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Crystal structure of a non-*P*4/*nnc* vesuvianite from Asbestos, Quebec

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ABSTRACT

The crystal structure of an Fe-free vesuvianite from Asbestos, Quebec, was determined. The sample has the tetragonal space group *P*4/*n,* unlike most reported vesuvianites, which have *P*4/*nnc.* This vesuvianite has cell parameters of $a = 15.504(2)$ and $c = 11.808(2)$ with a final R value of 5.48% for 3623 unique reflections with $|F|_o > 3\sigma|F|_o$. The crystal shows a weak acentricity and a number of violations of glide-plane extinction criteria. The formula is $(Ca_{18.68}Mn_{0.06}Mg_{0.26})Al_4Al(Al_{6.51}Mg_{1.49})(Si_{17.49}Al_{0.51})O_{69}(OH)_{9.0}$.

The arrangement of atoms along each fourfold axis is ordered and periodic, but it is also polar. The space group in vesuvianite is determined by the pattern of the two fourfold axes per unit cell. Gradation exists in vesuvianite from an ordered *P*4/*n* to a completely disordered *P*4/*nnc* vesuvianite. Domains with an ordered *P*4*nc* pattern can account for the acentricity found in the Asbestos vesuvianite.

INTRODUCTION

There have been several crystal-structure determinations of vesuvianite since the original model proposed in 1931 by Warren and Modell. Structures by Coda et al. (1970), Rucklidge et al. (1975), and Fitzgerald et al. (1986) were determined in the tetragonal space group *P*4/*nnc,* although additional space groups were reported by Arem and Burnham in 1969. Giuseppetti and Mazzi (1983) have also reported one of these non-*P*4/*nnc* vesuvianites. This study examines an Fe-free, non-*P*4/*nnc* vesuvianite and the relationships of space group, associated asymmetry, and crystal structure of this very complex mineral.

EXPERIMENTAL METHODS

The crystal used in this analysis was from a fairly large find of pocket crystals at the Jeffrey mine, Asbestos, Quebec. It was supplied by Dr. George Robinson, currently at the National Museum of Canada at Ottawa. The vesuvianite was a single crystal of medium-lilac color and was taken from a group of individual crystals each approximately 1 cm in length. The sample was analyzed using an ARL-SEMQ electron microprobe at an operating voltage of 15 kV and a beam current of 0.15 μA. The data were corrected using Bence-Albee factors. The standards used (Jarosewich et al., 1979) were hornblende (Si, Al, Fe, Mg, K, Ti, Na), wollastonite glass (Ca), apatite (F), and manganite (Mn). Water was calculated from the structure determination. The chemical analysis of this vesuvianite is shown in Table 1 and is remarkable for its Fe-free character and high Al content.

The sample was ground to a sphere 0.37 mm in diameter and was affixed to a fine glass fiber. The unit-cell parameters provided in Table 2 were obtained from the least-squares fit of the angular settings of 25 reflections. Careful examination of the reflection data was made to determine if the Asbestos crystal conformed to the requirements of space group *P*4/*nnc.* Analysis of the systematic absences revealed numerous violations of all three glide-plane extinction criteria, proving that the true symmetry was not *P*4/*nnc.*

Material from the same crystal group was sent for a centrosymmetry determination to the North American Philips Corporation, where it was kindly analyzed by G. M. Loiacano. Samples were ground and the particles separated into fractions ≥125, 125–75, <75–45, and <45 μm. The samples were matched with the index oil at $n = 1.705$, and the procedures of Dougherty and Kurtz (1976) were followed for optical second-harmonic generation (SHG) tests. The sample gave the following results, reported as $I_{2\omega}/I_{2\omega,SiO_2}$, the ratio of SHG signal intensity to that of a quartz standard: for the fraction ≥ 125 μm (12 mV)—0.005; <125–75 μm (10 mV)—0.004; <75–45 μm (36 mV)—0.014; <45 μm (30 mV)—0.012. The Asbestos vesuvianite is therefore weakly but definitely acentric. However, calculation of E values from the structure-factor data gave a value for $|E^2 - 1|$ nearly equal to 1.0, which is near the theoretical value of 0.94 for a centric crystal.

Table 2 gives data collection and structure-refinement information. Refinements were made using a SHELXTL structure-solving package (revision 3.0) and a Data General Nova 4 computer. Neutral-atom scattering factors were obtained from the *International Tables for Crystallography* (1974). Refinement was first carried out in *P*4, the space group suggested by the glide-plane extinction violations. The results strongly indicated that a space group with higher symmetry was needed, i.e., data throughout showed strong correlations between pairs of coordinates, thermal parameters were often negative, standard deviations were unacceptably large, and the refinement would not converge.

