The crystal structure of vesuvianite from Nakatatsu mine: reinvestigation of the cation site-populations and of the hydroxyl groups

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Abstract

Refinement of the crystal structure of a vesuvianite $[\text{Ca}_{18.6} (\text{Mn}_{0.3} \text{Fe}_{0.7}) (\text{OH})_2 (\text{Mg}_{2.1} \text{Fe}_{0.7} \text{Ti}_{0.5} \text{Al}_{4.7}) \text{Al}_{4.2} (\text{OH}, \text{O})_8 \text{Si}_{18.2} \text{O}_{68}]$; $a = 15.561(8)$ $c = 11.777(7)$ Å; space group $P4/nnc$] from Nakatatsu mine, Fukui Prefecture, central Japan, was carried out by a least-squares method with X-ray single-crystal data. The final R index for 1901 observed independent reflections is 0.030. From site population refinement and observed interatomic distances of cation sites, the C-sites (square antiprism) and B-sites (tetragonal pyramid) are half occupied by Ca^{2+} and Fe^{2+} (+ Mn^{2+}), respectively, the A-sites (octahedron) are almost completely occupied by Al, and the AlFe-sites (octahedron) are occupied by Mn^{2+} , Fe^{2+} , Mg^{2+} , Fe^{3+} , Ti^{4+} and Al^{3+} . From bond-valence calculations, the proton donor atoms are both O(10) and O(11). The cation site-populations and the hydroxyl groups of the structure models reported by earlier studies have been compared and reviewed.

Based on the structure analysis, the chemical formula of vesuvianite belonging to the space group $P4/nnc$ should be written as $\text{Ca}_{19} (\text{Mn}, \text{Fe}^{2+}) (\text{F}, \text{OH})_2 (\text{Mg}, \text{Fe}^{2+}, \text{Mn}, \text{Al}, \text{Fe}^{3+}, \text{Ti})_8 \text{Al}_4 (\text{OH}, \text{F}, \text{O})_8 (\text{SiO}_4)_{10} (\text{Si}_2\text{O}_7)_4$.

Introduction

Vesuvianite is a well-known silicate mineral and occurs frequently in metasomatised limestones and in skarns associated with ore deposits. The structural investigation was carried out first by Warren and Modell (1931). Their crystal structure model was checked and refined by Coda *et al.* (1970) and Rucklidge *et al.* (1975).

The general formula of vesuvianite is given in "Rock Forming Minerals" by Deer, Howie and Zussman (1982). It comes from the structural determinations by Coda *et al.* (1970) and by Rucklidge *et al.* (1975). Their structure models differ in the site preference for cations and in the number of the hydroxyl groups though their specimens do not differ so much in the geological conditions. The proposed three formulae are summarized as follows based on 78 (O, OH, F);

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Deer, Howie and Zussman (1982)

Coda *et al.* (1970)

Rucklidge *et al.* (1975)

In this study, the structure of vesuvianite has been refined in order to determine the structure parameters accurately. Bond-valence calculations are also carried out to recognize the hydroxyl groups. The results of the structure analyses reported by earlier studies are reviewed, and then the crystal chemistry and chemical formula are discussed.

Experimental

A brownish acicular specimen of vesuvianite was obtained from Nakatatsu mine, Fukui Prefecture, central Japan. The specimen was divided into two pieces; one was ground into a sphere with a diameter of 0.24 mm for X-ray experiments, and the other was used for a microprobe analysis. Table 1 presents the chemical composition obtained by using a HITACHI XMA-5A electron microprobe analyzer.

Weissenberg photographs indicated that Laue group is $4/mmm$, and the systematic absences (reflections of $hk0$ only present with $h + k = 2n$, $h0l$ only with

TABLE 1. Microprobe analyses of vesuvianite from Nakatatsu mine.

