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THE CRYSTAL STRUCTURES OF THREE CANADIAN VESUVIANITES

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ABSTRACT

The crystal structures of vesuvianites from Great Slave Lake, N.W.T., Bancroft, Ontario, and Wakefield, Quebec, have been determined from data collected on four-circle diffractometers. The three samples belong to the space group *P4/nnc* and have similar chemistry and cell parameters ($a = 15.516$, 15.558, 15.543; $c = 11.769$, 11.810, 11.791 Å). Full-matrix least-squares refinement of the structures, including anisotropic temperature factors, gave conventional *R* values of 0.039, 0.047 and 0.05.

The structures are virtually identical, and very similar to that proposed by Coda *et al.* (1970). There are four more oxygen atoms in the unit cell than proposed by Warren & Modell (1931) in their original determination. The formula which most correctly describes the contents of one unit cell is

$$2[Ca_{19}Al_4Fe(Al,Mg,Fe)_8Si_{18}O_{70}(OH)_8]$$

INTRODUCTION

The crystal structure of vesuvianite from Bric Camula, Italy was recently described by Coda *et al.* (1970), who found significant differences when compared with the original structure of Warren & Modell (1931). Before the recent work was published, the present studies were underway, and independently almost identical structures were found.

There has been much discussion concerning the formula of vesuvianite (which was well summarized by Ito & Arem, 1970). The cell content proposed by Warren & Modell (1931) was

$$2[Ca_{20}Al_8(Mg,Fe)_4Si_{18}O_{68}(OH)_8]$$

and this fitted into the structure which they ingeniously derived from that of grossular garnet. Their proposed structure was checked by comparison of 41 observed and calculated structure factors, which gave fair agreement. Study of this structure suggests that the atoms lying on the 4-fold axis, the only part not included in the garnet analogy, should be the subject of further investigation. Warren & Modell suggested that the only atoms on the 4-fold axis were 2 Ca atoms separated by 2.84Å, each coordinated by square antiprisms which shared one of their square faces. Coda *et al.* have determined a structure which is similar to that of Warren & Modell but has a new distribution of atoms along the 4-fold axis. They propose an additional two oxygens (4 per cell) between which they favour a hydrogen bond, and four cation positions (8 per cell) which are statistically occupied by two Ca and two Fe atoms (with minor Ti and Mn). The disordered occupancy of one-half atom per site still has Ca in an 8-fold square antiprism coordination, but the Fe is in 5-fold coordination in a square pyramid. This model, which gave satisfactory agreement of observed and calculated structure factors, led them to suggest the formula

$$2[Ca_{19}(Mg,Fe,Al,Ti,Mn)_5Al_8(O,OH)_{10}(SiO_4)_{10}(Si_2O_7)_4].$$

EXPERIMENTAL

In this work samples of vesuvianite from three Canadian localities were studied. Specimens from Turnback Lake near Great Slave Lake, N.W.T., previously described by Meen (1939), R.O.M. #M19485 kindly supplied by Dr. R. I. Gait, and #2 the Davis Pegmatite, York River complex, Bancroft, Ontario, kindly supplied by Dr. G. M. Anderson, were investigated at the University of Toronto. Sample #3 (cat. #4-555, National Mineral Collection, from Wakefield, Quebec, Geological Survey of Canada) was studied at the National Research Council.

All three samples were brown in colour with chemical and crystal data as listed in Table 1. Analyses for samples #1 and #2 were performed with an ARL-EMX electron probe using the method described by Rucklidge *et al.* (1970). The analysis for sample #3 was performed at the Mines Branch, Dept. of Energy Mines and Resources, Ottawa. The actual crys-

TABLE 1. CRYSTAL AND CHEMICAL DATA FOR VESUVIANITES

Crystal data	#1 Gt. Slave L.	#2 Bancroft	#3 Wakefield
Space group	$P4/nnc$	$P4/nnc$	$P4/nnc$
a(Å)	15.516(3)	15.558(4)	15.5430(12)
c(Å)	11.769(2)	11.810(3)	11.7905(7)
V(Å)^3	2833.3	2858.6	2848.4
D_{meas}	3.432* g/cm^3	--	--
D_{calc}	3.443 g/cm^3	3.431 g/cm^3	3.430 g/cm^3
Electron probe analysis			
SiO_2	36.6	36.4	37.0
Al_2O_3	15.7	14.1	17.0
BeO*	1.07	--	--
TiO_2	0.19	4.59	0.95
Fe_2O_3†	5.16	5.54	4.05
MnO	0.50	0.26	n.d.
MgO	2.17	0.81	1.79
CaO	35.6	33.6	37.5
Na_2O	0.04	1.17	n.d.
F	2.03	--	--
H_2O††	1.48	2.38	2.46
	100.5	99.6	100.8
-O ≡ F	0.85		
	99.7		

