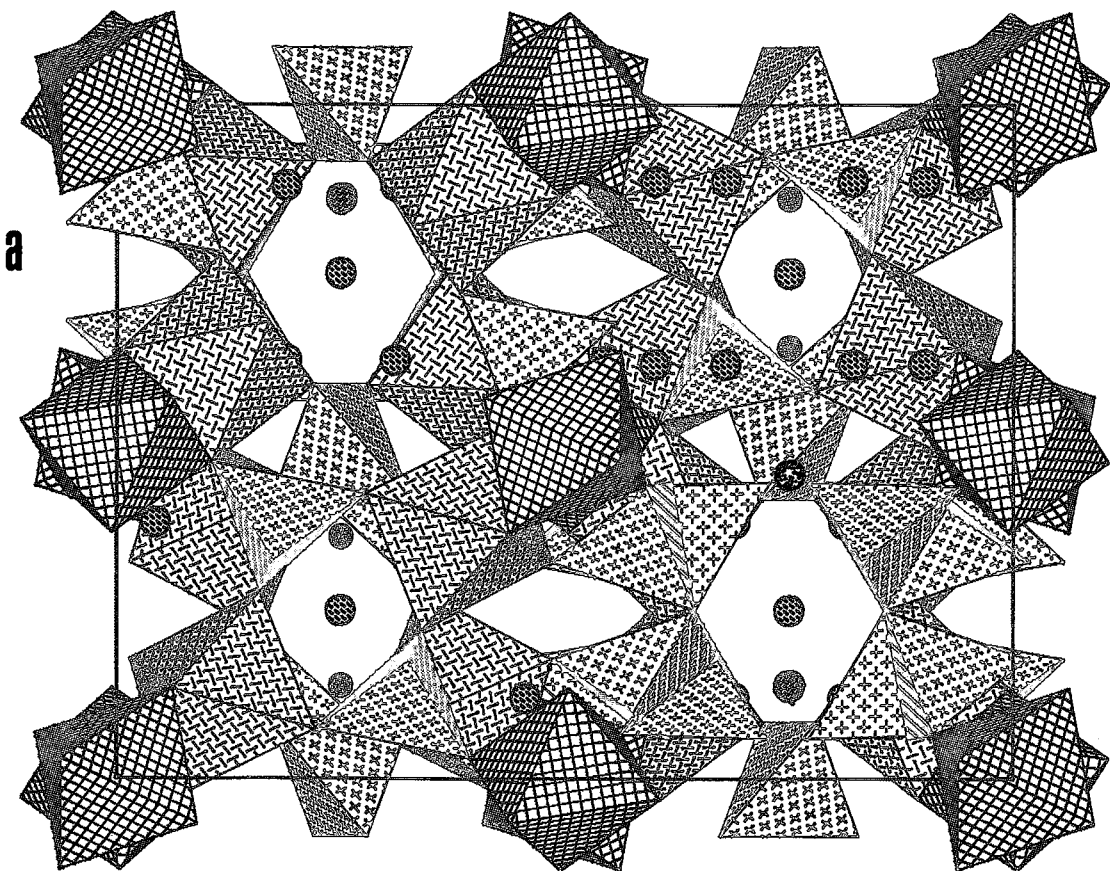
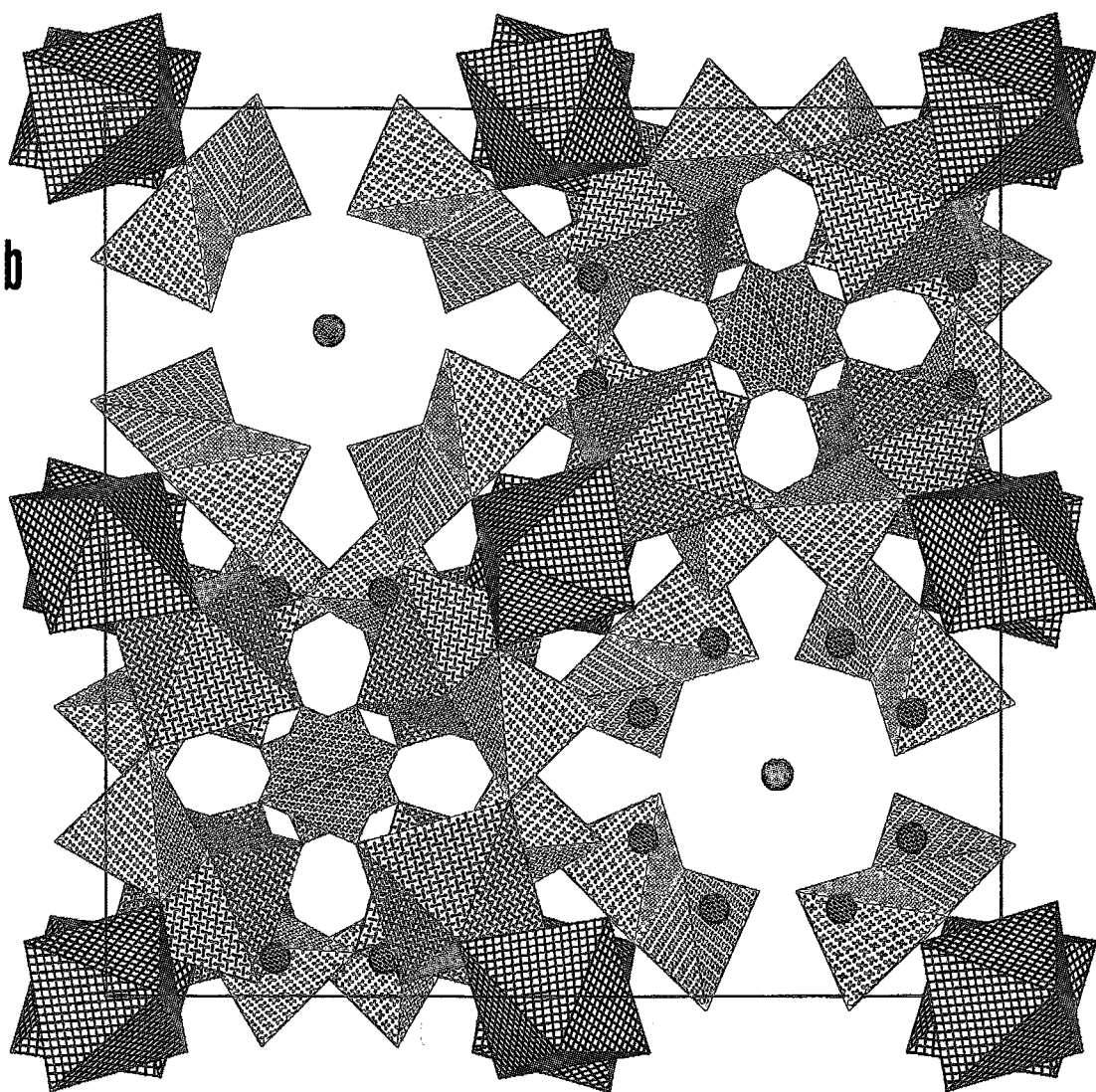


TABLE 1. SITE NOMENCLATURE FOR VESUVIANITE

This Study	Warren & Modell (1931)	Coda <i>et al.</i> (1970)	Rucklidge <i>et al.</i> (1975)	Giuseppetti & Mazzi (1983)
Z(1)	Si ₁	Si(1)	Si(1)	Si(1)
Z(2)	Si ₂	Si(2)	Si(2)	Si(2)
Z(3)	Si ₃	Si(3)	Si(3)	Si(3)
X(1)	Ca ₁	Ca(1)	Ca(1)	Ca(1)
X(2)	Ca ₂	Ca(2)	Ca(2)	Ca(2)
X(3)	Ca ₃	Ca(3)	Ca(3)	Ca(3)
X(4)	Ca ₄	Ca(4)	C	Ca(4)
Y(1)	-	B	B	M(3)
Y(2)	Al	A	A	M(1)
Y(3)	(Mg, Fe)	Al	AlFe	M(2)
OH	OH	O(11)	OH	O(11)

in vesuvianite. Here, we propose a new nomenclature of sites that is more conformable with that for other rock-forming silicate minerals. This is given in Table 1, along with equivalent positions from previous studies.

FIG. 1. (a) Projection of the vesuvianite structure down [100]; (b) projection of the vesuvianite structure down [001]. The Y(2) octahedra are blue, the Y(3) polyhedra are green, and the Z(1), Z(2) and Z(3) tetrahedra are red. The blue spheres represent the X(1), X(2) and X(3) cations. The purple, black and green spheres represent X(4), Y(1) and O(10) ions, respectively.



PREVIOUS WORK

The crystal structure of vesuvianite (Fig. 1) was solved by Warren & Modell (1931). They showed that it is closely related to that of grossular, but with additional atoms on the fourfold axes. Their basic structure has $P4/nnc$ symmetry, and consists of rods of the garnet structure separated by channels along Z . Two Ca atoms were placed along this channel, each coordinated by oxygen arranged at the vertices of face-sharing square antiprisms.

Coda *et al.* (1970) confirmed the basic validity of the Warren-Modell model, but discovered an additional oxygen atom on the fourfold axis that runs down the center of the prominent channels. They suggested that this O(10) is a hydroxyl group, and presented a single-crystal infrared-absorption spectrum to support this assignment. These authors also focused their attention on the arrangements of Ca and Fe atoms down the fourfold axis. Their structural refinement showed that the channel Ca position, here designated X(4), is only half-occupied. This is in accord with the short X(4)-X(4) distance of $\sim 2.8 \text{ \AA}$, which suggests that only one of this pair of sites can be occupied by Ca in any particular instance. Thus there is local order associating Ca at X(4) with a vacancy at the adjacent X(4) site. They also identified another

cation position, Y(1), on the fourfold axis, half-occupied by (Fe, Mg). The Y(1)-X(4) distance is $\sim 1.4 \text{ \AA}$. This distance is too short for the simultaneous occupancy of adjacent Y(1) and X(4) positions, and again a situation of local order must prevail whereby occupancy of one X(4) position must be accompanied by a vacancy at the adjacent Y(1) site (Fig. 2).

Rucklidge *et al.* (1975) confirmed the basic results of Coda *et al.* (1970) on three crystals of vesuvianite from Great Slave Lake, N.W.T., Bancroft, Ontario, and Wakefield, Quebec. Further $P4/nnc$ refinements of vesuvianite are given by Allen & Burnham (1983a), Valley *et al.* (1985), Yoshiasa & Matsumoto (1986), and Fitzgerald *et al.* (1986a). Some recent studies (Giuseppetti & Mazzi 1983, Allen & Burnham 1983b, Allen 1985, Fitzgerald *et al.* 1986b, 1987) have shown that cation ordering at the Y(1) and X(4) sites can reduce the symmetry of vesuvianite to $P4/n$, a subgroup of the normal $P4/nnc$ space group. However, the reasons for such ordering are not clear.

These structural ambiguities, coupled with the wide range of possible substitutions, have made it difficult to determine an adequate general formula for vesuvianite. This has important ramifications for petrological studies, particularly in terms of the development of an adequate activity-model for

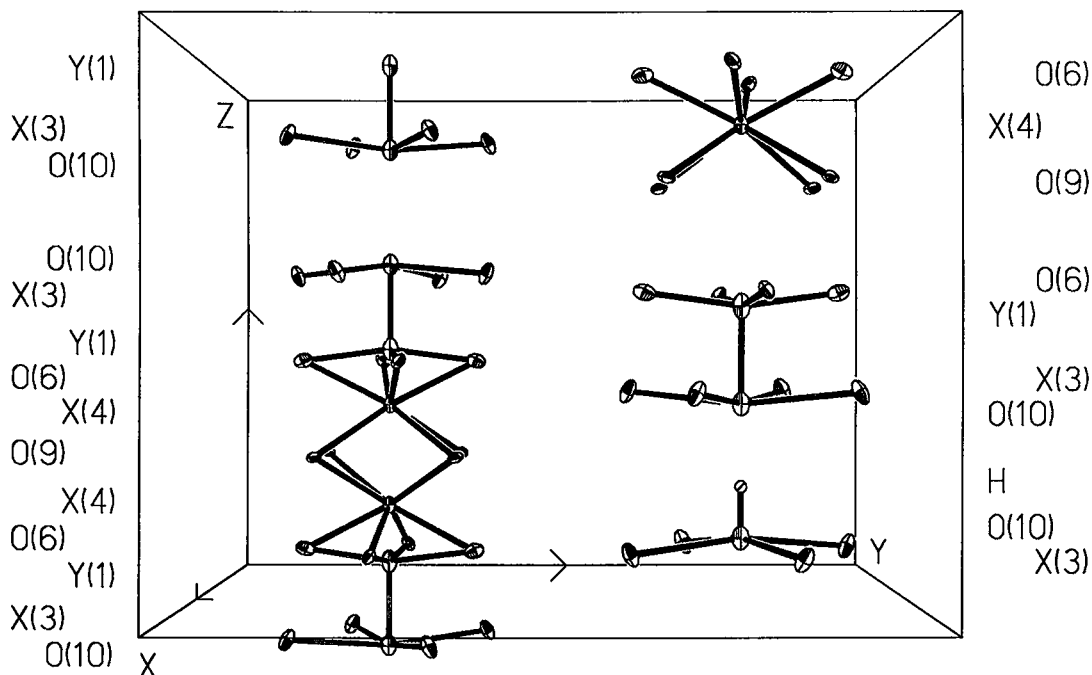


FIG. 2. Perspective view of the atomic arrangement down the channels; left: coordination with each of the Y(1) and X(4) positions occupied; right: an arrangement of singly occupied Y(1) and X(4) sites.

TABLE 2. STRUCTURAL FORMULAE PREVIOUSLY PROPOSED FOR VESUVIANITE

$4[\text{Ca}_{10}\text{Al}_4(\text{Mg}, \text{Fe})_2\text{Si}_9\text{O}_{34}\text{OH}_4]$	Warren & Modell (1931)
$2[\text{X}_{19}\text{Y}_{13}\text{Z}_{18}(\text{O}, \text{OH}, \text{F})_{78}]$ X = Ca (Na, K, Mn) Y = (Al, Fe ³⁺ , Fe ²⁺ , Mg, Ti, Zn, Mn), Z = Si	Machatschki (1932)
$4[\text{X}_{10-u}\text{Y}_{6+u}\text{Z}_6(\text{O}, \text{OH}, \text{F})_{38}]$ $u \leq 1$ X = Ca (Na, K, Mn) Y = (Al, Fe ³⁺ , Fe ²⁺ , Mg, Ti, Zn, Mn), Z = Si	Barth (1963)
$\text{Ca}_{18}(\text{Ca}_{2-x}\text{Mg}_x)\text{Mg}_2(\text{Mg}_{2-y}\text{Al}_y)\text{Al}_8(\text{Al}_y\text{Si}_{2-y})\text{Si}_{18}\text{O}_{68}(\text{OH})_8$ $0 \leq x < 1.5, 0 < y < 1.5$	Ito & Arem (1970)
$2[\text{Ca}_{19}(\text{Mg}, \text{Fe}, \text{Al}, \text{Ti}, \text{Mn})_2\text{Al}_8(\text{O}, \text{OH})_{10}(\text{SiO}_4)_{10}(\text{Si}_2\text{O}_7)_4]$	Coda <i>et al.</i> (1970)
$2[\text{Ca}_{19}\text{Fe}(\text{Fe}, \text{Ti}, \text{Mn}, \text{Mg}, \text{Al})_8\text{Al}_4\text{Si}_{18}\text{O}_{70}(\text{OH}, \text{F})_8]$	Rucklidge <i>et al.</i> (1975)
$2[\text{Ca}_{19}(\text{Al}, \text{Mg}, \text{Fe}, \text{Mn}, \text{Ti})_{13}\text{Si}_{18}\text{O}_{70}(\text{OH}, \text{F})_8]$ or $2[\text{Ca}_{19}(\text{Al}, \text{Fe})_{10}(\text{Mg}, \text{Fe})_2\text{Si}_{18}\text{O}_{70}(\text{OH})_8]$	Deer <i>et al.</i> (1982)
$2[\text{X}_{18}(\text{C}_i\text{B}_j)\text{A}_x\text{Y}_8\text{Z}_{18}(\text{O}, \text{OH}, \text{F})_{78}]$ $0 \leq i \leq 1, j = 2 - i$ X = Ca, Na, K, Fe ²⁺ , Mn Y = Al, Mg, Fe ²⁺ , Fe ³⁺ , Ca, Ti, Cr, Mn, Cu, Zn Z = Si, Al, B = Mg, Fe ²⁺ , Fe ³⁺ , Cu, Zn C = Ca, Na, Fe ²⁺ , Mn	Allen (1985)
$2[\text{Ca}_{19}\text{Al}_{11}\text{Mg}_2\text{Si}_{18}\text{O}_{68}(\text{OH})_8]$	Hoisch (1985)

thermodynamic calculations. On the basis of their crystal-structure results, Warren & Modell (1931) proposed the formula given in Table 2. However, the chemical data then available showed more (Al, Mg, Fe) and less Ca than provided for by this formula. A year later, Machatschki (1932) proposed an empirical formula based on published chemical data on vesuvianite. Barth (1963) took a similar approach, and concluded that chemical data should be normalized to a total of 38 anions. Studies on the experimental stability of vesuvianite suggested a formula based on 76 anions (Ito & Arem 1970).