SiO ₂	36.51	Si	18.19
TiO ₂	1.38	Ti	0.51
Al ₂ O ₃	15.10	Al	8.85
Cr ₂ O ₃	0.0	Cr	0.0
FeO*	3.28	Fe	1.38
MnO	0.63	Mn	0.27
MgO	2.79	Mg	2.06
CaO	34.91	Ca	18.63
Na ₂ O	0.0	Na	0.0
K ₂ O	0.01	K	0.0
Total** (wt.%)	94.61	Total*** (mol.%)	49.89
H ₂ O (calc)	3.05		

*Total iron as FeO

**Excluding H₂O

***Calculated on the basis of 73 oxygens per formula unit

TABLE 2. Crystal data and information for structure analysis

a (Å)	15.561(8)
c	11.777(7)
V (Å ³)	2851.6
Space group	$P4/nnc$
D calc (g.cm ⁻³)	3.42
Radiation used	MoK α (0.71069 Å) 40 KV 20 mA
Monochromator	graphite
Crystal size (mm)	0.24 (dia)
Crystal shape	spherical
μ (MoK α) (cm ⁻¹)	28.59
Diffractometer	Philips PW1100
Scan type	ω
2θ range (°)	10–70
No. of indep. reflections used for refinement with $F_o > 3\sigma(F_o)$	1901
R	3.04%
R_w	3.71%
S	1.145

$h + l = 2n$, and hhl only with $l = 2n$) were consistent with space group $P4/nnc$. The reflection data for structure refinement were collected on the Philips PW 1100 four-circle diffractometer with graphite-monochromatized MoK α radiation. Cell constants were refined using 12 reflections. Crystal data and experimental conditions are given in Table 2. The intensities of reflections within $2\theta = 10 - 70^\circ$ were measured by ω scan mode. The data were corrected for Lorentz and polarization factors, and for the absorption effect ($\mu R = 0.34$ for MoK α radiation). The 1901 reflections, $|F_o| \geq 3\sigma|F_o|$, were used in the refinement.

The refinement was initiated with the positional parameters reported by Rucklidge *et al.* (1975), using the program ORXFLS4 (Busing *et al.*, 1962; Johnson, 1969). Scattering factors were taken from “*International Tables for X-ray Crystallography*” (1974). Anomalous dispersion corrections were made for all atoms. Mg and Mn–Ti atoms were regarded as Al and Fe, respectively, in the refinement, since their scattering factors are not easily distinguishable from those of Al and Fe. The octahedral sites were assumed to be occupied by Al and Fe only. Several cycles of least-squares refinements resulted in convergence to an R index ($= \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$) of 0.0304 with anisotropic thermal parameters. A difference Fourier synthesis showed likely position for the hydrogen atom at the distance of about 0.6 Å from O(11), and the

TABLE 3. Positional parameters and site-occupancies for vesuvianite from Nakatatsu mine.

Atom	Site occupancy		x	y	z
Ca(1)			-0.25	0.25	0.25
Ca(2)			-0.18907(3)	0.04388(3)	0.37952(5)
Ca(3)			-0.09935(4)	-0.17919(4)	0.88720(5)
C	0.470	Ca	-0.25	-0.25	0.13908(24)
B	0.467	Fe	-0.25	-0.25	0.05336(26)
AlFe	{	0.909 Al	-0.11271(5)	0.12099(5)	0.12661(6)
		0.091 Fe			
A	1.0	Al	0.0	0.0	0.0
Si(1)			-0.25	0.25	0.0
Si(2)			-0.18074(5)	0.04081(5)	0.87140(6)
Si(3)			-0.08316(5)	-0.15073(5)	0.36462(6)
O(1)			-0.22050(12)	0.17277(12)	0.08583(17)
O(2)			-0.11777(12)	0.16006(12)	0.27981(16)
O(3)			-0.04843(12)	0.22231(12)	0.07599(17)
O(4)			-0.06184(12)	0.10622(12)	0.47021(16)
O(5)			-0.17024(12)	0.01452(12)	0.17895(17)
O(6)			-0.11840(14)	-0.27192(13)	0.05864(17)
O(7)			0.05564(13)	0.17364(13)	0.32181(19)
O(8)			-0.06070(12)	-0.09068(12)	0.06677(17)
O(9)			-0.14442(12)	-0.14442	0.25
O(10)	1.0	F	-0.25	-0.25	0.85585(57)
O(11)			-0.00398(11)	0.06191(12)	0.13708(16)
H(11)*			0.430	0.478	0.324

*not refined

peak height was $0.6 \text{ e}\text{\AA}^{-3}$.