Cell content

#1. $2[Ca_{18.8}Fe(Fe_{.11}Ti_{.01}Mn_{.03}Mg_{.20}Al_{.65})_{7.88}Al_4Si_{18}O_{70.5}(OH_{.61}F_{.39})_8 \cdot Be_{1.27}]$

#2. $2[(Ca_{.94}Na_{.06})_{19.0}Fe(Fe_{.14}Ti_{.21}Mn_{.01}Mg_{.07}Al_{.57})_{8.13}Al_4Si_{18}O_{70.6}(OH)_8]$

#3. $2[Ca_{19.5}Fe(Fe_{.06}Ti_{.04}Mg_{.17}Al_{.73})_{7.88}Al_4Si_{18}O_{70.4}(OH)_8]$

*Taken from Meen (1939). †Fe calculated as Fe_2O_3
-- not determined; n.d. not detected
††Calculated to give 16(OH,F) per cell

tals used for *x*-ray analysis were different from those on which the probe analyses were performed, but are believed to be representative.

All three samples contain more than 4% Fe_2O_3 (total Fe calculated as Fe_2O_3) and may therefore be classed as 'high Fe' vesuvianites, when compared with the variety of analyses given by Deer *et al.* (1962). The differences between the analyses are unremarkable except that #2 contains a relatively high TiO_2 content. The dark brown colour of the crystals is presumably related to the high Fe content. The 3 cell contents correspond closely to the 'ideal' one of Coda *et al.* (1970), which we have chosen to rearrange slightly as:

$$2[Ca_{19}Fe(Fe,Ti,Mn,Mg,Al)_8Al_4Si_{18}O_{70}(OH,F)_8]$$

All three crystals belong to the space group $P4/nnc$, as was unambiguously determined from long-exposure Weissenberg and precession photographs taken with Mo$K\alpha$ and Cu$K\alpha$ radiations. No extra reflections violating $P4/nnc$ extinction requirements were observed.

Crystal #1 was a rather irregular tetragonal prism, crystal #2 an irregular rectangular prism flattened in the c direction, and crystal #3 from Wakefield, Quebec, was ground into a sphere in a Nonius crystal grinder. All three crystals were mounted separately on Picker four-circle diffractometers for intensity data collection. Mo$K\alpha$ radiation was used for data collection on all three crystals and several standard reflections were monitored during this process to check for stability of the electronic system and possible crystal misalignment. A summary of the experimental methods employed is given in Table 2. The data were reduced in the usual way and corrected for Lp factors.

Scattering factors used in the least-squares refinement of data from all crystals were those reported by Cromer & Mann (1968). Anomalous dispersion corrections were made for all atoms except oxygen and corresponding f' and f'' values were taken from Cromer & Lieberman (1970).

TABLE 2. SUMMARY OF EXPERIMENTAL METHODS AND RESULTS

	#1 Gt. Slave Lake	#2 Bancroft	#3 Wakefield
Crystal size	0.24x0.24x0.30mm	0.36x0.21x0.17mm	0.17mm radius
Radiation used	Zr-filtered Mo$K\alpha$	Zr-filtered Mo$K\alpha$	monochromatized Mo$K\alpha$
Instrument	Picker FACS-1	Picker FACS-1	automated Picker
2θ-θ scan speed	1°/min	1°/min	2°/min
Background	2 x 40 sec	2 x 20 sec	2 x 30 sec
Std. reflections meas.	2 every 60 refl.	2 every 60 refl.	3 every 25 refl.
Data up to $(\sin\theta/\lambda)$ max.	0.70	0.70	0.80
No. of independent reflections measured	2082	2045	4281
No. of 'observed' refl.	1727(3σ)	1701(3σ)	3390(1.65σ)
Absorption corrections	not applied	not applied	spherical
Weighting scheme	unit weights	unit weights	statistical
Final R value	0.039	0.047	0.050
Final R_w	0.050	0.059	0.044

Despite initial problems of fitting the data to the structure model of Warren & Modell (1931), who had used a left-handed system of axes, it became clear that their model was essentially correct, though the electron density distribution along the 4-fold axes indicated serious discrepancies. The interpretation of this distribution is somewhat subjective, but it can be satisfactorily explained by the model of Coda *et al.* (1970), that there is a statistical distribution of ½ cations over 2 sets of positions with 4-fold multiplicity, and 4 oxygens, O(10). As there are many different possibilities for assigning the Ca, Al,Fe,Mg,Mn and Ti cations to the various sites, least-squares refinement of site occupancies, as well as positional coordinates, was undertaken using the program of Finger (1967), for crystals #1 and #2. This program allows two atom types to be assigned to each site whose occupancy is to be refined, and it will then indicate the best combination of these atoms in the site. Where more than two elements may be accommodated in a single site, as for instance Fe,Ti, Mn,Mg and Al which may occur together in an octahedral site, a composite of two major elements of contrasting atomic number was chosen, *e.g.* Fe and Al to give the same average scattering factor as the complete set. The result, while not absolute, indicates where the heavier and lighter elements should be placed. For samples

#1 and #2 this site occupancy refinement unambiguously assigned Al alone to the 8-fold centrosymmetric *A* site, Fe alone to the 4-fold disordered half-occupied *B* site, Ca alone to the 4-fold disordered half-occupied *C* site, and the balance of cations Al,Fe,Mg,Mn to the 16-fold general AlFe site.