Since the crystal was only slightly acentric, with a probable

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Table 1. Electron-microprobe analysis of Asbestos vesuvianite

Oxide	wt%
CaO	36.99
K_2O	0.01
Na_2O	0.00
Al_2O_3	21.62
MgO	2.46
TiO_2	0.02
MnO	0.14
FeO	0.05
SiO_2	37.07
F	0.02
H_2O_{calc}	2.51
Total	100.89
$-(O = F)$	0.01
Total	100.88

Table 2. Crystal and structure-refinement data at 22°C

Crystal system	tetragonal
Space group	*P4/n*
a (Å)	15.504(2)
c (Å)	11.808(2)
V (Å)^3	2838.2(8)
Z	2
Color	lilac
Crystal size	0.37-mm sphere
Radiation	graphite-monochromatized Mo$K\alpha$
Diffractometer	Nicolet R3
μ_l (cm^{-1})	25.07
Scan speed (°/min)	var 3–10
2θ scan range (°)	$4.0 < 2\theta < 60.0$
Scan technique	omega
Data collected	$+h, +k, +l$
Scan width (°)	$0.8 \pm \Delta(\alpha_1 - \alpha_2)$
Weighting factor g*	0.00085
Unique reflections	4060
Unique data with $(F_o) > 3\sigma(F_o)$	3623
Standard reflections	3/97
Parameters refined	297
Data/parameter ratio	12.2
R %(F_o)	5.48
R_w %(F_o)	6.32

* $w^{-1} = \sigma^2(F_o) + g(F_o)^2$.

symmetry higher than *P*4, refinement was then attempted in *P4/n*, a centric space group. The atomic coordinates of Rucklidge et al. (1975) were used, as in the *P*4 refinement, but the coordinates had to be translated to a new origin at $\bar{1}$ to conform to the requirements of *P4/n*. The problems apparent in the *P*4 refinement vanished, and a final *R* of 5.48% was reached. Least-squares refinement by blocked-cascade methods used anisotropic temperature factors for all atoms, although no attempt was made to include H-atom contributions.

Refinement problems resulted from a rather odd vesuvianite that seemed to belong exactly to no space group. The violations of glide-plane extinction criteria were present, as was the acentricity, yet the structure would refine only in *P4/n*. Refinement was also carried out in *P4/nnc* after the *P4/n* refinement was complete. The value of *R* remained high throughout the refinement, and distinct peaks, which could not be accounted for, remained on a difference map.

Ca was assigned to the C site and Al to the A position, following the terminology and site assignments of Rucklidge et al. (1975). Al was also assigned to the B site and the general Al-Fe site. Table 3 gives the atomic coordinates, and Table 4 gives the anisotropic temperature factors for the Asbestos vesuvianite.

DISCUSSION

The Asbestos vesuvianite is a previously undescribed type of this mineral, both in its Fe-free character and in the degree to which it deviates from *P4/nnc* symmetry.

The high Al content (21.62%) and lack of Fe and Ti cations make site assignments fairly straightforward. The C site on the fourfold axis contains Ca, as in the vesuvianites described by Rucklidge et al. (1975) and a cuprian vesuvianite from Franklin, New Jersey, analyzed by the authors (Fitzgerald et al., 1986). Al is assigned to the A position with its shorter bond length, and Al and Mg to the general Al-Fe position with its slightly longer bond length (Table 5). During the refinement, Al alone was actually assigned to the Al-Fe position, as least-squares cannot differentiate between Al and Mg. The larger Mg^{2+} ion should show a preference for this site rather than the smaller A site.

The B site shows shorter overall bond lengths than the same site in other vesuvianites. This is understandable in view of the presence of Fe in this position in the crystals studied by Rucklidge et al. (1975) and the presence of Cu in the Franklin vesuvianite (Fitzgerald et al., 1986). The mean bond length of 2.031 Å is not accurate in that this average includes O(6) and O(10) distances to a vacant B site. When these are eliminated, the mean becomes 1.873 Å. The latter value, the B–O(6) bond length of 1.935(3) Å, and the B–O(10) bond length of 1.810(6) Å are all too short for Mg but reasonable for Al. In contrast, Valley et al. (1985) assigned Mg^{2+} to the B site in a vesuvianite from Georgetown, California, which they refined in space group *P4/nnc*. Refinement in *P4/nnc* averages distances between B and neighboring oxygens, thereby making it impossible to distinguish between B occupied and B unoccupied. This averaging gives apparent bond lengths longer than actual bond lengths.