The positional parameters, site occupancies and the thermal parameters are listed in Tables 3 and 4. Cation-oxygen distances and proton donor-acceptor distances calculated using RSDA-4 program (Sakurai 1967) are given in Table 5.

Discussion

Polyhedral (tetrahedral and octahedral) representation of vesuvianite structure is partially shown in Fig. 1. The structure contains ten sets of crystallographically non-equivalent cation-sites; one 9-coordinated site (Ca(3)), three distinct 8-coordinated sites (Ca(1), Ca(2), C), one 5-coordinated site (B), two distinct 6-coordinated sites

TABLE 4. Anisotropic thermal parameters ($\times 10^5$) for vesuvianite from Nakatatsu mine.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca(1)	106(4)	48(3)	67(6)	0.0	0.0	0.0
Ca(2)	55(2)	77(2)	96(3)	7(1)	-5(2)	4(2)
Ca(3)	94(2)	84(2)	257(4)	18(2)	-49(2)	-23(2)
C	51(6)	51	263(23)	0.0	0.0	0.0
B	51(5)	51	808(30)	0.0	0.0	0.0
AlFe	53(3)	56(3)	87(5)	4(2)	9(3)	-4(3)
A	48(4)	44(4)	122(6)	3(3)	0(5)	-6(5)
Si(1)	55(3)	55	91(9)	0.0	0.0	0.0
Si(2)	48(2)	55(2)	93(5)	2(2)	-6(3)	4(3)
Si(3)	83(3)	41(2)	91(4)	4(2)	7(3)	2(3)
O(1)	94(7)	52(6)	111(12)	6(5)	-1(8)	-16(8)
O(2)	74(7)	95(7)	124(13)	-10(6)	-37(8)	6(8)
O(3)	89(7)	58(6)	121(12)	9(5)	-1(8)	-3(8)
O(4)	85(7)	53(7)	136(13)	-4(5)	-21(8)	13(8)
O(5)	88(7)	95(7)	137(13)	46(6)	14(8)	-3(8)
O(6)	198(9)	84(7)	166(13)	28(6)	29(9)	23(8)
O(7)	67(7)	135(8)	195(14)	18(6)	8(8)	6(9)
O(8)	67(6)	72(7)	123(12)	11(5)	29(7)	5(7)
O(9)	101(6)	101	105(16)	-18(8)	-9(9)	9
O(10)	63(8)	63	2002(80)	0.0	0.0	0.0
O(11)	44(6)	74(6)	131(12)	-12(5)	-13(7)	-19(7)

(A, AlFe), and three distinct 4-coordinated sites (Si(1), Si(2), Si(3)) [the designations of cation-sites are in accordance with those of Rucklidge *et al.* (1970)]. The Ca(1), C, B, A, and Si(1) sites are on the special positions and the other sites are on the general positions. The existence of both double tetrahedra Si_2O_7 and isolated tetrahedra SiO_4 is characteristic for this crystal structure. The tetrahedra bridge the vertices (except the O(11) vertex) of the octahedra (A, AlFe). The A-octahedra share the edge O(4)–O(11) with the AlFe-octahedra. While the partial structure of vesuvianite along the inversion axis is somewhat like that of grossular, the partial structure along the four-fold rotation axis is peculiar, e.g. disordered disposition of half occupied tetragonal pyramid (B) and half occupied square antiprism (C) exist (Coda *et al.*, 1970; Rucklidge *et al.*, 1975).