For crystal #3, the XRAY (Stewart *et al.* 1972) system of programs was used, and in this case site occupancies of one atomic species were refined. The refinement was therefore an attempt to match the observed and calculated electron density, and no significance was attached to the particular scattering factors used. The final electron distribution, however, agrees well with the analyses of crystals #1 and #2. Table 3 shows the final atomic coordinates for the three vesuvianites. The nomenclature of the atoms and the coordinates given are chosen so as to be easily compared with the data of Warren & Modell (1931), but because we used a right-handed system the signs for the *x* coordinates are opposite. Anisotropic temperature factors are given in Table 4, and Table 5 shows some of the more important interatomic distances in various coordination polyhedra. The table containing observed and calculated structure factors, has been deposited with the National Science Library.*

Figure 1 is a stereodiagram of one unit cell. In Figure 2 the details of atoms on the 4-fold axis are shown. Figure 2a shows the two complete sets of occupied *C* and *B* positions for crystal #3, while Figure 2b shows a possible real arrangement of singly occupied *C* and *B* sites as they must exist in one part of the disorder.

DISCUSSION

The anions OH and O(10) are the only ones in the structure which are not bonded to Si atoms and this is the reason that OH was so assigned. Our attempts to locate the H atoms were unsuccessful, and for this reason we cannot say whether there is H associated with O(10) as Coda *et al.* (1970) suggest.

Our assignment of pure Al to the centrosymmetic *A* site depends upon the mean octahedral