Coda *et al.* (1970) and Rucklidge *et al.* (1975) suggested new formulae based on their structural data (Table 2). Both formulae have 19 X and a total of 13 Y cations, with 78 anions rather than the 76 of earlier studies. They differ only in the disposition of the 13 Y cations and in their approach to normalization procedures. Coda *et al.* (1970) recalculated their analytical data on the basis of 19 Ca ions, whereas Rucklidge *et al.* (1975) normalized their data on the basis of 18 Si ions.

Deer *et al.* (1982) tested both methods, but saw no reason to alter their usual procedure of renormalizing analytical data to the total number of anions, in this case, 78(O,OH,F). They also pointed out that the Y-group cations are undivided,

and that although the formula of Rucklidge *et al.* (1975) fits the samples studied by them, many other samples of natural vesuvianite have less than 1 Fe p.f.u. (per formula unit). As a result, Deer *et al.* (1982) proposed two general formulae for vesuvianite (Table 2).

Hoisch (1985) studied the results of Coda *et al.* (1970) and Rucklidge *et al.* (1975) and decided that data should be normalized on the basis of 50 cations p.f.u. Allen (1985) proposed a structural formula, and also suggested that analytical results should be recalculated on the basis of 50 cations and 78 anions p.f.u., charge balance being maintained by adjusting the O²⁻/OH⁻ ratio.

How well do these formulae and normalization schemes fit a large number of analytical data for vesuvianite from diverse localities? In this study, we present the results of a large number of analyses of vesuvianite from a variety of localities. This data-set allows us to evaluate all the possible formulae and normalization schemes, and examine the ranges of composition found in vesuvianite.

EXPERIMENTAL

Seventy-six samples of vesuvianite from approximately 50 different localities were examined in this study (Table 3). In most cases, there is only

TABLE 3. VESUVIANITE SAMPLES

AUSTRALIA		NORWAY	
V1	Bowling Alley Point, Nundle, N.S.W.	V47	Stromsheim, Setesdal
		V48	? ? ?
CANADA		PAKISTAN	
V2	Silence Lake mine, Raft River, B.C.	V49	Hindubagh, Baluchistan
V3	Frye's Island, Charlotte Co., N.B.		
V4	Turnback Lake, N.W.T.	SWEDEN	
V5	Long Lake mine, Olden Twp., Ont.	V50	Långban
V6	York River, Dungannon Twp., Ont.		
V7-V8	Black Lake, Megantic Co., Que.	TAIWAN	
V9	Coleraine Twp., Megantic Co., Que.	V51	Feng Tien mine
V10-V22	Jeffrey mine, Richmond Co., Que.		
V23	Laurel, Que.	U.S.A.	
V24-V26	Mt. Saint Hilaire, Que.	V52	Brooks Mountains, AK
V27	Quebec	V53	Seward Peninsula, AK
V28-V30	Templeton Twp., Ottawa Co., Que.	V54	Magnet Cove, AR
V31	Wakefield Twp., Ottawa Co., Que.	V55	Big Sandy Draw, Mohave Co., AZ
V32	Marne Claim, Y.T.	V56	Bill Waley mine, Tulare Co., CA
V33-V34	Richardson Mountains, Y.T.	V57-V58	Butte Co., CA
CZECHOSLOVAKIA		V59	El Dorado Co., CA
V35	Hazlov, near Cheb	V60	Plumas Co., CA
GREECE		V61	San Benito Co., CA
V36	Xanthi	V62	Tulare Co., CA
ITALY		V63	Italian Mountain, CO
V37	Ala Piedmont	V64-V65	Sanford, York Co., ME
V38	Ariccia, Rome	V66	Woodstock, ME
V39	Bellecombe, Aosta	V67-V68	Franklin, Sussex Co., NJ
V40	Monte Somma	V69	Ludwig, NV
JAPAN		V70	Amity, Orange Co., NY
V41	Chichibu mine, Saitama Pref.	V71	Olmstedville, Essex Co., NY
		V72	Mt. Belvidere, Eden Mills, VT
		V73	? ? ?
KENYA		U.S.S.R.	
V42	Magadi	V74	Lupikko, Fennoscandia
		V75	Wilui River, Yakutskaya A.S.S.R.
MEXICO		UNKNOWN	
V43	Cerro de Los Muertos, Chihuahua	V76	? ? ?
V44-V45	Laguna del Jaco, Chihuahua		
MOROCCO			
V46	Othuren		

*Some of these numbers differ from those of Groat (1988).

one sample per locality, although there are 13 from the Jeffrey mine (Quebec), and three each from Mont Saint-Hilaire and Templeton Township (both in Quebec). Some samples (V1, V2, V32, V51) have not been described in any previous studies.

Electron-microprobe analysis

The electron-microprobe analyses were done with a JEOL 733 instrument, equipped with one energy-dispersion (ED) spectrometer and four automated wavelength-dispersion (WD) spectrometers. All WD analyses were done with an accelerating potential of 15 kV and a sample current of 25 nA. Data on standards were collected to 0.25% precision or for 25 seconds, whichever was less. Each element was collected to 0.5% precision or for 50 seconds. The beam was intentionally defocused to a diameter of 20 μm , except for samples with fine banding, for which a 10 μm beam was used. Back-scattered electron

(BSE) imaging was routinely used to investigate compositional differences. For vesuvianite, which is made up of relatively light elements, it was possible to detect a difference of 0.5 in average Z in the back-scattered image. The ED spectrometer was used to preview spectra and to identify accessory phases.

The data were collected and reduced with the Task program by Tracor Northern, which was set up to routinely analyze for F, Na, Mg, Al, Si, S, Cl, K (later replaced by Cr), Ca, Ti, Mn, Fe and Zn, and to look for Ce. If cerium was detected, a second list of elements was used to analyze for La, Ce, Pr, Nd, Sm, Eu and Gd. Other elements (Cu, Pb, Bi, Th) were added if seen in the ED spectra, and if Th was found, U was sought as well. Boron analyses were done separately, because of a necessary (manual) change in voltage (15 to 5 kV), a change in slit width, and realignment of the column.

Data reduction was done using conventional

ZAF techniques. Rare-earth-element data were corrected for line overlaps using the methods of Roeder (1985). The following standards were used: diopside (Si), almandine (Al, Mg, Fe), titanite (Ti), willemite (Mn, Zn), synthetic nichromate (Cr), cuprite (Cu), gehlenite (Ca), riebeckite (Na, K), REE glass S-254 (La, Ce, Pr, Nd, Gd), crocoite (Pb), bismutotantalite (Bi), monazite (Th), elbaite (B), anhydrite (S), fluor-riebeckite (F) and tugtupite (Cl). The analytical data are listed to two decimal places because of low standard deviations on minor elements and low detection-limits.

Atomic absorption spectroscopy (AAS)

Analyses for Be and Li were done with a Varian AA-975 atomic absorption spectrophotometer. Samples were dissolved using a mixture of HF and HClO₄. A K buffer was added to each sample to minimize ionization of Li in air-acetylene. One vesuvianite sample (V32; Marne Claim, Y.T.) was analyzed at regular intervals to provide a measure of experimental precision. The relative standard deviation on seven analyses of V32 was 11% for Li and 6% for Be. Detection limits were ~5 ppm for Li and ~2 ppm for Be.

Determination of ferrous iron

The ferrous iron determinations were done using the modified "Pratt" titration method described by Donaldson (1982). Nitrogen was bubbled through all solutions before use to minimize sample oxidation. A number of internal standards were used, and in each case, the measured amount of Fe²⁺ was equal to the accepted value. One vesuvianite sample (V32) and one standard (SY-2) were analyzed at regular intervals to provide a measure of experimental precision. The standard deviations for eight analyses of SY-2 and V32 were 0.04 (1.10%) and 1.46 relative %, respectively.

Determination of H₂O and CO₂

The H₂O and CO₂ determinations were done with a modified LECO 521 furnace, in which each sample was heated to ~1200°C by an RF induction coil. A current of oxygen gas was passed over the sample and then to a glass bulb containing magnesium perchlorate, which selectively absorbs H₂O. A second bulb containing "ascarite" was used to trap CO₂. The amount of H₂O and CO₂ present was determined by weighing the bulbs between each analysis. The standards SY-2 and PCC-1 were analyzed at regular intervals to provide a measure of experimental precision. Five analyses of PCC-1 gave average values of 4.64(1) wt. % H₂O and 0.17 wt. % CO₂; these compare well

with the accepted values of 4.70 wt. % H₂O and 0.15 wt. % CO₂ (Govindaraju 1989). For SY-2, the averages of five determinations were 0.48(8) wt. % H₂O and 0.55(1) wt. % CO₂; the accepted values are 0.43 wt. % H₂O and 0.46 wt. % CO₂ (Govindaraju 1989).

Unit-cell dimensions

Unit-cell dimensions were determined with a Nicolet R3m single-crystal diffractometer. A random-orientation rotation photograph was taken, and the horizontal and vertical spacings of 25 reflections were used as input to the orientation routine, which aligned on 2θ, ω and χ for each reflection while keeping φ constant. The reflections were indexed, and unit-cell parameters and orientation matrix were refined using a least-squares procedure. Both constrained (tetragonal) and unconstrained cells were calculated, with the latter transformed such that a₂ was always greater than a₁.

RESULTS

A total of 464 microprobe analyses were performed on the 76 samples; results of these analyses are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. Selected results referred to in the text are given in Table 4.

A total of 39 AAS analyses for Li and Be were carried out on 30 different samples from various localities. The results (Table 4) show a maximum of 0.04 wt. % Li₂O and 0.15% wt. % BeO in the samples examined. Thus Li and Be are present in vesuvianite only in very minor amounts.

Boron was found in six of the 49 samples analyzed for B. Only a few points on each section were analyzed for B because (1) of time constraints, and (2) the points had to be analyzed manually. An average B₂O₃ value was added to the results of all other analyses from the same section.

Thirty-nine determinations of ferrous iron were done on 25 different samples. The amount of Fe³⁺ in each sample was obtained by subtracting the measured Fe²⁺ value from the (average) amount of Fe obtained from the microprobe analysis. The Fe²⁺/Fe³⁺ ratio was then used to calculate the amounts of ferrous and ferric iron present in each sample (Table 4).

Initially, H₂O was calculated by charge balance, assuming 78 anions p.f.u. and all Fe as ferrous. Because of the amount of material required (~1 g), only 22 H₂O and CO₂ analyses were carried out on 18 different samples. The amount of H₂O ranges from 0.61 to 5.37 wt. %. In most cases, the

TABLE 4. SELECTED RESULTS OF CHEMICAL ANALYSES (wt.%) OF VESUVIANITE*

	V2-2	V3-3	V6-2	V12-5	V29-7	V32-2	V33-2	V38-15	V44-7	V45-1	V50-4	V53-2	V56-3	V58-2	V61-7	V62-2	V67-3	V68-2	V68-4	V75-5
SiO ₂	37.07	37.02	36.76	37.03	36.11	35.96	37.47	35.56	36.32	36.32	35.98	34.08	35.01	36.49	32.66	35.59	35.57	36.09	35.14	35.99
Al ₂ O ₃	16.83	16.21	15.15	17.04	11.38	14.26	17.26	11.73	13.94	12.67	13.84	11.69	12.13	17.87	5.54	12.65	15.87	16.63	18.34	11.84
TiO ₂	0.71	0.00	4.67	0.52	0.65	1.66	0.69	0.95	1.74	5.06	0.00	2.80	0.43	0.00	6.85	0.63	0.05	0.05	0.00	0.93
MgO	1.72	3.90	1.26	2.17	5.63	1.67	1.80	5.21	4.89	3.79	4.15	1.83	4.84	3.01	5.03	4.81	0.91	1.19	3.47	6.59
MnO	0.35	0.00	0.00	0.06	0.19	0.36	0.80	0.17	0.06	0.06	3.80	0.20	0.13	0.00	0.28	0.09	1.97	1.23	1.42	0.06
FeO	3.49	0.20	3.19	1.42	4.58	2.91	3.16	4.96	2.09	1.68	1.27	7.43	3.67	0.05	4.58	4.14	2.40	1.41	0.27	2.30
Fe ₂ O ₃	0.89	1.47	1.91	1.92	1.92	3.73	0.37	3.73	0.37	0.36	1.27	0.36	3.76	0.96	4.14	1.24	2.40	1.41	0.27	2.30
CaO	35.34	36.17	34.09	36.70	34.79	34.49	35.64	35.37	36.27	34.96	34.53	31.60	35.31	35.91	27.36	35.85	35.44	35.06	31.84	35.89
Na ₂ O	0.06	0.00	0.88	0.00	0.00	0.11	0.11	0.04	0.00	0.00	0.00	0.39	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.27
Li ₂ O	0.00	0.00	0.00	0.00	0.00	1.38	0.27	0.77	0.45	0.51	0.00	3.62	0.00	0.00	14.74	0.00	0.00	0.00	0.00	0.27
B ₂ O ₃	0.00	0.00	0.00	0.00	2.99	0.00	0.00	1.46	1.46	0.51	0.00	3.18	0.00	0.00	0.00	1.44	0.00	0.00	0.00	3.02
SiO ₃	0.11	0.35	0.00	0.00	0.28	0.00	0.12	1.00	1.00	0.18	0.00	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.18	0.50
F	2.99	0.00	0.00	0.00	0.64	2.35	3.15	0.71	0.84	0.75	1.25	1.83	0.00	0.00	0.00	0.44	1.34	1.81	1.33	0.50
Cl	0.00	0.00	0.00	0.00	0.00	0.21	0.00	0.00	0.00	0.22	0.16	0.05	0.00	0.00	0.00	0.07	0.00	0.00	0.00	0.00
H ₂ O ₁	1.66	4.24	2.45	2.80	0.49	1.56	1.63	2.45	1.42	1.80	2.89	1.92	0.86	2.96	1.41	1.41	1.41	2.06	2.57	0.61
H ₂ O ₂	1.32	2.75	2.45	2.80	0.49	1.43	1.35	2.45	1.42	1.80	2.89	1.92	1.28	2.80	2.09	2.06	2.57	2.10	2.32	1.03
O=F, Cl	101.42	99.56	98.45	99.65	99.31	99.54	102.08	99.50	100.48	98.37	98.35	99.10	99.32	97.25	99.13	98.37	98.93	98.90	98.27	99.40
TOTAL	100.16	99.56	98.45	99.65	99.04	98.50	100.75	99.20	100.13	98.00	97.78	98.32	99.32	97.25	99.13	98.16	98.37	98.14	97.71	99.19

* Analyses of boron-bearing vesuvianite are normalized on 19 X cations; those of boron-free vesuvianite on 50 total cations. Measured. † Calculated for charge balance. Additional components (wt.-%): V2, Li₂O 0.02, BaO 0.11; V32, Li₂O 0.03, BaO 0.02; V33, BaO 0.15; V50-4, B₂O₃ 0.48; V53-2, ThO₂ 1.50; V61-7, La₂O₃ 3.79, Ce₂O₃ 8.69, Pr₂O₃ 0.70, Mg₂O₃ 1.37, SiMg₂O₃ 0.19; V67-3, CaO 0.46, ZnO 2.35; V68, BaO 0.06; V68-2, CaO 1.55, ZnO 1.47, PbO 0.31; V68-4, K₂O 0.03, CaO 0.32, ZnO 1.75, PbO 2.06.

measured H₂O content and the amount calculated from averaged microprobe data correlate quite well, but there is a systematic difference between the two sets of results. The highest measured H₂O content (5.37 wt.%) belongs to a fibrous vesuvianite from Mont Saint-Hilaire, Quebec (V25). The calculated H₂O content is much lower (2.10 wt.%), suggesting that the sample was not completely free of adsorbed water, despite heating at 110°C for 12 hours.