The coordination polyhedra of oxygen atoms around calcium atoms are shown in Fig. 2. Ca-polyhedra share the edges with each other, and Ca(3)-polyhedra share the faces (O(6)–O(7)–O(10)) with other Ca(3)-polyhedra.

TABLE 5. Cation-oxygen interatomic distances (Å)

Ca(1) – O(1) *4	2.322(2)	AlFe – O(1)	1.922(2)
– O(2) *4	2.513(2)	– O(2)	1.906(2)
	2.418	– O(3)	1.960(2)
		– O(4)	2.062(2)
Ca(2) – O(1)	2.484(2)	– O(5)	1.981(2)
– O(2)	2.425(2)	– O(11)	1.930(3)
– O(3)	2.372(2)		1.960
– O(4)	2.450(2)		
– O(5)	2.424(2)	A – O(4) *2	1.945(2)
– O(5)	2.340(2)	– O(8) *2	1.871(2)
– O(6)	2.927(2)	– O(11)*2	1.881(2)
– O(8)	2.322(2)		1.899
	2.468		
		Si(1) – O(1) *4	1.636(2)
Ca(3) – O(3)	2.434(2)		
– O(6)	2.499(2)	Si(2) – O(2)	1.644(2)
– O(7)	2.555(2)	– O(3)	1.635(2)
– O(7)	2.510(2)	– O(4)	1.675(2)
– O(7)	2.372(2)	– O(7)	1.614(2)
– O(8)	2.594(2)		1.642
– O(10)	2.616(9)		
– O(11)	2.449(2)	Si(3) – O(5)	1.633(2)
– O(6)	2.997(2)	– O(6)	1.602(2)
	2.558	– O(8)	1.622(2)
		– O(9)	1.655(1)
			1.628
C – O(6) *4	2.282(2)		
– O(9) *4	2.666(2)	O(10) – O(10)	2.49(9)
	2.474	O(11) – O(7)	2.808(3)
		O(11) – H(11)	0.6
B – O(6) *4	2.077(2)		
– O(10)	2.33(7)		
	2.135		

From site population refinement and the observed mean interatomic distances of cation-sites, the C- and B-sites are half occupied by Ca and Fe(+Mn), respectively, the A-sites are almost completely occupied by Al, and the AlFe-sites are occupied by Mn, Fe, Mg, Ti, and Al. These results are consistent with cation distributions obtained by Rucklidge *et al.* (1975), but are different from those by Coda *et al.* (1970) (Table 6); the cation distributions of two distinct octahedral sites of vesuvianite from Bric

FIG. 1. A section of vesuvianite structure illustrating the linkage of tetrahedra and octahedra. The elements of symmetry are also indicated. The height of the atoms is indicated in $1000y$. The stippled polyhedra are approximately at the levels $y = 0 \sim 1/4$ and the striped ones at $y = 1/4 \sim 1/2$.

Camula contain contradiction that the AlFe-site, which has larger cation-oxygen interatomic distances than the A-site, is occupied only by Al. Therefore, the authors re-examined vesuvianite from Bric Camula with the structure amplitude reported by Coda *et al.* Tables 7 and 8 present the positional and thermal parameters newly refined using the same procedure mentioned above. The R index is improved to 0.050 and the A-site, as opposed to Coda's result, is occupied only by Al.

Fig. 3 shows r (effective ionic radius) – CN (coordination number) plots (Shannon, 1976), and also indicates the radius of five-coordinated cation which occupies the B-site in vesuvianite. As a result, it appears that the B-site is occupied mainly by Fe^{2+} in agreement with the result from Mössbauer spectral studies of vesuvianites by Manning and Tricker (1975). The five coordinated Fe^{2+} is characteristic and is perhaps first confirmed by X-ray study.

FIG. 2. Coordination polyhedra of oxygen atoms around calcium atoms. The height of the atoms are indicated in 1000y.

TABLE 6. Comparison of site-occupancies and mean M–O distances of the octahedral sites of vesuvianites.