TABLE 3. ATOMIC FRACTIONAL COORDINATES, STANDARD DEVIATIONS AND ISOTROPIC TEMPERATURE FACTORS FOR VESUVIANITE

		#1 Great Slave Lake				#2 Bancroft				#3 Wakefield			
	Position*	x	y	z	B(Å)^2	x	y	z	B(Å)^2	x	y	z	B(Å)^2
Si(1)	4*d*	-0.25	0.25	0	0.59(5)	-0.25	0.25	0	0.55(5)	-0.25	0.25	0	0.71(3)
Si(2)	16*k*	-0.18095(8)	0.04039(8)	0.87113(8)	0.46(3)	-0.18077(10)	0.03960(10)	0.87142(13)	0.58(3)	-0.18083(5)	0.04058(5)	0.87117(8)	0.66(2)
Si(3)	16*k*	-0.08263(9)	-0.15099(8)	0.36485(11)	0.58(3)	-0.08349(11)	-0.15075(10)	0.36462(13)	0.63(3)	-0.08275(5)	-0.15068(5)	0.36481(7)	0.81(2)
Ca(1)	4*c*	-0.25	0.25	0.25	0.78(4)	-0.25	0.25	0.25	1.47(5)	-0.25	0.25	0.25	0.81(3)
Ca(2)	16*k*	-0.18893(6)	0.04379(6)	0.37938(8)	0.60(2)	-0.18907(8)	0.04441(8)	0.37936(10)	0.78(2)	-0.18903(3)	0.04377(4)	0.37959(6)	0.63(1)
Ca(3)	16*k*	-0.10047(6)	-0.17982(6)	0.88629(9)	0.88(2)	-0.10067(8)	-0.17941(8)	0.88598(11)	1.08(2)	-0.10024(4)	-0.17980(4)	0.88584(6)	1.22(2)
C	4*c*	-0.25	-0.25	0.14092(39)	1.44(10)	-0.25	-0.25	0.14123(53)	1.35(13)	-0.25	-0.25	0.13959(27)	0.90(6)
B	4*c*	-0.25	-0.25	0.05702(42)	1.67(11)	-0.25	-0.25	0.04521(46)	1.35(10)	-0.25	-0.25	0.04842(29)	2.50(7)
AlFe	16*k*	-0.11319(8)	0.12107(8)	0.12631(11)	0.68(4)	-0.11095(9)	0.12038(9)	0.12775(12)	0.55(3)	-0.11252(5)	0.12111(5)	0.12645(8)	0.70(3)
A	8*f*	0	0	0	0.55(5)	0	0	0	0.22(6)	0	0	0	0.76(3)
O(1)	16*k*	-0.22040(23)	0.17294(22)	0.08628(29)	0.85(7)	-0.21967(28)	0.17240(27)	0.08474(36)	0.88(8)	-0.22031(12)	0.17320(12)	0.08583(19)	0.84(4)
O(2)	16*k*	-0.11681(22)	0.15987(22)	0.27910(29)	0.90(7)	-0.11603(28)	0.15938(27)	0.27942(35)	0.89(8)	-0.11715(12)	0.15951(12)	0.27837(19)	0.96(4)
O(3)	16*k*	-0.04907(22)	0.22158(21)	0.07539(28)	0.75(6)	-0.04876(28)	0.22176(27)	0.07560(35)	0.73(7)	-0.04932(13)	0.22170(12)	0.07689(19)	0.87(4)
O(4)	16*k*	-0.06169(22)	0.10677(22)	0.47056(28)	0.79(7)	-0.06110(27)	0.10669(27)	0.47051(34)	0.73(7)	-0.06174(12)	0.10611(12)	0.47074(18)	0.83(3)
O(5)	16*k*	-0.16969(22)	0.01546(24)	0.17907(30)	1.02(7)	-0.17054(27)	0.01480(29)	0.17936(38)	0.96(8)	-0.16955(12)	0.01587(13)	0.17879(20)	1.09(4)
O(6)	16*k*	-0.11719(26)	-0.27076(23)	0.05942(31)	1.45(8)	-0.11913(31)	-0.27181(28)	0.05890(39)	1.28(9)	-0.11777(15)	-0.27110(13)	0.05877(19)	1.54(5)
O(7)	16*k*	0.05622(23)	0.17440(23)	0.32233(31)	0.91(7)	0.05680(29)	0.17486(30)	0.32239(40)	1.03(8)	0.05603(13)	0.17329(13)	0.32195(21)	1.11(4)
O(8)	16*k*	-0.06063(22)	-0.09039(21)	0.06656(29)	0.83(7)	-0.06083(27)	-0.09074(27)	0.06683(36)	0.80(8)	-0.06090(12)	-0.09017(12)	0.06540(19)	0.92(4)
O(9)	8*h*	-0.14457(22)	-0.14457(22)	0.25	1.01(9)	-0.14482(28)	-0.14482(28)	0.25	0.92(10)	-0.14406(13)	-0.14406(13)	0.25	1.09(6)
O(10)	4*c*	-0.25	-0.25	0.86625(73)	1.17(14)	-0.25	-0.25	0.86738(87)	1.12(16)	-0.25	-0.25	0.86066(60)	3.24(14)
OH	16*k*	-0.00425(21)	0.06216(21)	0.13628(27)	0.71(6)	-0.00463(27)	0.06174(27)	0.13521(34)	0.79(7)	-0.00441(12)	0.06214(12)	0.13594(17)	0.68(3)

*Number of positions and Wykoff notation for space group *P4/nno*, origin at $\bar{1}$. Standard deviations in parentheses refer to last figures.