NORMALIZATION OF THE FORMULA UNIT OF BORON-FREE VESUVIANITE

A number of normalization schemes have been proposed in previous studies. However, their applicability to a large number of compositions from many different localities has not been examined. In addition, these studies have not recognized boron as a significant component in some vesuvianite samples. As the details of the substitution of boron are not yet clear, we have divided the chemical data into boron-free and boron-bearing sets, and focused first on boron-free vesuvianite. There have been many suggestions as to the optimum way to calculate the formula unit of vesuvianite (Table 2), and they all involve particular assumptions concerning stereochemistry. As we wish to examine the stoichiometry of vesuvianite, it is important that we use the minimum number of assumptions in the initial process of normalization. Any normalization scheme based on the number of anions requires knowledge or assumptions about the valence states of transition metals (particularly Fe) and the H₂O content. We have only limited analytical information about these parameters, and consequently will not use anion-based methods of normalization at the moment. Any scheme based on the numbers of cations does not need any such data or assumptions, and thus should be used here. The details of the cation sites in vesuvianite (given for *P4/nnc* symmetry and *Z* = 2 for simplicity) are given in Table 5. There are four sites [designated *X*(1), *X*(2), *X*(3) and *X*(4); see Table 1 for correspondence to site notations used in previous studies] that have coordination numbers greater than six; these are collectively designated *X*, and there are 19 *X* sites p.f.u., allowing for the half-occupancy of the *X*(4) site. There are three *Y* sites [*Y*(1), *Y*(2), and *Y*(3)] that have coordination numbers [6] and [5]; there are 13 *Y* sites p.f.u., allowing for the half-occupancy of the *Y*(1) site. There are three *Z* sites [*Z*(1), *Z*(2) and *Z*(3)] that have the coordination number [4]; there are 18 *Z* sites p.f.u. Apart from the results for boron-bearing vesuvianite (Groat *et al.*, in prep.), there are no indications of any other occupied cationic sites in any of the structure

TABLE 5. ATOMIC POSITIONS IN VESUVIANITE

Site	Equipoint	Site Contents	Bonded Atoms
<i>Z</i> (1)	4d	Si	O(1) × 4
<i>Z</i> (2)	16k	Si	O(2) O(3) O(4) O(7)
<i>Z</i> (3)	16k	Si	O(5) O(6) O(8) O(9)*
<i>X</i> (1)	4c	Ca	O(1) × 4 O(2) × 4
<i>X</i> (2)	16k	Ca	O(1) O(2) O(3) O(4) O(5) × 2 O(6) O(8)
<i>X</i> (3)	16k	Ca	O(3) O(6)† O(7) O(7) O(7) O(8) O(10) OH
<i>X</i> (4)	4e	0.5 Ca	O(6) × 4 O(9) × 4
<i>Y</i> (1)	4e	0.5 Fe	O(6) × 4 O(10)
<i>Y</i> (2)	8f	Al	O(4) × 2 O(8) × 2 OH × 2
<i>Y</i> (3)	16k	Al, Fe	O(1) O(2) O(3) O(4) O(5) OH
O(1)	16k	O	<i>Z</i> (1) <i>X</i> (1) <i>X</i> (2) <i>Y</i> (3)
O(2)	16k	O	<i>Z</i> (2) <i>X</i> (1) <i>X</i> (2) <i>Y</i> (3)
O(3)	16k	O	<i>Z</i> (2) <i>X</i> (2) <i>X</i> (3) <i>Y</i> (3)
O(4)	16k	O	<i>Z</i> (2) <i>X</i> (2) <i>Y</i> (3) <i>Y</i> (2)
O(5)	16k	O	<i>Z</i> (3) <i>X</i> (2) × 2 <i>Y</i> (3)
O(6)	16k	O	<i>Z</i> (3) <i>X</i> (2) <i>X</i> (3) × 2 <i>X</i> (4) or <i>Y</i> (1)
O(7)	16k	O	<i>Z</i> (2) <i>X</i> (3) × 3
O(8)	16k	O	<i>Z</i> (3) <i>X</i> (2) <i>X</i> (3) <i>Y</i> (2)
O(9)	8h	O	<i>Z</i> (3) × 2 <i>X</i> (4)
O(10)	4e	O, OH	<i>X</i> (3) × 4 <i>Y</i> (1)
OH	16k	OH	<i>X</i> (3) <i>Y</i> (3) <i>Y</i> (2)

Space group *P4/nnc*.

*Bridging oxygen in Si₂O₇ group. †O(6) × 2 in some studies.

refinements. Thus the cations must be assigned among 19 *X*, 13 *Y* and 18 *Z* sites, a total of 50 sites. Of the various different cation-based schemes of normalization used (Table 2), the least-restrictive scheme is based on a total of 50 cations, as this makes no assumptions as to the distribution of cations over the sites. The only way in which this could be wrong is if there are significant vacancies at any of the *X*, *Y* or *Z* sites [apart from the half-occupancies of *X*(4) and *Y*(1) mentioned above].

SITE-GROUP OCCUPANCIES

We now examine the possible distributions of cations over the various groups of sites in the structure. If these distributions are crystal-chemically reasonable, it will suggest that the 50-cation scheme of normalization is adequate. If the site assignments are correct, then the cation sums corresponding to each group of sites should show normal distributions, with the mean values corresponding to the number of sites; the distributions should also show low skew and kurtosis (kurtosis indicates too many data-points in the tails of the distribution). If the means do not correspond to the numbers of sites, either we have wrongly assigned some cations, or we have used the wrong scheme of normalization. If we have failed to consider one (or more) cations that substitute in small amounts at a site, this may not materially affect the mean value, but will skew the distribution

to lower values and will increase the degree of kurtosis. Consequently, cation assignments are considered both on crystal-chemical and on statistical grounds.

The Z sites

These are all tetrahedrally coordinated, and are dominantly to completely occupied by Si. The principal question is whether any Al occupies these sites. Figure 3 shows a histogram of Si cations p.f.u. for the 388 B-free formulae (because not all of the samples were tested for B, some of these may be boron-bearing). The observed mean, 18.0(2), is statistically identical to the ideal value of 18. The histogram itself is almost perfectly Gaussian. Both skew and kurtosis are low (-0.03 and 0.32, respectively), indicative of a statistically normal distribution; the low value of skew indicates that all of the tetrahedrally coordinated sites are filled with Si, and that there is little or no Al-for-Si substitution.

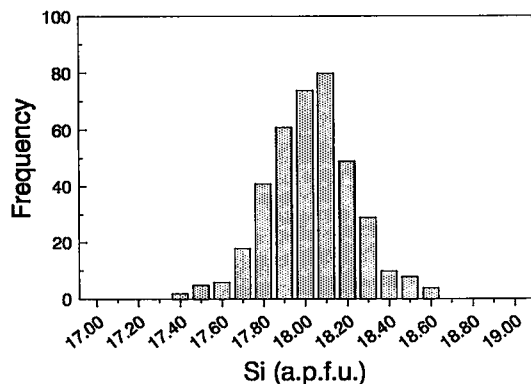


FIG. 3. Histogram of Si abundance (a.p.f.u.); mean, skew and kurtosis (based on 388 boron-free analyses) are 18.0(2), -0.03 and 0.32, respectively.

The X sites

These are all [8]- or [9]-coordinate, and are dominantly occupied by Ca. The formula of vesuvianite is commonly written with these sites completely assigned to Ca. A histogram of Ca abundance (a.p.f.u.) is shown in Figure 4a. The observed mean is 18.8(5), statistically identical to the ideal value of 19. However, the distribution is skewed toward lower values, and the tails are heavy with data points (skew and kurtosis are -3.24 and 15.55, respectively). Thus other elements are substituting for Ca at the [8]- and [9]-coordinate sites. Other elements detected in vesuvianite that

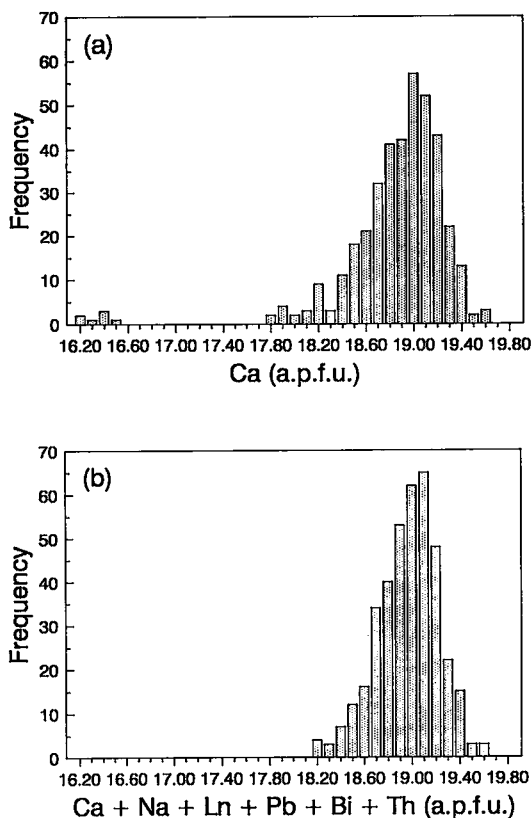


FIG. 4. X-site cation abundances (a.p.f.u.) in boron-free vesuvianite: (a) Ca, with mean, skew and kurtosis of 18.8(5), -3.24 and 15.55, respectively (low-Ca analyses are of sample V61); (b) ΣX (Ca + Na + Ln + Pb + Bi + Th), with mean, skew and kurtosis of 19.0(3), -0.38 and 0.22, respectively.

are appropriate for such coordinations are Na, Ln (the rare earths), Pb, Bi and Th. Including these cations into the X-site totals (Fig. 4b) shows a more normal distribution; the observed mean is 19.0(3); skewness and kurtosis are -0.38 and 0.22, respectively, indicating that these cations all occur at the X sites.

The Y sites

It is well known that the dominant cation occupying these sites is Al, with significant amounts of Mg and Fe (valence state usually unknown) and minor Ti. Presumably, other similar elements (Cr^{3+} , Mn, Cu^{2+} , Zn) also occur at these sites. In some cases (e.g., Cu^{2+}), this has been confirmed by structure refinement (Fitzgerald *et al.* 1986a). A

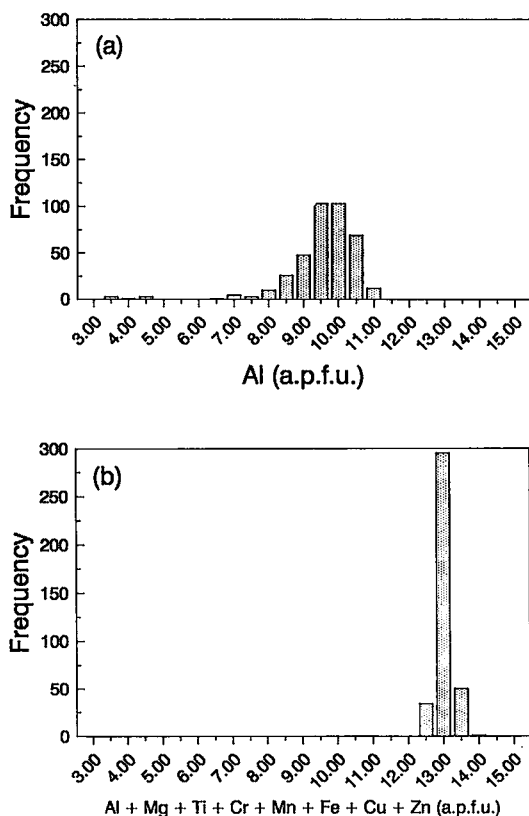


FIG. 5. Y-site cation abundances (a.p.f.u.) in boron-free vesuvianite: (a) Al, with mean, skew and kurtosis of 9.5(1.1), -3.08 and 13.88, respectively (low-Al analyses are of sample V61); (b) ΣY (Al + Mg + Ti + Cr + Mn + Fe + Cu + Zn), with mean, skew and kurtosis of 13.0(2), 0.64 and 0.87, respectively.

histogram of the Al abundance is shown in Figure 5a; the mean value is 9.5(1.1), with large values of skew and kurtosis, -3.08 and 13.88, respectively. The distribution of (Al + Mg + Fe + Ti + Cr + Mn + Cu + Zn) is shown in Figure 5b; the observed mean is 13.0(2), with skew and kurtosis values of 0.64 and 0.87, respectively, strong indications that all of these species occupy the Y sites.

General considerations

Cations have been assigned to the three groups of sites on the basis of charge and size. The sums of the cations for the three sites (i) are all equal to the number of corresponding sites in the structure, and (ii) are normally distributed in all cases, which suggest that the cations have been assigned to the

TABLE 6. MEAN CATIONIC ABUNDANCES AND WT. % OXIDE TOTALS FOR SELECTED VESUVIANITE ANALYSES

Reference	(1)	(2)	(3)	(4)
Number of Analyses	388	21	35	22
Mean Si	18.0(2)	17.7(2)	17.8(1)	18.01(8)
s	-0.03	-0.12	-0.48	0.41
k	0.32	-0.87	-0.35	-0.44
Mean Ca	18.8(5)	18.7(4)	18.9(2)	18.9(1)
s	-3.24	-1.61	-1.74	-0.64
k	15.55	2.10	4.77	0.38
Mean Al	9.5(1.1)	7.2(7)	10.00(7)	9.5(5)
s	-3.08	1.44	-0.46	0.41
k	13.88	1.03	-0.61	-1.51
Mean ΣX	19.0(3)	18.9(2)	18.9(1)	19.02(9)
s	-0.38	-1.07	-0.13	-0.13
k	0.22	1.74	-0.16	-1.16
Mean ΣY	13.0(2)	13.4(2)	13.2(2)	12.97(7)
s	0.64	0.68	1.04	0.16
k	0.87	-0.23	0.24	-0.99
Mean Totals	98.9(9)	98.8(1.0)	98.8(4)	98.5(6)
s	-0.33	-1.28	-0.11	0.15
k	0.53	1.78	-0.38	-1.27

Based on 50 cations (less B, S) and 78 anions.

s = skewness; k = kurtosis

$\Sigma X = (\text{Ca} + \text{Na} + \text{K} + \text{Ln} + \text{Pb} + \text{Bi} + \text{Th} + \text{U})$

$\Sigma Y = (\text{Al} + \text{Ti} + \text{Mg} + \text{Mn} + \text{Fe} + \text{Cr} + \text{Cu} + \text{Zn})$

(1) WD analyses of B-free samples. (2) WD analyses with B.

(3) WD analyses from Allen (1985).

(4) WD analyses from Hoisch (1985).

correct groups, and also suggest that the 50-cation scheme of normalization is correct. Because the sums for the Z sites are normally distributed about 18 a.p.f.u. for $Z = \text{Si}$, normalization on 18 Si a.p.f.u. also is justified. However, we prefer to use the 50-cation method, as it does not rely on a single measurement.

The 50-cation scheme works well for our analytical data-set. How does it work for other analytical results in the literature? Table 6 shows analogous results for some recent microprobe studies (Allen 1985, Hoisch 1985). We see the same pattern as above, further confirming both the 50-cation scheme of normalization and the cation assignments.

THE CHEMICAL FORMULA OF BORON-FREE VESUVIANITE

Cation contents and site occupancies

The total number of cations is constrained by the normalization procedure to a sum of 50, but the assignments of cations to specific groups has no such restriction. We have already shown that our cation sums to the X, Y and Z groups are

normally distributed, with low skew and kurtosis, and sums equal to the number of sites in the ideal structure. It remains to be shown that the distribution of all cations is crystal-chemically compatible with the known stereochemistry of the structure.

Figure 6a shows the observed $\langle Z-O \rangle$ distances from several published refinements of the structure of B-free vesuvianite. There are three populations, corresponding to the three crystallographically distinct sites in the normal $P4/nnc$ vesuvianite structure. For each site, the dispersion of $\langle Z-O \rangle$ distances is small, indicating that the occupancies of the Z sites in every case are essentially identical, and that these structures all contain the same amount of Si. For the compositions of boron-free vesuvianite presented here, the distribution of Si contents is symmetrically Gaussian, and the observed mean value of the Si content is 18.0(2). This shows that there is no significant substitution of other cations (*i.e.*, Al) for Si in boron-free vesuvianite.

Figure 6b shows the observed $\langle X-O \rangle$ distances from published structure-refinements. Again there are three sharp maxima, which correspond to the X(1), X(2) and X(3) sites; values for the half-occupied X(4) site are more dispersed. Simple arguments based on ionic radii suggest that those sites can potentially be occupied by alkaline earth, alkali and REE cations, and the histograms of Figure 4 support this contention.

The medium-sized trivalent and divalent cations constitute the Y group, and occupy the [5]- and [6]-coordinate sites in the structure. Figure 6c shows the observed $\langle Y-O \rangle$ distances for the published structure refinements of the vesuvianite. Together with the site occupancies reported by previous structure-refinements, these suggest that Y(1) is occupied by Fe, Cu, Zn and Mg(?), Y(2) is occupied primarily to exclusively by Al, and Y(3) is occupied by Al, Mg, Fe and Ti. In addition, MAS NMR (Magic Angle Spinning Nuclear Magnetic Resonance) work by Phillips *et al.* (1987) indicates that Al also can occupy the Y(1).

Anion contents

We have seen above that there are 50 cations in the unit formula of vesuvianite. If the (OH + F)⁻ content and the valence states of all the cations were known, then the anion content would be fixed by the electroneutrality principle. However, this is not the case, and we have to resort to other means.