No.	Locality	a c (Å)	R -factor	Mean inter-atomic distances (Å) and occupied cations		Reference
				A-site	AlFe-site	
1	Bric Camula	15.565 11.816	7.9%	1.912 A+M +F	1.957 A	Coda <i>et al.</i> (1970)
2	"	"	5.0%	1.900 A	1.967 A+M +F	This study
3	Gt. Slave L.	15.516 11.769	3.9%	1.893 A	1.948 A+M +F	Rucklidge <i>et al.</i> (1975)
4	Bancroft	15.558 11.810	4.7%	1.894 A	1.956 A+M +F	"
5	Wakefield	15.543 11.791	5.0%	1.890 A	1.947 A+M +F	"
6	Nakatatsu M.	15.561 11.777	3.0%	1.899 A	1.960 A+M +F	This study

A; Al, M; Mg, F; Ti+Mn+Fe

TABLE 7. Positional parameters and site-occupancies for vesuvianite from Bric Camula.

Atom	Site occupancy	<i>x</i>	<i>y</i>	<i>z</i>
Ca(1)		−0.25	0.25	0.25
Ca(2)		−0.1891(1)	0.0443(1)	0.3797(2)
Ca(3)		−0.1016(1)	−0.1818(1)	0.8870(2)
C	0.492 Ca	−0.25	−0.25	0.1491(7)
B	0.418 Fe	−0.25	−0.25	0.0339(5)
AlFe	{ 0.909 Al 0.091 Fe	−0.1124(1)	0.1209(1)	0.1262(2)
A	1.0 Al	0.0	0.0	0.0
Si(1)		−0.25	0.25	0.0
Si(2)		−0.1807(1)	0.0407(1)	0.8714(2)
Si(3)		−0.0840(2)	−0.1511(2)	0.3647(2)
O(1)		−0.2202(4)	0.1731(3)	0.0853(5)
O(2)		−0.1168(4)	0.1604(4)	0.2794(6)
O(3)		−0.0478(4)	0.2225(4)	0.0752(6)
O(4)		−0.0613(4)	0.1068(4)	0.4702(5)
O(5)		−0.1708(4)	0.0139(4)	0.1777(6)
O(6)		−0.1201(4)	−0.2722(4)	0.0590(5)
O(7)		0.0556(4)	0.1728(4)	0.3213(6)
O(8)		−0.0608(4)	−0.0916(4)	0.0665(6)
O(9)		−0.1452(4)	−0.1452	0.25
O(10)	1.0 F	−0.25	−0.25	0.8658(11)
O(11)		−0.0040(4)	0.0606(4)	0.1363(5)

Rucklidge *et al.* (1975) could not give a full discussion for the hydroxyl groups in the structure, but supposed that O(11) was the only hydroxyl group. So their chemical formula has a smaller number of hydroxyl than Coda's. The conclusion of Coda *et al.* that the proton donor atoms are both O(10) and O(11) can be justified by bond-valence calculations. The valence sums for the oxygen atoms of vesuvianite studied by Rucklidge *et al.* and by the present authors (Table 9) are calculated according to Donnay and Allmann's method (1970). The sums for O(10) and O(11) are close to the expected value of 1.0 v.u. for a hydroxyl group.

The magnitude of thermal parameters for the B and O(10) atoms along the four-fold rotation axis are significantly greater than the others. The root-mean-square thermal displacements for these atoms along the *c* axis are presented in Table 10. It appears that the displacements of the positions of these atoms occur due to the statistical arrangements (Coda *et al.*, 1970; Rucklidge *et al.*, 1975) along the four-fold rotation axis and that these displacements have effects on apparent thermal