TABLE 4. ANISOTROPIC TEMPERATURE FACTORS FOR VESUVIANITE

	#1 Great Slave Lake						#2 Bancroft						#3 Wakefield					
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Si(1)	62(5)	62(5)	84(14)	0	0	0	64(6)	64(6)	85(17)	0	0	0	46(3)	46(3)	141(10)	0	0	0
Si(2)	46(4)	46(4)	86(7)	-1(3)	-4(5)	7(5)	58(6)	62(6)	95(9)	1(4)	-1(6)	3(6)	41(2)	50(2)	124(5)	1(2)	-3(3)	-7(3)
Si(3)	86(5)	37(4)	90(8)	4(4)	0(5)	-3(5)	97(6)	43(5)	92(9)	0(5)	-3(6)	-7(6)	80(3)	43(2)	129(5)	5(2)	5(3)	-3(3)
Ca(1)	127(7)	67(7)	63(10)	0	0	0	202(11)	128(10)	190(15)	0	0	0	81(4)	47(4)	122(8)	0	0	0
Ca(2)	55(3)	71(3)	99(5)	6(2)	-7(4)	0(4)	71(4)	93(4)	115(7)	5(3)	-5(4)	2(5)	37(2)	59(2)	103(4)	5(1)	-5(2)	1(2)
Ca(3)	78(3)	68(3)	212(6)	16(3)	-44(4)	-16(4)	91(4)	85(4)	271(9)	11(3)	-54(5)	31(5)	73(2)	66(2)	278(5)	-21(1)	-49(3)	22(3)
C	109(10)	109(10)	216(33)	0	0	0	87(13)	87(13)	383(46)	0	0	0	32(5)	32(5)	273(24)	0	0	0
B	62(8)	62(8)	860(49)	0	0	0	32(9)	32(9)	709(45)	0	0	0	45(4)	45(4)	910(33)	0	0	0
AlFe	64(5)	67(5)	112(8)	-3(3)	9(5)	-2(5)	66(5)	57(5)	76(9)	-12(4)	15(5)	-8(5)	48(3)	47(3)	131(6)	1(2)	11(3)	-2(4)
A	43(8)	43(8)	118(12)	13(5)	-1(8)	1(8)	19(9)	16(9)	75(14)	10(6)	4(9)	6(9)	48(4)	52(4)	148(8)	3(3)	-1(5)	-4(5)
O(1)	122(13)	73(11)	118(20)	-10(10)	-3(13)	8(13)	87(15)	81(15)	143(26)	-2(12)	4(17)	34(17)	86(6)	44(7)	131(13)	-2(5)	-8(9)	-12(9)
O(2)	78(12)	99(13)	166(21)	-30(12)	-36(13)	6(13)	94(16)	90(16)	140(26)	-21(12)	-13(17)	12(17)	61(6)	72(7)	179(15)	-9(5)	-27(8)	8(9)
O(3)	89(12)	70(12)	121(20)	0(12)	17(13)	-16(13)	102(16)	60(14)	95(24)	14(12)	12(17)	7(16)	76(6)	55(7)	144(13)	3(5)	1(8)	-6(9)
O(4)	85(12)	81(12)	150(32)	-4(10)	-28(13)	40(13)	78(16)	76(15)	109(25)	11(12)	-18(16)	7(16)	72(7)	42(6)	156(14)	-2(5)	-20(8)	10(8)
O(5)	87(13)	132(14)	138(21)	45(10)	-2(14)	7(14)	86(15)	111(17)	146(27)	23(13)	23(17)	25(18)	73(7)	100(7)	164(14)	-29(6)	25(9)	11(9)
O(6)	200(16)	91(14)	189(23)	34(11)	29(16)	47(14)	169(19)	90(17)	185(27)	30(13)	24(19)	52(18)	172(7)	76(7)	227(16)	-38(6)	34(9)	-42(11)
O(7)	73(12)	105(13)	188(21)	11(10)	3(14)	5(14)	87(16)	113(17)	187(27)	12(13)	7(18)	-16(18)	51(6)	97(7)	217(15)	12(5)	-4(9)	15(9)
O(8)	72(12)	78(12)	177(21)	-3(10)	29(13)	17(13)	64(15)	75(15)	175(27)	0(12)	22(16)	13(17)	47(6)	56(6)	213(15)	-8(5)	48(9)	-16(8)
O(9)	134(11)	134(11)	97(26)	-57(15)	-24(16)	24(16)	121(14)	121(14)	89(31)	22(19)	1(19)	-1(19)	102(6)	102(6)	107(18)	-17(8)	-22(9)	21(9)
O(10)	111(16)	111(16)	422(59)	0	0	0	115(21)	115(21)	327(67)	0	0	0	43(8)	43(8)	1229(77)	0	0	0
OH	74(12)	88(12)	93(19)	-13(10)	-19(13)	-7(12)	85(15)	81(15)	106(25)	-2(12)	-7(16)	-11(16)	53(6)	49(6)	113(13)	7(5)	1(8)	12(8)

The values given in this table have been multiplied by 10^5. Standard deviations are in parentheses.

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*This table has been deposited with the Depository of Unpublished Data. Copies may be obtained on request to: Depository of Unpublished Data, National Science Library, National Research Council of Canada, Ottawa, Ontario, Canada.