The refined crystal-structures of boron-free vesuvianite show the presence of 78 anions (p.f.u.), 68 of which can be unequivocally identified as O²⁻ on the basis of bond-valence arguments. Table 7 shows the bond-valence arrangement for an

example of boron-free vesuvianite. The bond-valence sums around O(1) to O(9) are all approximately equal to 2 v.u., showing them to be O²⁻ anions. This leaves 10 additional anions (p.f.u.), labeled OH and O(10), for which the bond-valence sums are much less than 2.0 v.u., suggesting that these anions are (OH + F)⁻ rather

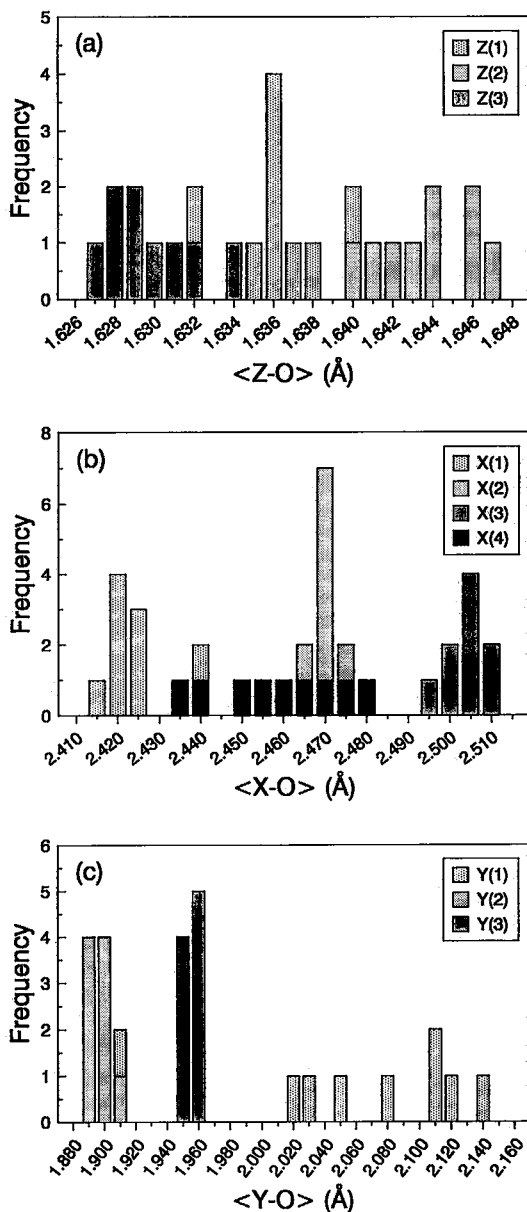


FIG. 6. Interatomic distances from several published structure-refinements of boron-free vesuvianite: (a) $\langle Z-O \rangle$ distances (Å); (b) $\langle X-O \rangle$ distances (Å); (c) $\langle Y-O \rangle$ distances (Å).

TABLE 7. BOND-VALENCE* TABLE FOR BORON-FREE VESUVIANITE V12₁†

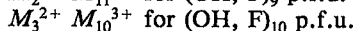
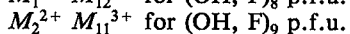
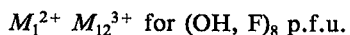
	Z(1)	Z(2)	Z(3)	X(1)	X(2)	X(3)	X(4)	Y(1)	Y(2)	Y(3)	Σ
0(1)	0.956 ₁ ^{x4}			0.339 ₁ ^{x4}	0.239					0.497	2.031
0(2)		0.941		0.226 ₁ ^{x4}	0.270					0.515	1.952
0(3)		0.946			0.307	0.257				0.470	1.980
0(4)		0.869			0.264				0.456 ₁ ^{x2}	0.360	1.949
0(5)			0.969		0.266					0.432	2.006
					0.339						
0(6)			1.046		0.102	0.240	0.354 ₁ ^{x4}	0.412 ₁ ^{x4}			2.154
0(7)		1.013				0.201					1.762
						0.238					
						0.310					
0(8)			1.005		0.351	0.184			0.541 ₁ ^{x2}		2.081
0(9)			0.905 ₁ ^{x2}				0.188 ₁ ^{x4}				1.998
0(10)						0.207 ₁ ^{x4}		0.509			1.337
OH						0.234			0.538 ₁ ^{x2}	0.500	1.272
Σ	3.824	3.769	3.925	2.260	2.138	1.957	2.168	2.157	3.070	2.774	

*Calculated from the curves of Brown (1981).

†Subscripts refer to different crystals from the same sample.

than O²⁻. However, there has been considerable debate over what proportion of these 10 anions are (OH + F)⁻, and a careful examination of this point is warranted.

The general formula of vesuvianite can be written as X₁₉Y₁₃Z₁₈O₆₈W₁₀, where X, Y, Z and W are as defined previously. The X sites are occupied predominantly by divalent cations, and the Z sites are occupied primarily (entirely) by tetravalent cations. The only significant polyvalent substitutions occur at the Y sites, where divalent (Mg, Fe²⁺, Mn), trivalent (Al, Fe³⁺) and tetravalent (Ti⁴⁺) cations occur. The total possible variation in anionic charge is from 146⁻ to 156⁻, corresponding to between ten OH⁻ and zero OH⁻. In the models previously proposed (Table 2), the charge variation is from 146⁻ to 148⁻, corresponding to 8(OH)⁻ and 10(OH)⁻, respectively. In order to produce electroneutrality, the required charge arrangements at the Y sites (ignoring Ti⁴⁺) are:



In most cases, the Fe²⁺/Fe³⁺ ratio is unknown; consequently the M²⁺ or M³⁺ contents are unknown. However, the Al content provides a minimum M³⁺ content that can indicate a limit on the possible variation. The variation in Al content as a function of the remaining Y cations in boron-free vesuvianite is shown in Figure 7a. The sum of the Y cations should be 13 a.p.f.u., and the data points scatter about the ideal line. In addition, the amount of Al varies continuously

from 6 to 11 a.p.f.u., at which point there is a sharp cutoff. Figure 7b examines (Al + Fe³⁺) as a function of (Mg + Fe²⁺ + Ti) in those samples for which we have determined the Fe²⁺/Fe³⁺ ratio; again we see this cutoff at M³⁺ = 11 atoms p.f.u., suggesting that this is a limit on the incorporation of trivalent cations into vesuvianite. However, in terms of aggregate charge at the Y site, the substitution (Mg + Fe²⁺) + Ti \rightleftharpoons 2(Al + Fe³⁺) can effectively increase the total charge. This point is examined in Figure 7c, which shows the variation of [Al + Fe³⁺ + 2Ti] as a function of [Mg + Fe²⁺ - Ti] [the former variable gives the amount of trivalent cations (Al + Fe³⁺) together with the amount of Mg + Ti (= 2Ti) that have "equivalent" trivalent charge; the latter variable gives the amount of divalent cations (Mg + Fe²⁺) corrected for the amount of Mg associated with Ti]. This substitution falls about the ideal 13-cation line, with maximum "effective" trivalent charge content of 11.5 p.f.u. For the moment, we will restrict our discussion to the implications of this on the total distribution of charge in the structure. According to the range of M³⁺ and (OH + F)⁻ contents outlined above, a maximum effective M³⁺ value of 11.5 a.p.f.u. corresponds to an (OH + F)⁻ content of 8.5 a.p.f.u.; there are other possible substitutions that can increase this (OH + F)⁻ content, and thus 8.5 a.p.f.u. is a lower limit to (OH + F)⁻ variation (established partly from the empirical observation of Figure 7c).

The only other possible polyvalent substitution at the Y site that does not involve the X or Z group cations is Mg + OH⁻ \rightleftharpoons Al + O²⁻, which produces

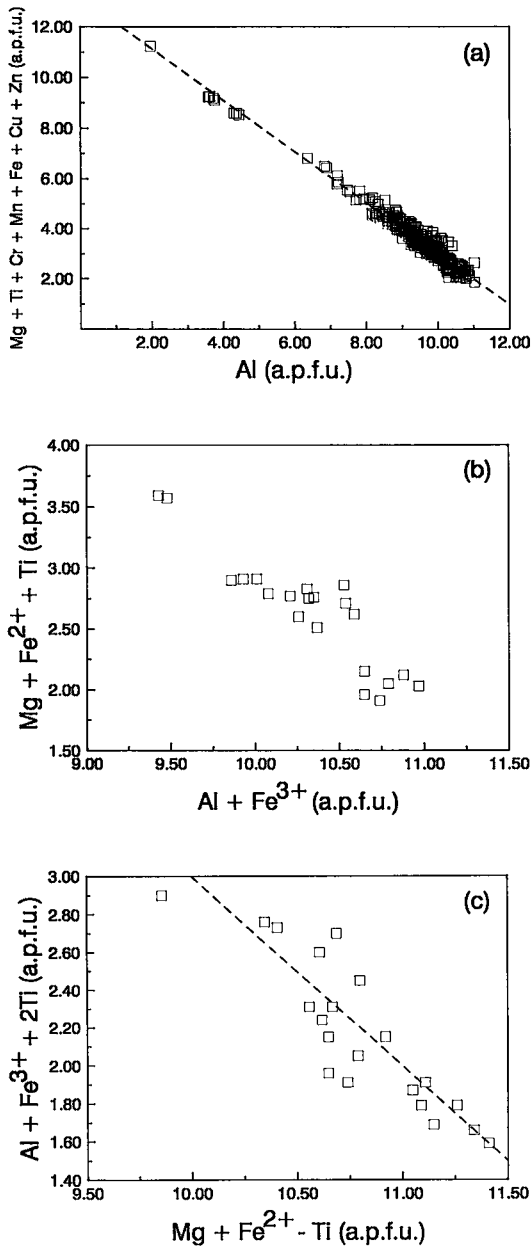


FIG. 7. (a) Variation of Al content as a function of other Y-site cations for boron-free vesuvianite. The dashed line represents an ideal Y-site content of 13 atoms p.f.u. The low-Al analyses are of sample V61. (b) $(\text{Al} + \text{Fe}^{3+})$ as a function of $(\text{Mg} + \text{Fe}^{2+} + \text{Ti})$ for those samples with analyzed $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios. (c) Variation of $(\text{Al} + \text{Fe}^{3+} + 2\text{Ti})$ as a function of $(\text{Mg} + \text{Fe}^{2+} - \text{Ti})$.

a variable OH^- content. The upper limit for $(\text{OH} + \text{F})^-$ is 10 a.p.f.u. [if we assume that no other anions except OH and O(10) can be hydroxyl],

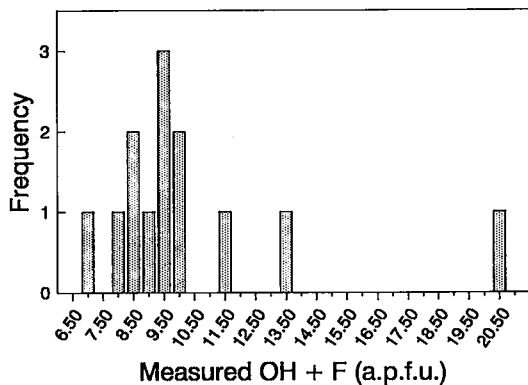
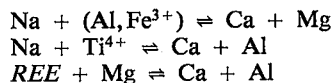


FIG. 8. The distribution of measured $(\text{OH} + \text{F})^-$ contents p.f.u.

which gives an upper $\text{Mg}(\text{Fe}^{2+} + \text{Mn})$ limit of 3 a.p.f.u. What do our experimentally determined $(\text{OH} + \text{F})^-$ contents indicate in this regard? Figure 8 shows the distribution of measured $(\text{OH} + \text{F})^-$ contents p.f.u.; the mean value is 9.6 a.p.f.u., with the variation ranging from 7.0 to 20.5 a.p.f.u. Most of the determinations fall between the predicted limits of 8.5 and 10.0 $(\text{OH} + \text{F})^-$ a.p.f.u. However, there are significant outliers to higher values. The highest measured OH^- content (20.5 a.p.f.u., 5.37 wt.% H_2O) is for a fibrous vesuvianite (V25) from Mont Saint-Hilaire. As pointed out earlier, the fibrous nature of this sample suggests that it may not have been free of adsorbed H_2O when analyzed. The next highest value (V3) is for a microcrystalline sample that may have suffered from the same problem. With this rationalization for the outliers, the small number of data points we have do seem to support the suggested range of $(\text{OH} + \text{F})^-$ content. Thus, we can summarize the charge-balance restrictions in the following way: the content of trivalent cations can only be in the range 10–11.5 a.p.f.u., with a corresponding $(\text{OH} + \text{F})^-$ range of 10–8.5 a.p.f.u. Additional H_2O determinations are needed to test this model. Despite this, the current data do suggest a substitution of the type $\text{Mg} + \text{OH}^- \rightleftharpoons \text{Al} + \text{O}^{2-}$ in vesuvianite. We can write the possible formula as $X^{2+}_{19}(M^{3+}_{10.0-11.5}M^{2+}_{3.0-0.5})Z^{4+}_{18}\text{O}_{68}(\text{OH},\text{F})_{10.0-8.5}\text{O}^{2-}_{0.0-1.5}$.

Note that this formula ignores any heterovalent substitutions at the X and Z sites. It is possible that heterovalent substitutions at the Y site could be coupled to compensating heterovalent substitutions at the X site. The stoichiometric possibilities are listed below:



The importance of these possible substitutions in vesuvianite is examined in the section on major- and minor-element chemistry.

CHANNEL CONFIGURATION IN VESUVIANITE

Much of the complexity in the crystal chemistry of vesuvianite arises because of the presence of channels through the framework of octahedra and tetrahedra. These channels incorporate significant amounts of *X*- and *Y*-type cations, together with additional anions and some boron. Some of the structural implications of the channel stereochemistry have been discussed previously (Coda *et al.* 1970, Rucklidge *et al.* 1975), but they have not been fully explored, particularly with regard to their influence on bulk chemistry. Consequently, an examination of the channel sites and their local environments follows.

Geometrical restrictions on occupancy

The sequence of sites down the channel in *P4/nnc* vesuvianite is illustrated in Figure 9; note that more than one unit cell (along *Z*) is shown. The separation between adjacent *Y*(1) and *X*(4) sites ranges from 1.0 to 1.4 Å, and as noted by many previous investigators, precludes simultaneous occupancy of adjacent *Y*(1) and *X*(4) sites. This implies that the sum of the *Y*(1) and *X*(4) cations cannot exceed half the number of *Y*(1) and *X*(4) sites (*i.e.*, cannot exceed 2 cations p.f.u.). Adjacent *X*(4) sites (Fig. 9) are separated by ~2.4 Å. This value is approximately equal to the $\langle \text{Ca-O} \rangle$ distances in vesuvianite, which suggests that adjacent *X*(4) sites also cannot be simultaneously occupied. Thus it seems reasonable to conclude that the Ca occupancy of the *X*(4) site also cannot exceed one half.

We conclude that the sum of the *Y*(1) and *X*(4) cations cannot exceed half the number of *Y*(1) + *X*(4) sites, and that the *X*(4) site cannot be more than half-occupied. Note that these arguments do not restrict both *Y*(1) and *X*(4) sites to be half-occupied, as has been assumed by some previous workers. For example, these restrictions allow (i) the *Y*(1) site to be fully occupied and the *X*(4) site to be empty (see configuration A in Fig. 9), (ii) both the *Y*(1) and *X*(4) sites to be half-occupied (configuration B, Fig. 9) and (iii) any configuration intermediate between these two end-members. We have concluded from the chemical analytical data that the *Y*(1) and *X*(4) sites are always half-occupied (see Fig. 2); this indicates that there must be an additional (as yet unknown) mechanism constraining the occupancies to configuration B (Fig. 9). This will be examined in more

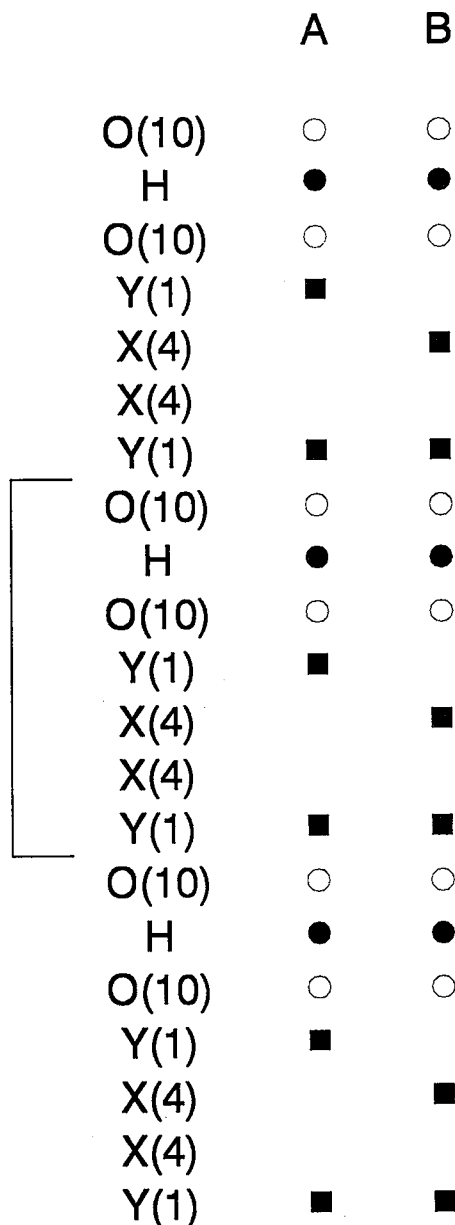


FIG. 9. The sequence of sites down the fourfold axes in *P4/nnc* vesuvianite: (a) the *Y*(1) site is fully occupied, the *X*(4) site is empty; (b) both sites are one-half occupied.

detail in a later paper that focuses on the structural aspects of vesuvianite.