TABLE 8. Anisotropic thermal parameters ($\times 10^5$) for vesuvianite from Bric Camula.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca(1)	151(14)	101(13)	81(29)	0	0	0
Ca(2)	107(7)	112(7)	133(18)	-4(5)	-1(9)	8(9)
Ca(3)	131(8)	163(8)	405(21)	37(6)	-81(10)	-95(11)
C	80(21)	80	263(82)	0	0	0
B	67(18)	67	208(71)	0	0	0
AlFe	88(10)	101(11)	96(26)	10(7)	6(12)	-20(12)
A	86(14)	94(14)	141(29)	14(11)	1(18)	-1(19)
Si(1)	99(11)	99	93(40)	0	0	0
Si(2)	79(9)	90(9)	105(24)	11(7)	8(12)	2(12)
Si(3)	140(10)	101(10)	116(24)	20(8)	-6(13)	-13(12)
O(1)	154(25)	100(24)	126(52)	1(18)	-68(31)	-9(30)
O(2)	115(24)	114(24)	329(72)	5(18)	-11(32)	43(33)
O(3)	144(24)	110(23)	163(52)	26(18)	-18(32)	-3(32)
O(4)	105(25)	111(24)	200(64)	0(17)	-32(31)	43(30)
O(5)	144(26)	253(30)	203(62)	17(22)	37(33)	-4(37)
O(6)	265(30)	133(26)	164(51)	20(21)	47(35)	48(32)
O(7)	153(26)	148(26)	173(59)	11(20)	-8(33)	-21(32)
O(8)	154(25)	115(24)	167(50)	-14(19)	19(31)	30(32)
O(9)	152(20)	152	154(72)	-38(29)	12(35)	-12
O(10)	273(32)	273	733(132)	0	0	0
O(11)	102(24)	176(26)	139(56)	-66(20)	15(31)	-47(31)

parameters of these atoms.

Based on the crystal structure analyses the chemical formula of vesuvianite belonging to the space group $P4/nnc$ should be written as follows with two formula unit per unit cell;

Vesuvianite has the following structural characteristics: both isolated $[\text{SiO}_4]$ and double $[\text{Si}_2\text{O}_7]$ tetrahedra exist; one of two kinds of octahedral sites is occupied by an aluminum ion in preference to the others; the other octahedral site is occupied by Mn^{2+} , Fe^{2+} , Mg^{2+} , Fe^{3+} , Ti^{4+} , and Al^{3+} ; the B-sites (tetragonal pyramid) and C-sites (square antiprism) are half occupied by Fe^{2+} (+ Mn^{2+}) and Ca^{2+} , respectively.

FIG. 3. Effective ionic radius (r) – coordination number (CN) plots (Shannon 1976). The radius of five-coordinated cation which occupies the B-site in vesuvianite are also indicated.

TABLE 9. Valence sums of the oxygen atoms in vesuvianites in valence units*

Anions	Nakatatsu	Gt. Slave L.**	Bancroft**	Wakefield**	Anion chemistry
O(1)	2.04	2.02	2.05	2.00	O ²⁻
O(2)	2.03	1.98	2.07	1.98	O ²⁻
O(3)	2.04	1.99	2.04	2.01	O ²⁻
O(4)	2.00	1.96	1.97	1.95	O ²⁻
O(5)	2.01	2.00	2.02	1.98	O ²⁻
O(6)	1.87	1.87	1.84	1.85	O ²⁻
O(7)	1.81	1.84	1.84	1.84	O ²⁻
O(8)	2.06	2.06	2.05	2.06	O ²⁻
O(9)	2.06	2.06	2.10	2.08	O ²⁻
O(10)	0.90	1.01	1.07	1.02	OH ⁻
O(11)	1.31	1.26	1.37	1.26	OH ⁻

*Expected values are 2.0 (v.u.) for O²⁻ and 1.0 for OH⁻.

Calculated total iron as FeO.

**Valence sums are calculated by present authors using Rucklidge's data.

TABLE 10. Portion of root-mean-square thermal displacements along the *c* axis.

Atom	Displacement along <i>c</i> axis (Å)
C	0.136
B	0.237
O(10)	0.375
Si(1)	0.080

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