TABLE 5. INTERATOMIC DISTANCES IN CATION COORDINATION POLYHEDRA

			#1 Gt. Slave L.	#2 Bancroft	#3 Wakefield
Si(1)	-O(1) (4X)		1.635(4)	1.638(4)	1.632(2)
Si(2)	-O(2)		1.639(5)	1.645(5)	1.650(2)
	O(3)		1.644(5)	1.647(5)	1.640(2)
	O(4)		1.674(5)	1.676(4)	1.684(2)
	O(7)		1.608(5)	1.610(5)	1.614(2)
		mean	1.641	1.644	1.647
Si(3)	-O(5)		1.633(5)	1.644(5)	1.643(2)
	O(6)		1.599(5)	1.605(5)	1.608(2)
	O(8)		1.622(4)	1.620(5)	1.624(2)
	O(9)^{b}		1.661(2)	1.659(3)	1.659(1)
		mean	1.629	1.632	1.634
Ca(1)	-O(1) (4X)		2.314(4)	2.343(4)	2.320(2)
	O(2) (4X)		2.519(5)	2.540(4)	2.521(2)
		mean	2.416	2.442	2.421
Ca(2)	-O(1)		2.482(5)	2.482(5)	2.490(2)
	O(2)		2.427(5)	2.426(4)	2.431(2)
	O(3)		2.363(4)	2.374(4)	2.383(2)
	O(4)		2.450(4)	2.462(4)	2.451(2)
	O(5)^{1}		2.417(5)	2.424(5)	2.426(2)
	O(5)^{4}		2.341(5)	2.337(4)	2.344(2)
	O(6)		2.893(6)	2.943(5)	2.908(2)
	O(8)		2.317(4)	2.329(4)	2.330(2)
		mean	2.468	2.472	2.470
Ca(3)	-O(3)		2.451(5)	2.459(5)	2.454(2)
	O(6)		2.492(5)	2.514(5)	2.499(2)
	O(7)^{5}		2.551(5)	2.555(5)	2.547(2)
	O(7)^{7}		2.481(5)	2.484(5)	2.501(2)
	O(7)^{13}		2.358(5)	2.353(5)	2.357(2)
	O(8)		2.609(5)	2.617(5)	2.607(2)
	O(10)		2.574(2)	2.579(2)	2.588(2)
	OH		2.458(5)	2.469(4)	2.461(2)
		mean	2.497	2.504	2.502
C (Ca)	-O(6) (4X)		2.296(6)	2.282(5)	2.289(3)
	O(9) (4X)		2.646(6)	2.647(5)	2.668(2)
		mean	2.471	2.464	2.479
B (Fe)	-O(6) (4X)		2.086(5)	2.070(5)	2.085(2)
	O(10)(1X)		2.245(11)	2.100(12)	2.214(8)
		mean	2.118	2.080	2.111
AlFe	-O(1)		1.907(5)	1.943(5)	1.921(2)
	O(2)		1.897(5)	1.893(4)	1.889(2)
	O(3)		1.944(5)	1.950(4)	1.937(2)
	O(4)		2.054(5)	2.074(4)	2.057(2)
	O(5)		1.960(5)	1.982(5)	1.960(2)
	OH		1.925(5)	1.891(4)	1.917(2)
		mean	1.948	1.956	1.947
A (Al)	-O(4) (2X)		1.944(4)	1.944(4)	1.939(2)
	O(8) (2X)		1.862(4)	1.874(4)	1.859(2)
	OH (2X)		1.873(4)	1.865(3)	1.873(2)
		mean	1.893	1.894	1.890

Standard deviations in parentheses refer to last decimal place. b indicates bridging oxygen in Si_2O_7 group. (nX) indicates multiplicity of bond. Superscripts refer to symmetry operation number. Equivalent positions in space group *P4/nnc* (origin at $\bar{1}$ were numbered 1,2....16 from left to right, top to bottom as printed in *International Tables for X-Ray Crystallography* (1962).

bond lengths of 1.893 (#1) and 1.894 (#2), (1.890 for #3), compared with 1.948 (#1) and 1.956 (#2), (1.947 for #3), in the general AlFe position, which presumably contains a higher proportion of larger ions. To support this view, site occupancy refinement indicated .998 Al, .002 Fe in *A* and .876 Al, .124 Fe in AlFe for #1, and 1.019 Al,-.019 Fe in *A* and .743 Al, .257 Fe in AlFe for #2. The negative atom fractions arise because the total occupancy was constrained to 1.000, and they thus appear to indicate ultra purity of one element species.

Perhaps it is significant that Fe is concentrated in the less symmetrical of the two octahedral sites. In this case, in a structure with such high symmetry, the distortion is very small, with the quadratic elongation parameters of Robinson *et al.* (1971) being 1.0065 for *A* and 1.0079 for AlFe in sample #1.

The most irregular coordination polyhedron for medium-sized cations is the square pyramid around the *B* site. The site occupancy refinement indicates that this disordered site, which should theoretically contain .5 of an atom, appears to have .558 Fe and -.058 Ca while the *C* site contains .040 Fe and .460 Ca in #1. In #2, *B* contains .431 Fe and .068 Ca with -.024 Fe and .524 Ca in *C*. The bond lengths shown in Figure 2b are consistent with this distribution of Fe and Ca. Perhaps one could go a step further and assign the *B* site to Fe^{3+} since this ion has been shown to be associated with the more distorted octahedral sites, *e.g.* in epidote (Burns & Strens 1967), or with 5-fold coordination sites as in yoderite (Fleet & Megaw 1962). This is not to say that Fe^{3+} is to be associated exclusively with the *B* site, but further discussion of this must await the results of Mössbauer measurements on this material. The *B*-O(10) distance seems quite variable with 2.245 in #1, 2.100 in #2 and 2.214 in #3. Coda *et al.* found *B*-O(6)