The *O*(10) position

Coda *et al.* (1970) identified the *O*(10) anion in

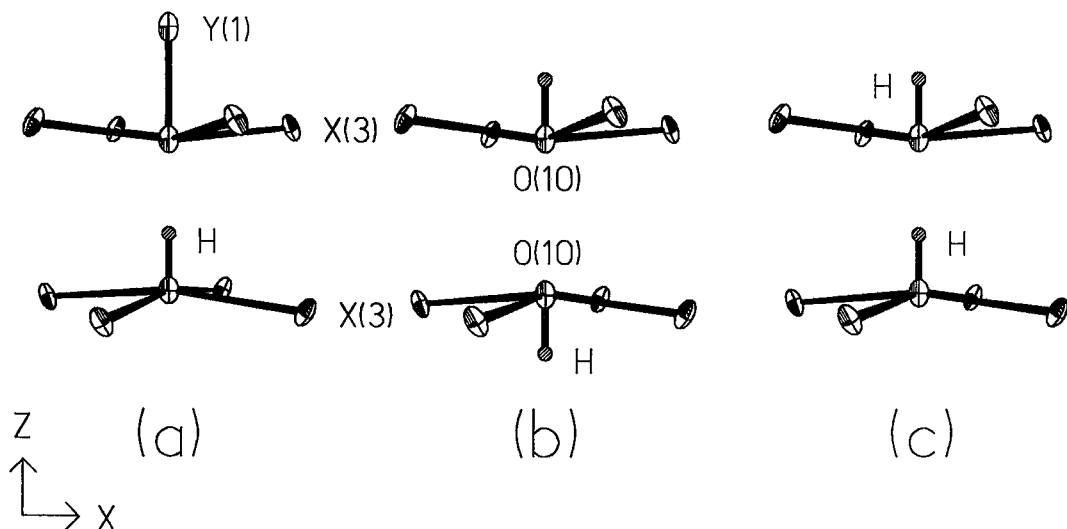


FIG. 10. Possible local O(10) anion configurations: (a) H between two O(10) anions; (b) H atoms on the outside of both O(10) atoms; (c) one H between the O(10) anions and one on the outside.

the channel of vesuvianite, and proposed that it is a hydroxyl group. There has since been considerable discussion as to the amount of hydroxyl present in vesuvianite, with contents ranging from 8 to 10 a.p.f.u.

The key question in the resolution of the character of the O(10) anion is whether or not the O(10) position can be occupied by a divalent anion. If (a local configuration of) O(10) is occupied by O^{2-} , it must receive a total bond-valence of 2.0 v.u. from the surrounding cations; is this possible? The local geometry around O(10) is shown in Figure 10. It is bonded to 4 X(3) cations and 1 Y(1) cation, receiving a bond-valence contribution of $(4 \times 0.207 + 0.509)$ v.u. for occupancies of these sites by Ca and Fe^{3+} , respectively; in this configuration, O(10) cannot be a divalent simple anion, as the bond-valence sum at the O(10) position is not ~ 2 v.u. Can different site-occupancies at X(3) and Y(1) change the local bond-valence sum to 2.0 v.u.? There seems to be no local configuration of cations (conformable with the general chemistry of vesuvianite) that can provide sufficient bond-valence to the O(10) site to allow occupancy by a divalent anion. Thus the O(10) position must be completely occupied by monovalent anions.

The O(10)–O(10) separation (see Fig. 10) is ~ 2.7 Å; this allows three possible H-bond configurations. If the H lies solely between the two adjacent O(10) atoms (A, Fig. 10), there is only room for one H, which must therefore be shared between two O(10) atoms. This would give a total H content of 9 atoms p.f.u. If the hydrogen lay on the other

side of O(10) (B, Fig. 10), then each O(10) could have an associated H. This would give a total H content of 10 atoms p.f.u. If a hydrogen lay between two adjacent O(10) atoms (C, Fig. 10), one of which has a hydrogen on the other side, the total H content would be 10 atoms p.f.u. Lager *et al.* (1989) have recently observed configuration A in a gem vesuvianite from Tanzania, the H lying between the two O(10) atoms, where it occupies a disordered off-center position (symmetrical hydrogen bonds are quite rare). If this result is generally the case, it further indicates that vesuvianite has a maximum H content of 9 atoms p.f.u.

The total bond-valence consequences of the half-occupied Y(1) and X(4) sites, and the observed H configuration in the neighborhood of O(10), are examined in Figure 11 for the boron-free vesuvianite V12. Starting at the top: (i) O(10) receives bond-valence from X(3) [4×0.207 for X(3) = Ca] and Y(1) [0.509 for Y(1) = Fe^{3+}] to give a sum of 1.337 v.u.; the remaining bond-valence (0.663 v.u.) will be supplied by the hydrogen to which it also is bonded. Thus the bond-valence requirements of the first O(10) oxygen are satisfied. (ii) Hydrogen receives 0.663 v.u. from O(10), and thus forms a hydrogen bond of valence 0.337 v.u. with O(10)a (Fig. 11). (iii) O(10) receives bond-valence from X(3) [4×0.207] and H (0.337 v.u.); this totals 1.165 v.u., far short of what its bond-valence requirements would be (2.0 v.u.) as an O^{2-} anion. We know that there is not another H attached to O(10) from the

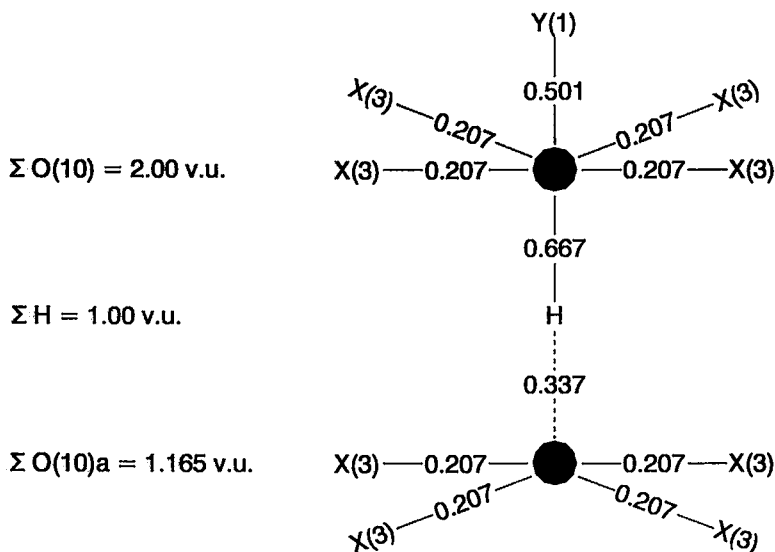


FIG. 11. Bond-valence arrangements around adjacent O(10) atoms in vesuvianite; bond-valence sums around locally distinct O(10) atoms are given on the left of the figure.

experimental results of Lager *et al.* (1989), and that the Y(1) site cannot be occupied (or the long-range occupancy would exceed one-half). There is one solution to this problem: if this O(10) is actually F, then the local bond-valence sum need only be 1.0 rather than 2.0 v.u., which satisfies the bond-valence requirements. However, it is not clear that this is an adequate general solution, as the problem of local configurations and bond-valence satisfaction within the channel still remains to be solved.

BORON-BEARING VESUVIANITE

A significant finding of this work is the recognition (or rediscovery, Jannasch 1884) of boron as a major constituent in some vesuvianite samples, up to ~ 4 a.p.f.u. Consequently, it has a major effect on the overall compositional variation of vesuvianite, as well as the renormalization procedure. Nothing is known about the details of the boron substitution in vesuvianite, and thus the best scheme for normalization of the formula unit is not apparent. Initially, we calculated the formula unit of boron-bearing vesuvianite based on 50 cations excluding B^{3+} , and examined the site-group occupancies as we did for boron-free vesuvianite. The distributions of values for each group of sites are shown in Figure 12. These distributions differ from those found in the boron-free vesuvianite (Figs. 3, 4 and 5). Neither the Z- or Y-site averages

correspond to their ideal values, indicating that the cation assignments in boron-bearing vesuvianite must be significantly different from those in boron-free vesuvianite.

The Z sites

The mean value of the Z cations (namely Si) is 17.7, with a standard deviation of 0.2, and skew and kurtosis values of -0.12 and -0.87 , respectively (Fig. 12a). Vacancies cannot be incorporated at the tetrahedrally coordinated sites in vesuvianite, as this leads to extreme bond-valence deficiencies at the coordinating oxygen atoms. Consequently, the following situations are possible: (i) other cations substitute (for Si) at the Z sites; (ii) the normalization scheme is wrong.

The X sites

The mean value of the X cation sums (Ca, Na, Ln, Pb, Bi, Th) is 18.9, with a standard deviation of 0.2, and skew and kurtosis values of -1.07 and 1.74, respectively (Fig. 12b). The mean value is statistically identical to the ideal value of 19.

The Y sites

The mean value of the Y cation sums (Al, Mg, Fe, Ti, Cr, Mn, Cu, Zn) is 13.4, with a standard deviation of 0.2, and skew and kurtosis values of

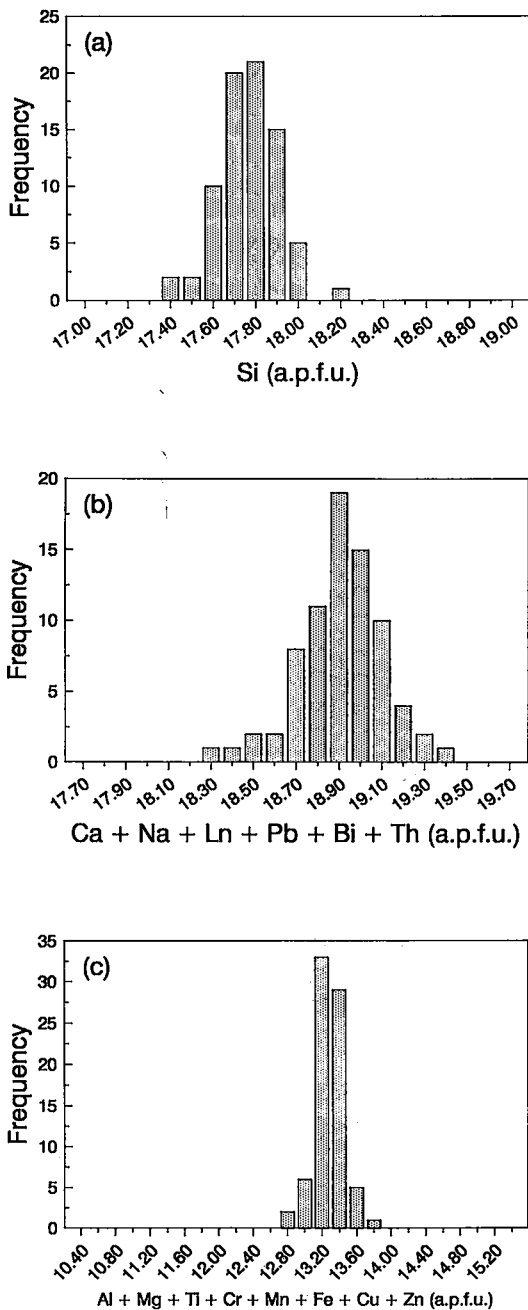


FIG. 12 (a) Si abundances (a.p.f.u.) in boron-bearing vesuvianite; mean, skew and kurtosis (based on 21 analyses) are 17.7(2), -0.12 and -0.87 , respectively: (b) ΣX (Ca + Na + Ln + Pb + Bi + Th) abundances (p.f.u.); mean, skew and kurtosis are 18.9(2), -1.07 and 1.74 , respectively: (c) ΣY (Al + Mg + Ti + Cr + Mn + Fe + Cu + Zn) abundances (p.f.u.); mean, skew and kurtosis are 13.4(2), 0.68 and -0.23 , respectively.

0.68 and -0.23 , respectively (Fig. 12c). As the number of Y cations exceeds the number of possible sites, either (i) one or more of the cations assigned to the Y group occupies non-Y type sites in the vesuvianite structure, or (ii) the normalization scheme is wrong.

General considerations

For two of the three groups of cations, the common explanation is that the 50-cation scheme of normalization is wrong for boron-bearing vesuvianite. However, this does not explain the pattern of observed sums at all the sites, and thus additional factors must be involved. The result for the X sites suggests that the normalization scheme underestimates the number of cations. There are two other lines of evidence, developed below, that also suggest this to be the case.

Charge-balance arguments

Crystal-structure refinements of six samples of boron-bearing vesuvianite (Groat *et al.*, in prep.) show that the anion contents of boron-free and boron-bearing vesuvianite are the same [$= 78 (O^{2-} + OH^- + F^-) = 156 - F$ negative charges]. The formula unit of any vesuvianite should contain sufficient cationic charge to neutralize the total anionic charge. The charge balance in one sample of boron-free and three samples of boron-bearing vesuvianite is examined in Table 8. For the boron-free vesuvianite, the positive and negative charges are approximately the same. The total cationic charge is systematically low in all three samples of boron-bearing vesuvianite for which we have both Fe^{2+}/Fe^{3+} values and analyzed H contents. This suggests that the total number of cations is slightly too low, and that the correct scheme of normalization should give slightly more than 50 cations excluding B^{3+} and H^+ .

TABLE 8. CATION CHARGES IN SELECTED VESUVIANITE SAMPLES

	Ideal	V12	V56	V61	V74
Si	72	71.0	69.9	71.4	71.0
Al	33	31.9	21.2	22.3	20.6
Ti	-	1.1	0.7	0.8	1.4
Fe ³⁺	-	2.0	4.3	4.6	2.6
Mg	4	2.1	6.7	7.2	9.6
Fe ²⁺	-	1.1	3.3	1.1	1.0
Ca	38	38.3	37.7	37.7	37.7
B	-	-	7.6	3.7	7.3
F	-	-	0.4	0.6	-
H	9	9.0	2.7	4.5	2.0
Σ	156	156.5	154.5	153.9	153.1

X-ray-scattering considerations

The crystal structures of all six crystals of boron-bearing vesuvianite (Groat *et al.*, in prep.) show two additional cation sites with coordination numbers of [3] and [4], respectively. The scattering power at these two sites considerably exceeds (by at least a factor of two) the amount of scattering possible from the analytically measured amounts of boron in each crystal. This indicates that the total number of cations (excluding B^{3+} and H^+) in each of these crystals exceeds 50 p.f.u. (assuming no vacancies at the *X*, *Y* and *Z* sites) and, consequently, that a 50-cation normalization scheme for boron-bearing vesuvianite is not adequate.

Formula-unit normalization for boron-bearing vesuvianite

All evidence points to an excess of "normal" cations over the non-boron ideal value of 50 cations per formula unit. There are two possible schemes: (i) normalization on $\Sigma Z = 18$ cations p.f.u., or (ii) normalization on $\Sigma X = 19$ cations p.f.u. As $[18 - \langle \Sigma Z \rangle]$ exceeds $[19 - \langle \Sigma X \rangle]$, normalization on $\Sigma Z = 18$ would produce an excess of *X* cations but with nowhere to put them. Consequently, the most satisfactory scheme of normalization for boron-bearing vesuvianite would seem to be $\Sigma X = 19$ cations p.f.u.

Relations between cation sums at the Y and Z sites

The mean values for the *Y*- and *Z*-group cation

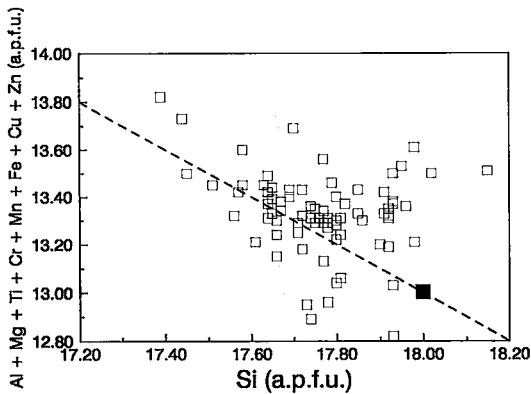


FIG. 13. Si versus ΣY (Al + Mg + Ti + Cr + Mn + Fe + Cu + Zn) in boron-bearing vesuvianite (a.p.f.u.). The dashed line represents a 1:1 relationship between *X*- and *Z*-site contents. The filled point at Si = 18, $\Sigma Y = 13$ a.p.f.u. represents ideal boron-free vesuvianite.

sums are 13.4 and 17.7 cations p.f.u., with standard deviations of 0.2 in each case. There is a weak negative correlation between sums of the *Y*- and *Z*-group cations (Fig. 13). Comparison with a reciprocal 1:1 relationship shows that there is usually an excess of *Y* cations over that needed to complete the occupancy of the *Z* sites, and consequently there will generally be an excess of "normal" cations that can satisfy the charge-balance and X-ray scattering requirements indicated by the results of both chemical analysis and structure refinement.