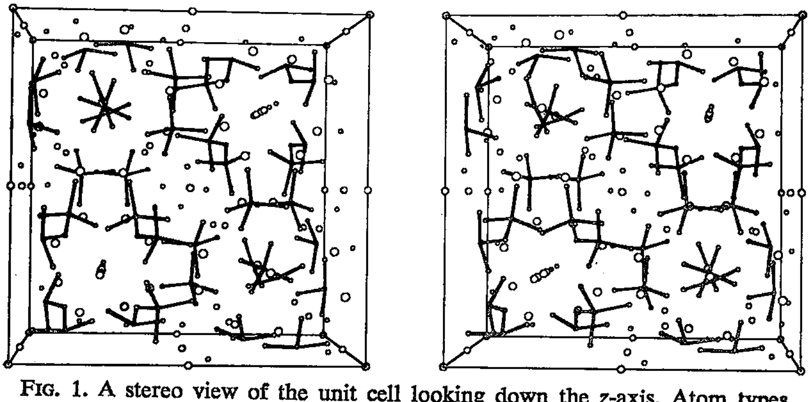

FIG. 1. A stereo view of the unit cell looking down the z-axis. Atom types are indicated by increasing radii: Si, O, OH, AlFe, *A*, *B*, *C*, Ca.

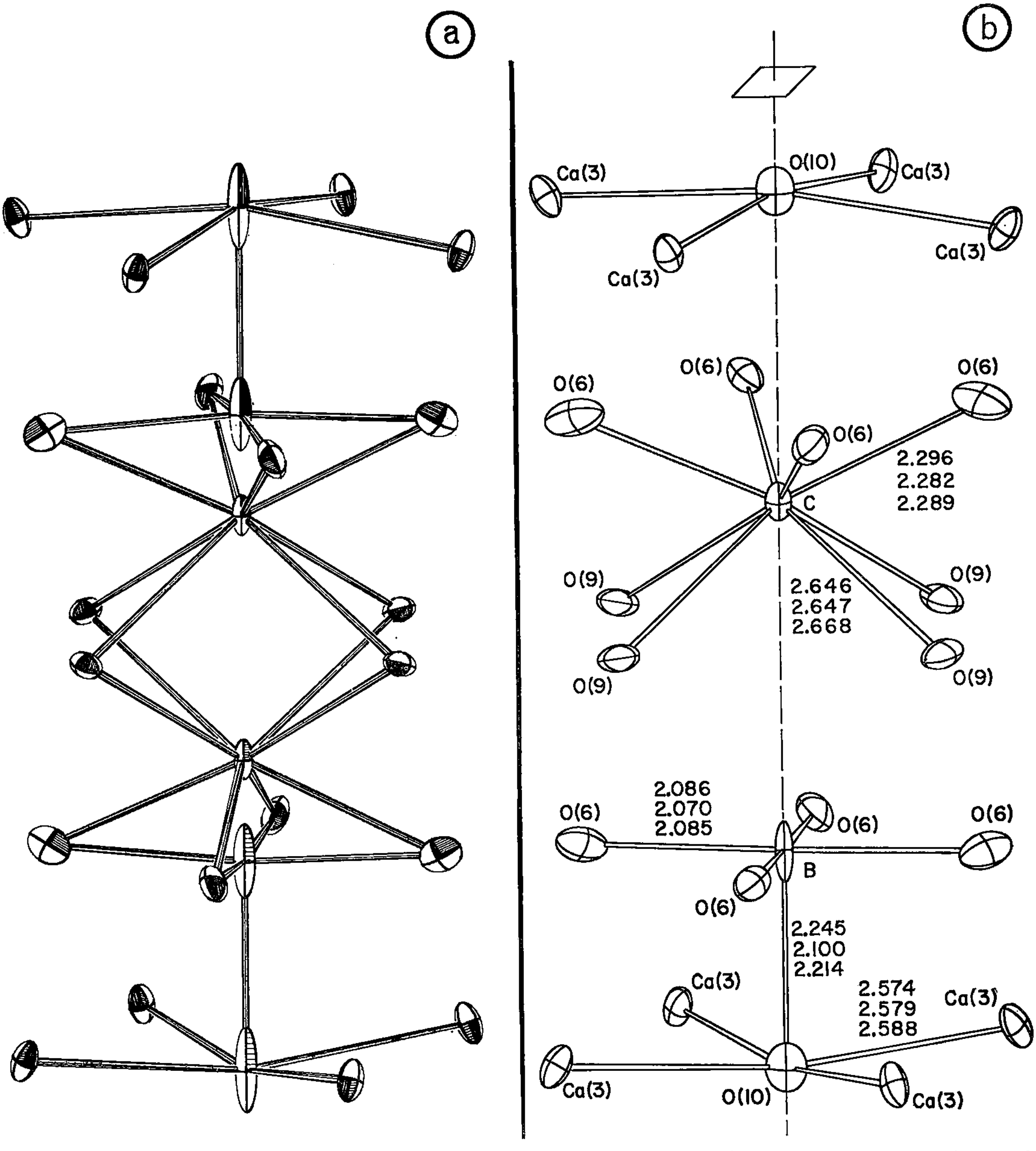

FIG. 2. The atomic arrangement along the 4-fold axes. (a) Coordination with each of the *B* and *C* positions occupied. (b) An arrangement of singly occupied *B*- and *C*-sites showing bond lengths derived for samples 1, 2 and 3.