THE INCORPORATION OF BORON IN VESUVIANITE

Inspection of the analytical data for boron-bearing vesuvianite shows that the increase in boron is accompanied by an increase in Mg and a decrease in both Al and OH. The coupling of B with Al is apparent (Fig. 14) from the prominent bimodal distribution of Al, with maxima at ~ 9.8 a.p.f.u. and at ~ 6.9 a.p.f.u. The higher mean value corresponds to boron-free vesuvianite, and the lower mean value corresponds to boron-bearing vesuvianite. Note that the relative number of analyzed samples in these two populations does not reflect the natural distribution of compositions; rather, it reflects the emphasis of our analytical work. However, the bimodal nature of Figure 14 does serve to

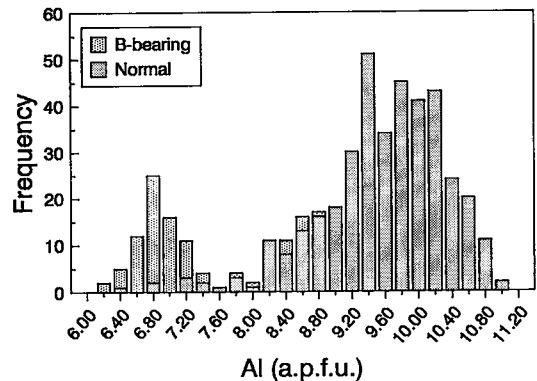


FIG. 14. Histogram of Al abundances for boron-free and boron-bearing vesuvianite (V61 not shown).

emphasize the coupling of high B with low Al in vesuvianite. Figure 15 shows the relationship between Al and Mg. Again, boron-free and boron-bearing vesuvianites constitute two distinct populations. Low Al and high B correlate with high Mg; this relationship should involve $(Mg + Fe^{2+})$ and $(Al + Fe^{3+})$, but Fe^{2+}/Fe^{3+} is unknown for many of the vesuvianite samples, and Mg and Al are sufficiently dominant in most cases that the

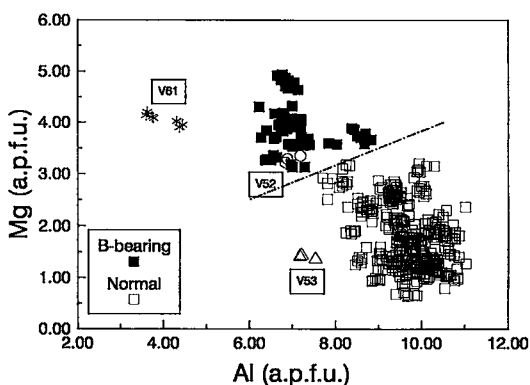


Fig. 15. Al versus Mg (a.p.f.u.) for boron-free and boron-bearing vesuvianite.

relationship is not obscured by ignoring Fe^{2+} and Fe^{3+} . Vesuvianite samples V52 and V53 are boron-free but lie in the field of boron-bearing vesuvianite. It is notable that these samples are also partially metamict, possibly leading to postcrystallization alteration. From Figures 14 and 15, we can conclude that the incorporation of B into vesuvianite also involves an increase in Mg and a decrease in Al.

There are three possible substitutions that lead to the incorporation of B into vesuvianite. All of these involve the loss of H, causing the change of OH^- to O^{2-} . The relationship between B and OH^- (+ F^-) is examined in Figure 16, both for calculated and measured OH^- values. For the calculated values, there is a negative correlation between B and OH^- , with the values scattering around the 1B:2H trend. Note that there are only a few samples for which we have measured OH^- , F^- , B and $\text{Fe}^{2+}/\text{Fe}^{3+}$. Nevertheless, a similar trend is ob-

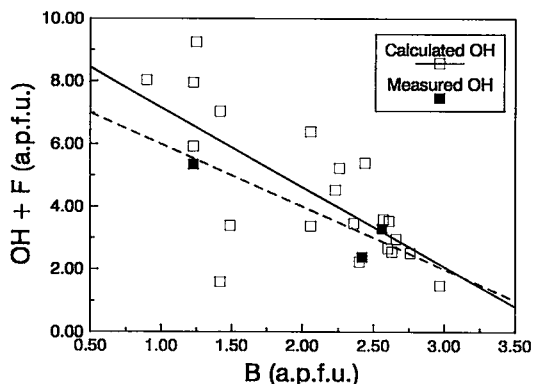


Fig. 16. B versus $(\text{OH} + \text{F})$ (a.p.f.u.). The dashed line represents a 1B:2H ratio, and the solid line is a linear fit to the data points.

served for these samples as well. This indicates that substitution (9), $\text{B} + \text{Mg} \rightleftharpoons 2\text{H} + \text{Al}$, is the principal mechanism for the incorporation of B into vesuvianite. This does not totally discount the other two mechanisms, as there is some structural evidence to suggest that substitution (10) may also be operative, although to a much lesser extent than substitution (9). In addition, boron-bearing vesuvianite does show Si values systematically less than the ideal value of 18.0 a.p.f.u. observed in boron-free vesuvianite, and small amounts of substitution (11) could possibly account for this. Evaluation of the presence of minor amounts of these substitutions must await the results of a detailed structural study of boron-bearing vesuvianite (currently in prep.).

PROPERTIES OF BORON-BEARING VESUVIANITE

The presence of boron in vesuvianite is of considerable geochemical and petrological significance. Fortunately, there are reliable and simple indicators of the presence of boron: (i) all samples of boron-bearing vesuvianite examined are optically positive, whereas all boron-free vesuvianite is optically negative. (ii) Boron-bearing vesuvianite has a longer a and a shorter c dimension than boron-free vesuvianite (see below, Fig. 21). (iii) Boron-bearing vesuvianite has low Al (+ Fe^{3+} ?) and high Mg (+ Fe^{2+} ?) compared to boron-free vesuvianite (see Fig. 15). (iv) Boron-bearing vesuvianite has much less OH^- (2–5 a.p.f.u.) than boron-free vesuvianite (8.5–10 a.p.f.u.).

These criteria indicate whether there is a significant amount of boron in vesuvianite. Such qualitative confirmation can indicate that analytical determination of boron content is worthwhile.

MAJOR- AND MINOR-ELEMENT CHEMISTRY

The data presented here give us the opportunity to examine the ranges and degree of importance of all the heterovalent and homovalent substitutions possible in the vesuvianite structure. The homovalent substitutions present no intrinsic problems, except for the determination of valence state in the transition metals (specifically Fe). Heterovalent substitutions are more complicated; the possible substitutions are shown in Table 9.

Calcium

There are up to 19 Ca cations in the formula unit, but limited substitution by the other large cations does occur. The average amount of Ca in the samples analyzed here is 18.8 atoms p.f.u., and Ca rarely falls below 18 cations p.f.u. Exceptions are the Ce-rich vesuvianite from San Benito

TABLE 9. POSSIBLE SUBSTITUTIONS IN VESUVIANITE

Starting formula/Additive component: $\text{Ca}_{18}(\text{Al}_{11}\text{Mg}_2)\text{Si}_{18}\text{O}_{38}(\text{OH})_0$		
Substitution	Site at which substitution occurs	Exchange operators
(1) $\text{Ln}^{3+} + \text{Na} \leftrightarrow 2\text{Ca}$	X	$\text{Ln}^{3+}\text{NaCa}_{-2}$
(2) $\text{Na} + \text{Al} \leftrightarrow \text{Ca} + \text{Mg}$	X, Y	$\text{NaAl}(\text{CaMg})_{-1}$
(3) $\text{Na} + \text{Ti}^{4+} \leftrightarrow \text{Ca} + \text{Al}$	X, Y	$\text{NaTi}(\text{CaAl})_{-1}$
(4) $\text{Ln}^{3+} + \text{Mg} \leftrightarrow \text{Ca} + \text{Al}$	X, Y	$\text{Ln}^{3+}\text{Mg}(\text{CaAl})_{-1}$
(5) $\text{Ln}^{3+} + \text{O}^{2-} \leftrightarrow \text{Ca} + \text{OH}^-$	X, O(10), OH	$\text{Ln}^{3+}\text{O}(\text{CaOH})_{-1}$
(6) $\text{Mg} + \text{Ti} \leftrightarrow 2\text{Al}$	Y	MgTiAl_{-2}
(7) $\text{Mg} + \text{OH}^- \leftrightarrow \text{Al} + \text{O}^{2-}$	Y, O(10), OH	$\text{MgOH}(\text{AlO})_{-1}$
(8) $\text{Ti} + \text{O}^{2-} \leftrightarrow \text{Al} + \text{OH}^-$	Y, O(10), OH	$\text{TiO}(\text{AlOH})_{-1}$
No substitutions are written involving Z-group cations in boron-free vesuvianite as there is no significant substitution for Si at the Z sites.		
(9) $\text{B}^{3+} + \text{Mg} \leftrightarrow 2\text{H} + \text{Al}$	T, Y, H(1)	$\text{BMg}(\text{H}_2\text{Al})_{-1}$
(10) $\text{B}^{3+} + 2\text{Hg} \leftrightarrow \text{H} + 2\text{Al}$	T, Y, H(2)	$\text{BMg}_2(\text{HAl}_2)_{-1}$
(11) $\text{B}^{3+} + \text{Al} \leftrightarrow 2\text{H} + \text{Si}$	T, Z*	$\text{BAl}(\text{H}_2\text{Si})_{-1}$
(12) $\text{Fe}^{2+} \leftrightarrow \text{Mg}$	Y	$\text{Fe}^{2+}\text{Mg}_{-1}$
(13) $\text{Cu}^{2+} \leftrightarrow \text{Mg}$	Y	$\text{Cu}^{2+}\text{Mg}_{-1}$
(14) $\text{Zn} \leftrightarrow \text{Mg}$	Y	ZnMg_{-1}
(15) $\text{Mn}^{2+} \leftrightarrow \text{Mg}$	Y	$\text{Mn}^{2+}\text{Mg}_{-1}$
(16) $\text{Fe}^{3+} \leftrightarrow \text{Al}$	Y	$\text{Fe}^{3+}\text{Al}_{-1}$
(17) $\text{F} \leftrightarrow \text{OH}$	OH, O(10)	$\text{F}(\text{OH})_{-1}$

*In boron-bearing vesuvianite, the Si sums tend to be less than the ideal value of 18, allowing substitutions at the Z sites.

County, California (V61), and an Sb-rich vesuvianite from Sarawak, Malaysia (Bradshaw 1972), which have minimum Ca values of 16.18 and 14.13 a.p.f.u., respectively. It is notable that in both of these cases, extensive substitution for Ca involves trivalent cations. Substitution of divalent (e.g., Pb^{2+}) and monovalent (e.g., Na) cations is much less extensive, rarely exceeding 0.5 a.p.f.u.

Rare-earth elements

These are fairly common as minor constituents in vesuvianite, but can reach significant levels (in this work, five samples of vesuvianite have in excess of 0.5 wt. % Ln_2O_3). The highest amounts recorded here are ~6 wt. % Ln_2O_3 (~1.2 a.p.f.u.) for V29 (Templeton Township, Quebec) and V38 (Ariccia, Italy), both boron-bearing vesuvianite; however, the other samples of boron-bearing vesuvianite contain only minor amounts of the REE. This association in V29 and V38 is presumably geochemical rather than crystal-chemical in origin. All samples of lanthanide-rich vesuvianite are relatively enriched in Fe. Again, this seems not to be of crystal-chemical significance. The structure of a REE-rich vesuvianite from San Benito County was refined by Fitzgerald *et al.* (1987). They stated that the REE substitute for Ca, Ti substitutes for Al at the Y(2) site, OH is an oxygen atom rather than a hydroxyl, and Mg substitutes for Al at the Y(2) site to maintain overall charge-balance. For this vesuvianite sample, the analytical results of Fitzgerald *et al.* (1987) give an anomalously low Si content, and the formula unit (normalized on 50

cations) has 0.72 Al assigned to the Z-group cations. This result does not agree with a previous analysis of a REE-bearing vesuvianite from this locality (Murdoch & Ingram 1966). Consequently, we reanalyzed a sample from this locality (Table 4, V61). The Si content is in line with that in all other samples of boron-free vesuvianite.

There are three possible substitutions involving the incorporation of REE at the X sites (Table 9). The San Benito County vesuvianite, V61, is particularly informative here as it contains virtually no Na, eliminating the $\text{Ln}^{3+} + \text{Na} \rightleftharpoons 2\text{Ca}$ and $\text{Na} + \text{Ti}^{4+} \rightleftharpoons \text{Ca} + \text{Al}$ substitutions in this sample. The other notable features of this sample are the extremely low Al content (~3.6 Al p.f.u.) and the very high Ti content. This indicates that the substitutions $\text{Ln}^{3+} + \text{Mg} \rightleftharpoons \text{Ca} + \text{Al}$ and $\text{Mg} + \text{Ti} \rightleftharpoons 2\text{Al}$ are the principal mechanisms for incorporating Ln^{3+} and Ti into the San Benito vesuvianite. The other possible mechanism involves substitution of O^{2-} for OH^- ; however, there are insufficient data on Ln^{3+} and OH^- contents of vesuvianite to test whether this substitution is of any significance. The situation in the other REE-bearing samples is less clear, both because of the smaller amounts of REE present, and because the presence of boron in two of these samples complicates the chemical variations.

Sodium

The most Na-rich samples occur in altered alkali syenites and related rocks. A vesuvianite from the nepheline gneiss complex near York River, Ontario (V6; Osborne 1930) contains ~0.88 wt. % Na_2O (0.85 atoms p.f.u.). A partly metamict sample from Alaska (V53), found in syenite boulders with nepheline and cancrinite (Himmelberg & Miller 1980), has 0.38–0.44 wt. % Na_2O . About half of the samples examined contain no Na; most of these are from rodingites associated with serpentinites.

Na occurs at the X sites. There are three possible substitutions for this (1, 2 and 3, Table 9). As shown in Figure 17 (and discussed in the section on Ti), Na and Ti are not correlated where Ti is less than 0.6 Ti p.f.u., but show a positive 1:1 correlation at larger values (except for REE-rich vesuvianite, e.g., V61, which has no Na). In most cases, vesuvianite does not contain electron-microprobe-detectable REE, eliminating substitution (1). This leaves substitutions (2), $\text{Na} + \text{Al} \rightleftharpoons \text{Ca} + \text{Mg}$, as the only possible polyvalent substitution to account for the incorporation of Na into vesuvianite at low values of Na and Ti.

Potassium

Only one sample of vesuvianite (V68) out of ~40

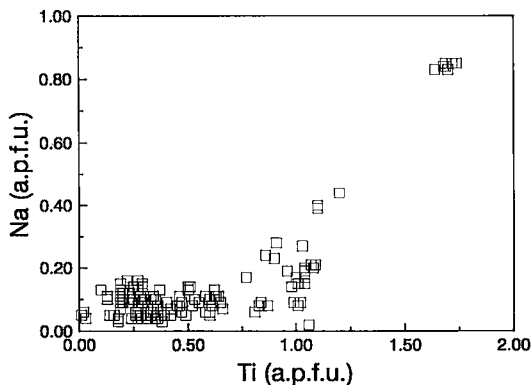


FIG. 17. Ti versus Na (a.p.f.u.; non-zero values for both only) showing their correlation at high Ti values.

analyzed for K contains electron-microprobe-detectable amounts (*i.e.*, above 0.04 wt. % K_2O). This is possibly because the *X* sites are too small to accommodate K. Analyses of a leached vesuvianite (V73) show up to 0.35 wt. % K_2O . The lack of K in all other samples suggests that detectable K is due to a minor admixed phase.

Lead

Analyses of the unusual Cu-rich vesuvianite from Franklin, N.J. (V68) show 0.31–2.06 wt. % PbO (0.04–0.28 atoms p.f.u.). No Pb was found in the other sample from this locality (V67), and this is the only report of Pb in vesuvianite. Pb replaces Ca in the structure.

Bismuth

Up to 2.49 wt. % Bi_2O_3 (0.32 atoms p.f.u.) occurs in the Mn-rich vesuvianite from Långban, Sweden (V50). No previous studies have reported Bi in vesuvianite. Bi replaces Ca in the vesuvianite structure, possibly at the *X*(3) site.

Thorium

The partly metamict, Fe- and Ln-rich vesuvianite from Alaska (V53) contains 1.43–1.50 wt. % ThO_2 (0.17–0.18 atoms p.f.u.). Thorium presumably replaces Ca in the structure. No U was detected in this sample.

Aluminum

The bimodal distribution of Al among the vesuvianite samples analyzed of this study (Fig. 14) correlates with the presence or absence of B.

However, as there are a disproportionate number of analytical data on boron-bearing vesuvianite, the sizes of the two maxima (Fig. 14) do not represent the natural proportion of the two types.

Al occurs primarily at two sites in the structure, Y(2) and Y(3), both of which are coordinated by oxygen atoms and hydroxyl groups in an octahedral arrangement. Phillips *et al.* (1987) have shown by MAS NMR that Al also occurs in [5]-coordination, presumably at the Y(1) site. Thus any substitutions involving Al can potentially occur at any or all of the three Y sites.

The ideal formula of vesuvianite contains up to 11.5 "effective" trivalent a.p.f.u. (Fig. 7c). However, the Al (and Al + Fe^{3+}) content does not exceed 11 a.p.f.u. in the samples examined by us (Figs. 7a, b, c). In addition, Al does not go below 8.00 a.p.f.u., except in boron-bearing vesuvianite and in V61 (San Benito County), in which the extensive substitution of Ln^{3+} also involves reduction in the Al content at the Y sites. For boron-bearing vesuvianite, the excess charge introduced into the structure by the incorporation of boron is partly compensated by the replacement of Al by Mg, leading to very low Al contents.

Magnesium

The Mg content ranges from 0.84 to 6.69 wt. % MgO (0.64–4.93 a.p.f.u.). The most Mg-rich sample is from Wilui River, U.S.S.R. (V75), and a Mn- and Zn-rich "cyprine" from Franklin, N.J. (V67) has the lowest Mg content.

Mg occupies the Y sites in the structure. Twelve of the thirteen Y sites constitute (four) linear edge-sharing octahedral trimers, with the Y(2) site in the middle and the Y(3) site at both ends (Fig. 2). Mean bond-lengths in several refined structures suggest that most substitutions for Al in this trimer occur at the Y(3) sites. Both Hoisch (1985) and Allen (1985) have suggested the following coupled substitution [(6) in Table 9]: $Mg^{2+} + Ti^{4+} \rightleftharpoons 2Al^{3+}$, in which Mg and Ti replace Al at neighboring Y(3) sites. Local charge-balance is maintained by changing bond lengths. It is unlikely that this substitution can account for all divalent cations at the Y(3) sites, as the amount of Ti in most samples is low. Other Mg substitutions of potential importance are numbers (2), (4), (6), (7), (9) and (10) in Table 9. For boron-free vesuvianite, substitution (2) should involve a decrease in the amount of Mg over the value of 2 a.p.f.u. As this is not observed, this mechanism is not of importance. As discussed in the section on the lanthanides, substitution (4) can be very important. However, in REE-free vesuvianite, this mechanism is obviously not applicable. Of key interest in the chemistry of boron-free vesuvianite is substitution

(7), discussed above in connection with charge-balance aspects of the structure. The substitution $\text{Mg}(+ \text{Fe}^{2+}) + \text{OH}^- \rightleftharpoons \text{Al}(+ \text{Fe}^{3+}) + \text{O}^{2-}$ also is an important mechanism for producing significant variations in $\text{Mg}(+ \text{Fe}^{2+})$ content in boron-free vesuvianite. As all the *Y* sites coordinate OH, the local environment of this substitution is not obvious, and more complete analyses must be performed before this particular substitution can be substantiated.

The most important mechanism for producing variation in Mg content of vesuvianite is the substitution involving boron: $\text{B} + \text{Mg} \rightleftharpoons 2\text{H} + \text{Al}$. This substitution is responsible for the highest Mg values, which thus occur in boron-bearing vesuvianite.

Iron

Although not an essential constituent of vesuvianite, iron is present in all samples analyzed, in amounts ranging from 0.19 to 7.43 wt.% FeO (all Fe as FeO; 0.08–3.26 a.p.f.u.). The most Fe-rich sample is a partly metamict vesuvianite from Alaska (V53), and the specimen with the least Fe is a “cyprine” (bright blue or green in color) from Norway (V48). In general, vesuvianite from rodingites has the lowest Fe contents.

Unfortunately, most modern analyses do not include $\text{Fe}^{2+}/\text{Fe}^{3+}$ determinations. As the roles of Fe^{2+} and Fe^{3+} in vesuvianite chemistry (as in all other minerals) are completely different, such analyses must be considered as deficient. Of the samples here that were analyzed for FeO, only 7 of the 25 samples have more ferrous than ferric iron ($\text{Fe}^{2+}/\text{Fe}^{3+} < 1.00$). The F- and Mn-rich vesuvianite from the Richardson Mountains, Yukon (V33) has the highest $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio (9.14). Most of the iron in the low-Fe vesuvianite from rodingites is ferric, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio being generally less than 0.50.

Fe is a *Y*-group cation; the stoichiometric arguments given above indicate that it does not occur at the *X* sites. Fe occurs at both the *Y*(1) and *Y*(3) sites, but site-occupancy refinements indicate that it does not substitute at the *Y*(2) site. Fe can be incorporated into the structure by the simple homovalent substitutions $\text{Fe}^{2+} \rightleftharpoons \text{Mg}$ and $\text{Fe}^{3+} \rightleftharpoons \text{Al}$. The simplest constraints on its variation are thus due to charge balance. However, the variation of both Fe^{2+} and Fe^{3+} in vesuvianite has a much more restricted range than the isovalent Mg and Al, and it is unclear, as yet, whether this is due to crystal chemical or to geochemical constraints.

There is one general chemical relationship involving Fe. As shown in Figure 18, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio seems independent of F content until approximately 3 F a.p.f.u.; a positive correlation

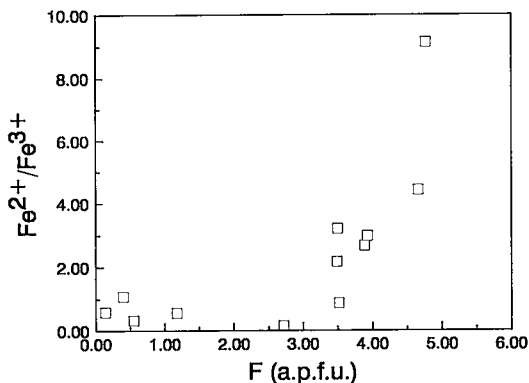


FIG. 18. F (a.p.f.u.) versus $\text{Fe}^{2+}/\text{Fe}^{3+}$ (non-zero values for F only).

is observed at higher F values. The correlation of $\text{Fe}^{2+}/\text{Fe}^{3+}$ with F at $F > 3$ a.p.f.u. is accompanied by analogous positive and negative correlations of Fe^{2+} and Fe^{3+} , respectively, with F. Normally Fe^{2+} tends to locally avoid bonding to F (the F avoidance “rule”), apparently in contrast to the observed correlation. At low values of F, there is no relationship between F and Fe. At higher values of F, presumably F begins to bond significantly to Fe^{3+} , which then locally orders at a different site that requires a change of valence state from Fe^{3+} to Fe^{2+} . This would account for the observed relationship of Figure 18. However, the specific details of this are not known, and must await detailed crystallographic studies.

Titanium

Titanium is a common accessory element in vesuvianite. The highest TiO_2 content presented here, 5.06 wt.%, 1.90 a.p.f.u., pertains to vesuvianite from Laguna del Jaco, Mexico (V45). Other analyses of this sample show only 0.26–1.33 wt.% TiO_2 (0.10–0.49 a.p.f.u.), so that there seems to be considerable local variability in the Ti-content of vesuvianite at this locality.

In general, the Ti-rich vesuvianite occurs in altered alkali syenites and related rocks. The sample from York River, Ontario (V6) contains 4.39–4.67 wt.% TiO_2 (1.64–1.67 a.p.f.u.). Ti can be incorporated into vesuvianite *via* substitutions (3), (6) and (8) (Table 9). Figure 17 shows the compositional data in regard to substitution (3). At Ti^{4+} values below 0.75 a.p.f.u., there is no correlation between Na and Ti^{4+} , and the Na contents are low (~ 0.05 a.p.f.u.). Above $\text{Ti}^{4+} = 0.75$ a.p.f.u., there is a positive correlation between Na and Ti, indicating that the substitution $\text{Na} + \text{Ti}^{4+} \rightleftharpoons \text{Ca} + \text{Al}$ is generally the principal substitution incorporat-

ing moderate to high levels of Ti into the vesuvianite structure. Substitution (6), $\text{Mg} + \text{Ti} \leftrightarrow 2\text{Al}$, is the principal mechanism incorporating Ti into the Ce-rich V61 vesuvianite. A mechanism also is needed to account for the incorporation of low levels of Ti into vesuvianite. Both substitutions (6) and (8) are possible, but the total variation is insufficient to allow the substitution scheme to be unequivocally resolved.

Seventeen of the 76 samples contain no detectable Ti. Most of these are from rodingites. The maximum amount of Ti found in a vesuvianite from Jeffrey, Quebec, is 1.20 wt.% TiO_2 (0.44 a.p.f.u.). All of the low-Ti samples from this locality are green, whereas all those with more than 0.10 wt.% TiO_2 are brown, confirming observations made by Manning (1975). Ti is generally considered to occupy the Y(3) site, although Manning (1975, 1976) suggested that it may occupy X(4), and Manning & Tricker (1975) suggested that it may also be found at Y(1). The general stereochemistry of Ti^{4+} in an oxygen-rich environment suggests that some of these assignments are unlikely, and much structural work is necessary to resolve the question of site occupancy of Ti in vesuvianite.

Manganese

Although most of the samples contain minor amounts of Mn, very few have more than 0.5 wt.% MnO. Manganese in the bright red Bi-rich vesuvianite from Långban, Sweden (V50), ranges from 3.10 to 3.80 wt.% MnO (1.32–1.61 a.p.f.u.). Both samples from Franklin, N.J., are rich in Mn; V67 contains 1.68–1.97 wt.% MnO (0.71–0.85 a.p.f.u.), and V68 contains 1.23–1.57 wt.% MnO (0.52–0.67 a.p.f.u.). One of the "cyprine" samples from Norway (V48) contains 0.95 wt.% MnO (0.39 a.p.f.u.), and the F- and Cl-rich vesuvianite from Long Lake mine in Ontario (V5) has 0.75–0.80 wt.% MnO (0.33–0.34 a.p.f.u.). The MnO content of the high-F vesuvianite from the Richardson Mountains, Y.T. (V33) ranges from 0.67 to 0.80 wt.% (0.28–0.33 a.p.f.u.). Although Arem (1970) stated that almost all samples contain trace amounts of Mn, no Mn was found in 15 of the 75 samples analyzed in this study. Mn is a chromophore in vesuvianite; a small amount in Fe-poor samples causes a pink or lilac color in hand specimen. Some of the crystals from Jeffrey, Quebec, have lilac-colored (Mn-rich) pyramidal faces capping green (Fe-rich) prisms.

Manganese can show two very different types of behavior in silicates; it can enter into solid solution with small and intermediate-sized divalent cations (e.g., Mg, Fe^{2+}), or it can enter into solid solution with large divalent cations (e.g., Ca). The behavior

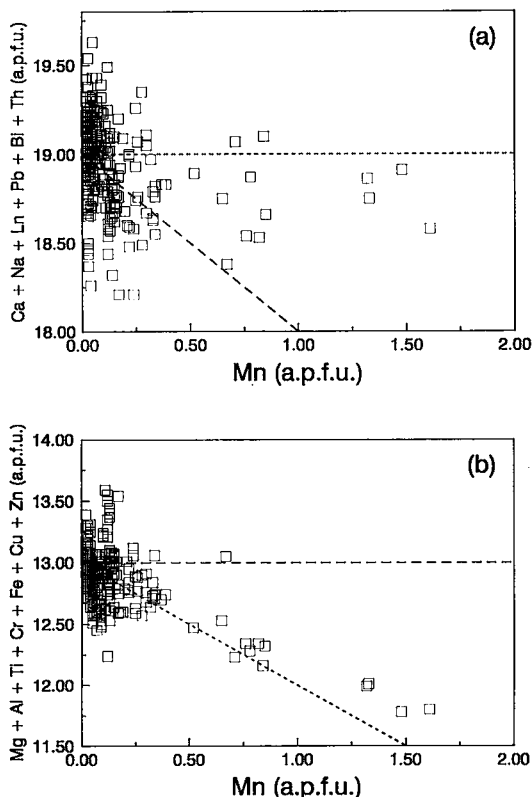


FIG. 19. Variation of Mn in vesuvianite: (a) ΣX versus Mn; (b) ΣY versus Mn. The cation sums do not include Mn, and the stronger broken lines denote the trend expected if Mn substituted at the X or Y sites, respectively.

of Mn (assumed to be divalent) is examined in Figure 19, which shows the sums of X and Y cations (excluding Mn) versus Mn content. There is no relationship between ΣX and Mn, whereas for high Mn contents, ΣX decreases in a 1:1 ratio with increasing Mn content. This indicates that in Mn-rich samples, Mn occurs at the Y sites. It is possible that at low Mn contents, some Mn may occur at the X sites, but there is no evidence for this in the chemical data presented here.

Chromium

A sample of dark green vesuvianite from Xanthi, Greece (V36) has the most Cr, with 0.34–0.63 wt.% Cr_2O_3 (0.13–0.24 a.p.f.u.); this is the sample described by Frenzel *et al.* (1969), who reported a maximum of 0.48 wt.% Cr_2O_3 . Other samples of vesuvianite contain only minor amounts of Cr.

In general, chromium-bearing vesuvianite has a vivid green color, as Cr is a strong chromophore. Chromium probably occurs at the Y(3) site in the structure. It is also notable that Cr-enriched vesuvianite tends to have little or no prism {100} development, the most prominent form being {101}.

Copper

Copper was found in vesuvianite from Franklin, N.J. (V67, V68) and Norway (V47, V48). Sample V68 contains 1.13–1.55 wt.% CuO (0.43–0.59 a.p.f.u.), and V67 has 0.41–0.63 wt.% CuO (0.16–0.24 a.p.f.u.). Copper in the Norwegian samples ranges from 0.44 to 0.94 wt.% CuO (0.16–0.35 a.p.f.u.).

All of these samples are "cyprine", although Fitzgerald (1985) found that some red and brown vesuvianite at Franklin contain as much Cu as the "cyprine" samples, and that the amount of Fe probably determines the color. The samples from Franklin also show a fibrous habit, commonly reported for "cyprine". The crystal structure of a copper-bearing vesuvianite was refined by Fitzgerald *et al.* (1986a), who concluded that Cu occupies the Y(1) site.

Zinc

Both copper-bearing samples from Franklin, N.J., also contain Zn, in amounts ranging from 1.43 to 2.35 wt.% ZnO (0.53–0.87 a.p.f.u.). The Pb-rich material (V68) contains slightly more Cu and less Zn than the other sample. Only trace amounts of Zn were found in other samples.

Zinc probably occupies the Y(1) or Y(3) sites. It is interesting to note that samples V67 and V68 contain 0.99–1.04 and 1.03–1.13 (Cu + Zn) a.p.f.u. respectively, enough to completely fill the Y(1) site; Cu and Zn possibly are ordered at Y(1) in these samples.

Silicon

Boron-free vesuvianite contains ~18 Si a.p.f.u., which suggests that there is no Al → Si or H → Si ("hydro-vesuvianite") substitution in the samples studied. The mean value for Si in boron-bearing vesuvianite is 17.7 a.p.f.u., normalized on the basis of 50 cations (less B and S). Thus either Si is replaced by another cation, or some of the Z sites are vacant. If vacancies occur at the Z sites, some oxygen atoms will locally show extreme bond-valence deficiencies, even allowing for the fact that other high-valence cations (*e.g.*, B³⁺, Al) may bond to some of the coordinating ions. If other cations replace Si at the Z sites, the only possibilities are Al, B (and possibly Fe³⁺, although we consider this

as very unlikely). These possibilities can only be resolved from a detailed experimental examination of the relevant local stereochemistry, and will be addressed in a forthcoming paper.

Boron

The highest amounts of boron (~3.18 wt.% B₂O₃) occur in samples from Templeton Township, Quebec (V29), and Tulare County, California (V56). The amount of boron in a particular sample may vary considerably, and two specimens (V44 and V75) show sector-zoning. Boron-bearing vesuvianite generally contains more Mg, less Al and less OH than those without boron. Four of the six samples also have high concentrations of lanthanide elements (although V56 has no detectable rare earths at all). Boron does not replace other cation species, which suggests that it occupies vacant site(s) in the structure. One possibility is the T site at (0.05, 0.05, 1/4), which is coordinated by 2 O(7) and 2 OH positions in an approximately tetrahedral arrangement. If this is the case, the coupled substitution B³⁺ + Mg²⁺ = 2H⁺ + Al³⁺ could account for the high Mg, low Al and low OH⁻ contents of the boron-bearing vesuvianite.

Fluorine

Most of the samples analyzed in this study contain minor to significant amounts of F. A vesuvianite from Richardson Mountains, Y.T. (V33) contains up to 3.15 wt.% F (4.84 a.p.f.u.). Both "cyprine" samples from Norway are F-rich; sample V48 had up to 2.82 wt.% F (4.32 a.p.f.u.). Four other samples (V4, V5, V72 and V71) gave analyses with more than 4 F a.p.f.u. Vesuvianite samples from altered alkali syenites and related rocks are generally described as being F-rich, but the material from York River, Ontario (V6), has no detectable fluorine (<0.6 wt.%). Vesuvianite from rodingites has only minor amounts of F. F⁻ presumably replaces OH⁻ at the OH and O(10) sites. At present, the relative site-preference of F⁻ for these two sites is unknown. However, as the amount of F in vesuvianite commonly exceeds the number of O(10) sites (*i.e.*, 2 sites p.f.u.), F⁻ must occupy the OH site in some high-F samples.

H₂O

Figure 20 is a histogram of calculated OH⁻ abundance. There is a bimodal distribution, with OH⁻ from analyses of boron-bearing vesuvianite clustered around 5.0 a.p.f.u., and the others centered about 9.0 a.p.f.u. The mean calculated OH⁻ content of the 76 boron-bearing analyses is 5.3(1.6) a.p.f.u. (50-cation normalization). For the

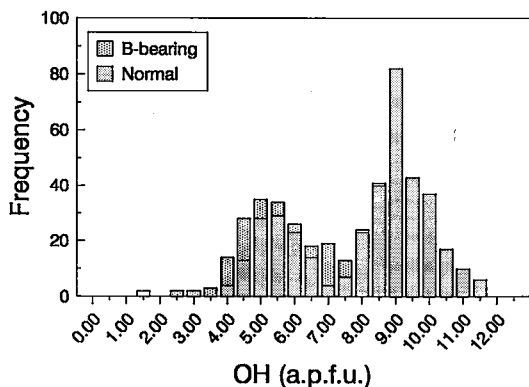


FIG. 20. Histogram of calculated OH abundance (a.p.f.u.) for boron-free and boron-bearing vesuvianite.