= 2.077 and *B*-O(10) = 1.978. The variation of the *B*-O(10) distance must arise from the peculiar bonding around the *B* site. *B* is almost in the plane of the square formed by 4 O(6) atoms, and so can vibrate freely perpendicular to this plane, *i.e.* strongly anisotropically along the 4-fold axis. The *B* site could thus be viewed as having coordination rather like an octahedron with one corner missing.

The occurrence of Be-bearing vesuvianite has been recorded from at least 3 localities (Hurlbut 1955) including that from Great Slave Lake (sample #1). Table 6 shows the structural formula which can be calculated for this sample, using electron probe analysis for all constituents except Be and H_2O, the former being determined by Meen (1939) and the latter calculated to give exactly 16 OH per cell. Fe^{3+}

TABLE 6. STRUCTURAL FORMULA OF GREAT SLAVE LAKE (#1) VESUVIANITE

	Wt. %	Cation prop.		Cation sites		
				4 Si(1)		
SiO_2	36.6	36.000		16 Si(2)		36
				16 Si(3)		
				4 Ca(1)		
CaO	35.6	37.520	37.60	16 Ca(2)		38
Na_2O	0.04	0.076		16 Ca(3)		
				2 Ca(4)	= 4 x ½'C'	
Fe_2O_3	2.70	2.000		2 Fe^{3+}	= 4 x ½'B'	
FeO	2.20	1.809	15.75	16 AlFe		
TiO_2	0.19	0.141				
MnO	0.50	0.417				
MgO	2.17	3.181				
Al_2O_3	15.7	10.202				
		8.000		8 Al	= A	
BeO	1.07	2.531		16 Be	???	
F	2.03	6.312	16.00	16 H		
H_2O	1.48	9.688				
	100.2					
-O≡F	0.85					
	99.3					

Total cation charge 305.9
Ideal anion charge (assuming 156 O,F) 305.7

Electron probe analysis except for Be and H_2O. For details of this and division of Fe^{2+} and Fe^{3+} see text. Cation proportions calculated assuming 36 Si atoms per cell.

and Fe^{2+} have been divided rather arbitrarily with all Fe^{3+} being assigned to the *B* site and Fe^{2+} to the AlFe site. Surprisingly, the ratio Fe^{3+}/Fe^{2+} determined in this way, 1.10, does not differ too much from that of .85 measured in Meen's original analysis. The role of Be in the crystal structure is unclear, but the structural formula, calculated by assuming 36 Si atoms, indicates that Be is in excess of the required complement of cations, and serves merely to balance charges. It is unlikely to substitute for any of the cations, requiring as it does a tetrahedral site. There is a general set of tetrahedral positions in the structure at -0.512, -0.086, 0.088 where the mean bond length to O(4), O(8), and OH would be 1.645Å. However, if 2.5 atoms of Be were statistically distributed over 16 sites, there would be less than 1 electron at each site, which would be difficult to detect. This possible BeO_4 tetrahedron has the disadvantage of sharing one of its faces with the AO_6 octahedron, and an edge with the $Si(3)O_4$ tetrahedron. There is no indication of any electron density in a difference Fourier map.

In conclusion it may be said the modified vesuvianite structure described here resolves some unsatisfactory aspects of the Warren & Modell structure. Firstly, the coordination of the Ca(3) atom, formerly [7] is now raised to [8] by the inclusion of the extra oxygen, O(10). This higher coordination number is also to be expected from the otherwise very compact nature of the structure. Secondly, the disordered arrangement of atoms along the 4-fold axis, which nevertheless allows a satisfactory refinement to be obtained, also permits one to speculate on the possible consequences of ordering the atoms on this axis. Several ordered models are possible, where the 4 sites presently occupied by ½ atoms are reduced to 2 fully occupied sites. Such ordering necessarily reduces the symmetry of the structure forcing it into a sub-group of *P4/nnc*, such as, for example *P4/n*. Certain violations of *P4/nnc* extinction requirements would be observed, such as have been noted by Arem & Burnham (1969). Because the major part of the structure would conform to *P4/nnc* with only the ordered, special positions, on the 4-fold axis, belonging to the sub-group, it might not be possible to identify the lower symmetry. Thus, a structure with true space group *P4/n* might be expected to have diffraction symmetry of *P4/nmm* or *P4* could appear to be *P4/mmm*, which were the space groups observed by Arem & Burnham. This would satisfactorily resolve the problem of fitting the vesuvianite structure into a space group containing an *m* symbol, but it is quite possible that an alternative explanation, such as submicroscopic twinning, exists. Until a satisfactory refinement is performed on a vesuvianite violating *P4/nnc* reflection conditions, we must reserve further speculation.

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