388 boron-free analyses, it is 8.0(1.9); this is considerably lower than 9.0, presumably because the "boron-free" data-set contains data for some boron-bearing samples that were not identified as such.

Figure 21 shows measured H_2O versus calculated H_2O (both wt. %). The observed trend suggests that H_2O calculations are good only for samples with up to 3.00 wt. % H_2O . Earlier, we suggested that the samples with highest analyzed H_2O had significant adsorbed H_2O involved in this analytical amount. Figure 21 also shows that boron-bearing vesuvianite has a low H_2O content. Samples V56 and V75 (both with ~ 2.90 wt. % B_2O_3) have the lowest H_2O contents (0.61 and 0.86 wt. %). This is approximately 2 OH^- a.p.f.u. Sample V62, with less B, ~ 1.44 wt. % B_2O_3 , has more H_2O (1.41 wt. % H_2O , or ~ 4 OH^- a.p.f.u.).

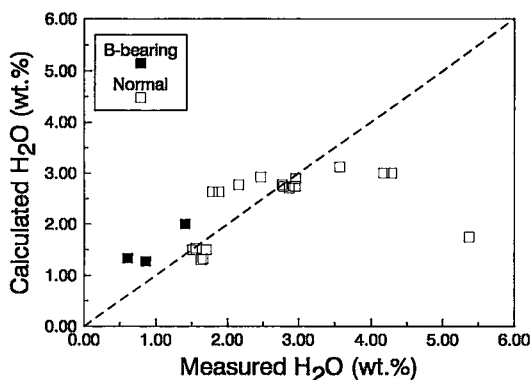


FIG. 21. Measured H_2O versus calculated H_2O (both wt. %). The dark squares represent data for boron-bearing vesuvianite. All Fe is assumed to be ferrous, except in cases where Fe^{2+}/Fe^{3+} is known.

CO_2

Only minor amounts of CO_2 were found in the samples analyzed. A boron-bearing sample, V56, has 0.50 wt. % CO_2 , and three other samples (V43, V60 and V62) contain in excess of 0.30 wt. % CO_2 . The role of CO_2 in the structure is unclear; we consider it likely that these small amounts result from carbonate inclusions, although because of the presence of (BO_3) groups in boron-bearing vesuvianite, we cannot totally discount the possibility of structural incorporation of (CO_3) groups.

Sulfur

Up to 1.00 wt. % SO_3 (0.37 a.p.f.u.) was found in the boron-bearing vesuvianite from Laguna del Jaco, Mexico (V44). This is probably the most S reported in vesuvianite. The other sample from this locality (V45) showed a maximum of 0.63 wt. % SO_3 (0.23 a.p.f.u.). Vesuvianite from Mont Saint-Hilaire in Quebec (V24) contains 0.87 wt. % SO_3 (0.32 a.p.f.u.). Many of the sulfur-bearing samples are rich in F, and some contain both S and Cl. However, the role of S in vesuvianite is unclear.

Chlorine

The F-rich vesuvianite from Long Lake mine in Ontario (V5) also contains up to 1.18 wt. % Cl (0.56 a.p.f.u.), and a sample from Amity, New York (V70), gave a maximum of 0.37 wt. % Cl (0.31 a.p.f.u.). Almost all of the chlorine-bearing samples contain significant amounts of F, and a few have both S and Cl. Like F^- , Cl^- presumably replaces OH^- in the vesuvianite structure.

Vector representation of vesuvianite composition

The vector method of representing mineral compositions is quite widely used at present, and a brief description of vesuvianite chemistry in these terms seems warranted. Explanations and applications of the method of vector representation in this context are given by Burt (1979, 1988, 1989) and Thompson (1981, 1982). The idea is very straightforward. If one defines a "starting formula", additional formulae may be derived by substituting one or more components of the original starting formula by other components. The starting formula is called the additive component, and the substitutions may be represented as vectors in compositional space. The vectors are called exchange operators and are simply represented in terms of their effect. Thus in olivine, we may define forsterite, Mg_2SiO_4 , as the additive component, and use the exchange operator $FeMg_{-1}$ to derive the formula of fayalite, Fe_2SiO_4 .

The origin of the exchange vectors is specified by one specific mineral composition called the additive component. Any end member can be used as the additive component; for vesuvianite, we will use the composition $\text{Ca}_{19}\text{Al}_{11}\text{Mg}_2\text{Si}_{18}\text{O}_{68}(\text{OH})_9\text{O}$. The more important substitutions are given in Table 9, both in conventional form and as exchange operators. These may be divided into two types, heterovalent exchange-operators, (1)–(11), and homovalent exchange-operators, (12)–(17). Estimation of the relative importance of the heterovalent exchange-operators is complicated by the common lack of information concerning the homovalent operators $\text{Fe}^{2+}\text{Mg}_{-1}$ and $\text{Fe}^{3+}\text{Al}_{-1}$ and the OH content. A detailed examination of compositional variations in vesuvianite as a function of paragenesis will appear elsewhere.

CELL DIMENSIONS

A total of 86 sets of cell dimensions were recorded from 71 different samples (Table 10). In most cases, the crystals used were from the bulk specimen, and were not taken from microprobe mounts or thin sections. Three of the samples are microcrystalline aggregates (V3, V58, and V76), and one is metamict (V73). The smallest unit-cell volume belongs to a copper-bearing sample from Norway (V48₂); the largest cell was recorded from a partly metamict sample from Alaska (V53). The *a* dimension varies considerably in vesuvianite (Fig. 22). However, most samples with *a* greater than 15.62 Å either contain boron (filled squares) or are partly metamict (V52, V53). Two of the samples with *a* greater than 15.62 Å contain no boron and

TABLE 10. CELL DIMENSIONS OF VESUVIANITE SAMPLES USED IN THIS WORK

Sample	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	Sample	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
V1	15.540(1)	11.809(1)	2851.7(6)	V37	15.535(1)	11.819(1)	2852.5(5)
V2	15.516(2)	11.781(1)	2836.3(7)	V38	15.708(2)	11.748(2)	2898.5(8)
V3	microcrystalline			V39	15.566(1)	11.841(2)	2869.1(5)
V4	15.527(1)	11.786(1)	2841.5(4)	V40	15.581(2)	11.833(1)	2872.8(8)
V5	15.648(2)	11.827(2)	2895.9(8)	V41	15.602(1)	11.854(1)	2885.5(5)
V6	15.591(2)	11.851(2)	2880.8(7)	V42	15.585(1)	11.830(2)	2873.3(6)
V7 ₁ *	15.546(2)	11.822(2)	2857.3(7)	V43 ₁	15.600(2)	11.786(2)	2868.1(7)
V7 ₂	15.544(1)	11.820(1)	2856.1(6)	V43 ₂	15.597(1)	11.767(1)	2862.3(5)
V7 ₃	15.501(1)	11.760(1)	2825.7(5)	V44	15.634(3)	11.747(3)	2872(1)
V8	15.529(2)	11.803(2)	2846(1)	V45	15.624(3)	11.780(5)	2876(2)
V9	15.535(2)	11.815(1)	2851.2(6)	V46	15.519(2)	11.773(2)	2835(1)
V10 ₁	15.523(2)	11.816(3)	2847.2(9)	V47 ₁	15.518(1)	11.786(1)	2838.2(6)
V10 ₂	15.507(2)	11.813(2)	2840(1)	V47 ₂	15.522(1)	11.780(1)	2838.2(5)
V10 ₃	15.522(2)	11.829(3)	2850(1)	V48 ₁	15.508(2)	11.763(3)	2829(1)
V11	15.537(1)	11.815(2)	2852.2(6)	V48 ₂	15.490(2)	11.765(2)	2822.9(7)
V12 ₁	15.522(1)	11.802(2)	2843.3(7)	V49	15.548(2)	11.826(2)	2858.7(7)
V12 ₂	15.521(1)	11.813(1)	2845.7(6)	V50	15.592(2)	11.780(3)	2864(1)
V12 ₃	15.538(3)	11.819(3)	2853(1)	V51	15.520(2)	11.807(1)	2844.0(6)
V13	15.518(1)	11.803(1)	2842.1(4)	V52 ₁	15.670(5)	11.759(9)	2888(3)
V14	15.531(2)	11.807(1)	2848.0(7)	V52 ₂	15.656(4)	11.736(4)	2876(2)
V15	15.537(2)	11.815(2)	2852.2(7)	V53	15.792(5)	11.993(8)	2991(3)
V16	15.543(2)	11.820(2)	2855.6(8)	V54	15.564(1)	11.827(2)	2864.8(6)
V17	15.526(1)	11.814(1)	2847.9(5)	V55	15.541(2)	11.789(2)	2847.2(7)
V18	15.532(1)	11.823(1)	2852.1(6)	V56	15.738(1)	11.730(2)	2905.2(6)
V19	15.526(2)	11.815(1)	2848.0(8)	V57 ₁	15.564(1)	11.833(2)	2866.5(6)
V20 ₁	15.529(2)	11.813(3)	2848(1)	V57 ₂	15.551(1)	11.820(1)	2858.4(4)
V20 ₂	15.689(2)	11.751(2)	2892.3(8)	V58	microcrystalline		
V20 ₃	15.512(1)	11.798(1)	2838.7(4)	V59	15.560(1)	11.827(1)	2863.5(6)
V21	15.540(1)	11.818(1)	2853.9(4)	V60	15.584(1)	11.822(1)	2870.8(5)
V22 ₁	15.519(1)	11.808(2)	2843.9(7)	V62	15.664(1)	11.769(1)	2887.8(5)
V22 ₂	15.520(1)	11.801(2)	2842.4(6)	V63	15.569(1)	11.811(2)	2862.9(6)
V23	15.529(2)	11.787(1)	2842.4(7)	V64	15.510(1)	11.763(2)	2829.8(5)
V24	15.562(1)	11.821(1)	2862.6(5)	V65	15.524(1)	11.764(1)	2834.9(5)
V25	15.552(2)	11.802(1)	2854.5(7)	V66	15.513(1)	11.779(2)	2834.5(6)
V26	15.545(2)	11.797(2)	2850.9(8)	V67 ₁	15.541(1)	11.787(2)	2846.7(6)
V27	15.539(1)	11.792(2)	2847.2(6)	V67 ₂	15.519(2)	11.771(1)	2834.7(6)
V28	15.539(1)	11.793(1)	2847.5(5)	V68	15.524(2)	11.793(2)	2841.8(7)
V29	15.730(1)	11.731(1)	2902.6(5)	V69	15.565(1)	11.831(2)	2866.5(5)
V30	15.547(2)	11.806(3)	2853.6(9)	V70	15.556(2)	11.811(2)	2858.3(7)
V31	15.530(1)	11.788(2)	2842.7(6)	V71	15.543(1)	11.791(1)	2848.4(5)
V32	15.557(1)	11.791(1)	2853.7(5)	V72	15.555(2)	11.833(1)	2862.8(7)
V33	15.510(2)	11.766(2)	2830(1)	V73	metamict		
V34	15.564(1)	11.774(2)	2851.9(6)	V74	15.651(2)	11.792(1)	2888.3(6)
V35	15.524(1)	11.777(1)	2838.1(4)	V75	15.750(1)	11.704(2)	2903.4(6)
V36	15.565(1)	11.839(2)	2868.0(5)	V76	microcrystalline		

*Subscripts refer to different crystals from the same sample.

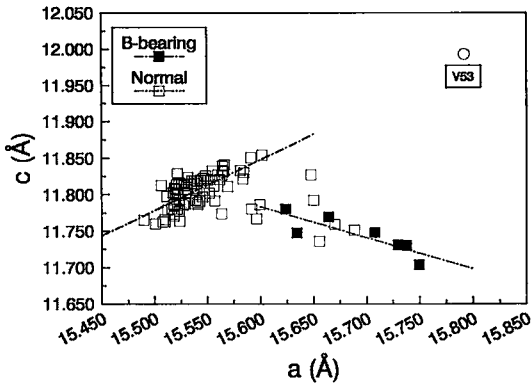


FIG. 22. Cell dimensions a versus c of vesuvianite. The dark squares represent boron-bearing vesuvianite; they are (left to right) V44, V45, V62, V38, V29, V56 and V75. The outlier represents V53, a partly metamict vesuvianite. The size of a symbol on this graph represents two standard deviations. The lines through the data points are not least-squares fits to the data, but were drawn solely as a guide to the eye. Samples of nominally boron-free vesuvianite that belong to the boron-bearing trend were not analyzed for boron and may be boron-bearing.

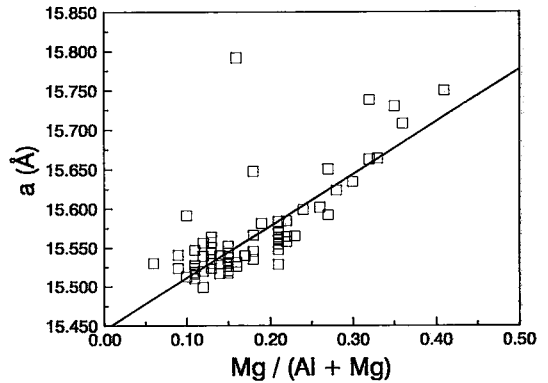


FIG. 23. $Mg/(Al + Mg)$ versus a . The solid line is a linear fit to the data points, minus the outlier (sample V53).

are nonmetamict (V5 and V20_p); the compositional reason for this is not apparent. The smallest a dimensions are from the copper-bearing sample from Norway. Ito & Arem (1970) found that synthetic and natural samples of copper-bearing vesuvianite all have a small unit-cell volume. The a cell length for copper-bearing samples in this study ranges from 15.490 to 15.541 Å, and seems relatively insensitive to variation in Cu content.

A graph of a against c (Fig. 22) shows that boron-bearing vesuvianite has a larger a dimension than boron-free vesuvianite, but a slightly smaller c dimension. Most of the remaining points define a general trend whereby a and c increase sympathetically. Samples of vesuvianite from rodingites seem to define a distinct group within this diagram. As vesuvianite from these localities is known to be Al-rich and Mg-poor, a was plotted against $Mg/(Al + Mg)$ (averaged analyses) for all of the samples (Fig. 23). There is an obvious inverse relationship between the a dimension and Al content, and a direct relationship between a and Mg. The relationship between a and $Mg/(Al + Mg)$ is expected, as the ionic radii of $^{[6]}Al$ and $^{[6]}Mg$ differ by 0.18 Å (Shannon 1976). There is no regular relationship between c and $Mg/(Al + Mg)$. Other elements (Ti, Fe, etc.) were plotted against a , c and V , but no correlations were seen.

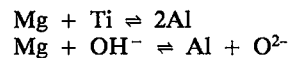
Ito & Arem (1970) found that a synthetic Mg-rich vesuvianite has a larger cell than most natural samples, and suggested that this was so because most natural samples contain F or are partially dehydroxylated. Numano *et al.* (1978) attributed the large unit-cell dimensions of some Japanese samples to high H_2O contents. Graphs of a , c and V against F and $(F + Cl + OH)$ (calc.) showed no such relationship in the samples examined here.

GENERAL SUMMARY

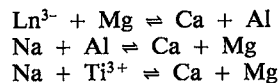
(i) The general chemical formula of vesuvianite can be written as $X_{19}Y_{13}Z_{18}T_{0.5}O_{66}W_{10}$, in which X stands for Ca, Na, Ln^{3+} , Pb^{2+} and Sb^{3+} , Y stands for Al, Mg, Fe^{3+} , Fe^{2+} , Ti^{4+} , Mn, Cu and Zn, Z = Si, T = B, and W stands for (OH,F,O)

(ii) Formula-unit normalization is best done on the basis of 50 ($X + Y + Z$) cations for boron-free vesuvianite, and 19 X cations for boron-bearing vesuvianite.

(iii) Examination of a wide variety of analytical data show the principal heterovalent substitutions in boron-free vesuvianite to be



with the more minor substitutions



occasionally reaching significant levels.

(iv) This study has recognized the incorporation of B into vesuvianite as a more common occurrence than was hitherto recognized.

(v) Results of chemical analyses of boron-bearing vesuvianite generally show less than 8.00 Al a.p.f.u., and more than 2.5 Mg a.p.f.u. It is apparent that the wide range of $Al^{3+} \rightleftharpoons Mg^{2+}$ and $O^{2-} \rightleftharpoons OH^-$ substitutions are due to the occurrence of B^{3+} in the structure. The principal substitution involved is $B^{3+} + Mg \rightleftharpoons 2H + Al$, with B locally replacing two hydrogen atoms, and Mg replacing Al at the Y sites in the structure. Boron-bearing vesuvianite also contains much less OH than boron-free vesuvianite. The latter have, on average, 9.0 OH a.p.f.u. compared with ~ 5.0 OH a.p.f.u. for boron-bearing vesuvianite. It is these "hidden" substitutions involving the very light elements hydrogen and boron that have given vesuvianite its apparently inexplicably wide range of chemistry.

(vi) Boron-bearing vesuvianite can be recognized by the following characteristics: (a) it is optically positive, whereas boron-free vesuvianite is optically negative; (b) the *a* dimension is greater than 15.62 Å, and the *c* dimension is less than 11.80 Å; (c) the Mg content is usually greater than 3 a.p.f.u., and the Al content is usually less than 8.5 a.p.f.u.

(vii) None of the vesuvianite samples analyzed contain Li or Be in significant quantities.

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