Vesuvianite has eleven different oxygen positions, with O(10) and O(11) the only oxygens not bonded to Si. Bond-strength calculations (Donnay and Allmann, 1970) show O(1) through O(9) to be oxygen ions with bond strengths near 2.0. The atom O(11), as in the Franklin vesuvianite (Fitzgerald et al., 1986), is an OH with a bond strength of 1.35 if the general site is occupied by Al, and 1.13 if the site is occupied by Mg, which it is one-third of the time. However, unlike the Franklin vesuvianite in which O(10) is also an OH, in the Asbestos vesuvianite, the O(10) site is an OH only when B is not occupied. The atom O(10) has a bond strength of 0.99 when B is not occupied, showing that in this situation O(10) is a hydroxyl. With B occupied, however, the bond strength increases to 1.7, strongly suggesting that in this case O(10) is an oxygen ion. Valley et al. (1985) reached the same conclusion in their study of a vesuvianite from Georgetown, California. In addition, the O(10)–O(10) distance of 2.75 Å suggests a H bond between the two. Figure 1

Table 3. Atomic coordinates (×10^4) and temperature factors (Å^2 × 10^3) for Asbestos vesuvianite

Atom	*x*	*y*	*z*	U_{iso}*
Si(1a)	−¼	¼	½	5(1)
Si(1b)	−¼	¼	0	6(1)
Si(2a)	−399(1)	3180(1)	1308(1)	5(1)
Si(2b)	−422(1)	1797(1)	3727(1)	5(1)
Si(3a)	795(1)	1506(1)	6364(1)	6(1)
Si(3b)	889(1)	3482(1)	−1335(1)	6(1)
Ca(1a)	−¼	¼	2498(1)	7(1)
Ca(2a)	1902(1)	−421(1)	6215(1)	7(1)
Ca(2b)	−457(1)	1880(1)	−1191(1)	7(1)
Ca(3a)	1782(1)	4005(1)	1222(1)	11(1)
Ca(3b)	3147(1)	3958(1)	−6043(1)	11(1)
Cac(1)	¼	¼	−3498(2)	9(1)
Cac(2)	¼	¼	−1499(22)	8(5)
Al(1a)	−1136(1)	1194(1)	1253(1)	8(1)
Al(1b)	−1229(1)	1111(1)	6266(1)	6(1)
Ala(1)	0	0	½	5(1)
Ala(2)	0	½	0	7(1)
Alb(1)	¼	¼	−297(2)	0(1)
Alb(2)	¼	¼	−4652	3
O(1a)	−2215(2)	1723(2)	858(2)	8(1)
O(1b)	−2823(2)	1733(2)	4144(2)	7(1)
O(2a)	−1187(2)	1574(2)	2808(2)	8(1)
O(2b)	−1166(2)	3384(2)	2239(2)	8(1)
O(3a)	−480(2)	2213(2)	768(2)	9(1)
O(3b)	−496(2)	2772(2)	4240(2)	7(1)
O(4a)	−638(2)	1054(2)	4728(2)	7(1)
O(4b)	−613(2)	3933(2)	326(3)	9(1)
O(5a)	−88(2)	3270(2)	−1757(2)	9(1)
O(5b)	−190(2)	1677(2)	6795(2)	8(1)
O(6a)	1290(2)	2719(2)	−576(3)	14(1)
O(6b)	1135(2)	2293(2)	5624(3)	12(1)
O(7a)	555(2)	1701(2)	3262(2)	9(1)
O(7b)	559(2)	3250(2)	1827(3)	10(1)
O(8a)	929(2)	4381(2)	−631(2)	8(1)
O(8b)	899(2)	603(2)	5687(2)	8(1)
O(9a)	1418(2)	1481(2)	7510(2)	9(1)
O(10a)	¼	¼	1235(5)	12(1)
O(10b)	−¼	−¼	−3568(5)	10(1)
O(11a)	−54(2)	592(2)	1369(2)	11(1)
O(11b)	−640(2)	40(2)	6351(2)	9(1)

Note: Estimated standard deviatioons (esd's) are in parentheses.

* Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Anisotropic temperature factors (Å^2 × 10^3) for Asbestos vesuvianite

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si(1a)	6(1)	6(1)	4(1)	0	0	0
Si(1b)	6(1)	6(1)	5(1)	0	0	0
Si(2a)	6(1)	5(1)	5(1)	0(1)	1(1)	1(1)
Si(2b)	5(1)	5(1)	6(1)	−0(1)	0(1)	0(1)
Si(3a)	7(1)	5(1)	5(1)	−0(1)	−0(1)	−1(1)
Si(3b)	9(1)	4(1)	5(1)	−1(1)	1(1)	−1(1)
Ca(1a)	11(1)	6(1)	4(1)	0	0	−1(1)
Ca(2a)	7(1)	8(1)	7(1)	0(1)	−1(1)	0(1)
Ca(2b)	9(1)	6(1)	7(1)	0(1)	0(1)	1(1)
Ca(3a)	11(1)	9(1)	14(1)	2(1)	−2(1)	−2(1)
Ca(3b)	10(1)	9(1)	13(1)	−3(1)	−1(1)	1(1)
Al(1a)	7(1)	8(1)	8(1)	−0(1)	1(1)	−0(1)
Al(1b)	6(1)	5(1)	7(1)	0(1)	0(1)	0(1)
Ala(1)	5(1)	5(1)	6(1)	−1(1)	1(1)	1(1)
Ala(2)	5(1)	5(1)	9(1)	1(1)	−0(1)	−1(1)
O(1a)	11(1)	7(1)	6(1)	1(1)	1(1)	1(1)
O(1b)	8(1)	6(1)	6(1)	1(1)	0(1)	−1(1)
O(2a)	7(1)	8(1)	9(1)	2(1)	−2(1)	0(1)
O(2b)	10(1)	9(1)	5(1)	1(1)	2(1)	−0(1)
O(3a)	10(1)	9(1)	8(1)	0(1)	−2(1)	0(1)
O(3b)	8(1)	7(1)	7(1)	0(1)	1(1)	−0(1)
O(4a)	8(1)	6(1)	7(1)	1(1)	−1(1)	1(1)
O(4b)	11(1)	6(1)	10(1)	1(1)	4(1)	2(1)
O(5a)	12(1)	7(1)	10(1)	1(1)	−2(1)	−2(1)
O(5b)	10(1)	8(1)	6(1)	−1(1)	1(1)	1(1)
O(6a)	20(2)	11(1)	11(1)	3(1)	0(1)	4(1)
O(6b)	16(1)	10(1)	11(1)	5(1)	−4(1)	−4(1)
O(7a)	9(1)	14(1)	6(1)	−1(1)	0(1)	3(1)
O(7b)	6(1)	10(1)	13(1)	−1(1)	1(1)	−1(1)
O(8a)	8(1)	6(1)	10(1)	−2(1)	0(1)	1(1)
O(8b)	6(1)	7(1)	12(1)	−3(1)	−3(1)	0(1)
O(9a)	9(1)	11(1)	7(1)	1(1)	−1(1)	−2(1)
O(10a)	10(2)	10(2)	15(3)	0	0	0
O(10b)	9(2)	9(2)	11(3)	0	0	0
O(11a)	13(1)	13(1)	7(1)	−1(1)	−0(1)	−4(1)
O(11b)	13(1)	8(1)	7(1)	1(1)	2(1)	0(1)

Note: The anisotropic temperature factor exponent takes the form $-2\pi^2(h_{11}^2a^{*2}U_{11} + k^2b^{*2}U_{22} \ldots 2hka^*b^*U_{12})$. Esd's are in parentheses.

shows the general structure of the Asbestos vesuvianite, and Figure 2 shows the arrangement of atoms along the fourfold axis.

On the basis of structural considerations and the chemical analysis, the formula may be written as

$$(Ca_{18.68}Mn_{0.06}Mg_{0.26})$$
$$Al_4Al(Al_{6.51}Mg_{1.49})(Si_{17.49}Al_{0.51})O_{69}(OH)_{9.0}.$$

This formula corresponds almost exactly with the structural model, another indication that O(10) and O(11) are properly identified as (O,OH) and OH, respectively.

CONCLUSIONS

Space group

Refinement of the Asbestos vesuvianite in the space group *P*4/*nnc* would necessitate ignoring numerous and real violations of glide symmetry. The refinement of this vesuvianite in *P*4/*n* then allows the violations of the second and third glide planes. Although the first glide plane is weakly violated, to reduce the symmetry still further to *P*4 is not representative of the major structure, and the *P*4 refinement of the Asbestos vesuvianite showed that this vesuvianite does not in fact have this symmetry.

Giuseppetti and Mazzi (1983) suggested the existence of *P*4*nc* vesuvianites, although their attempt at the refinement of one was a failure. The present study has demonstrated the existence of a vesuvianite that shows much stronger violations to the second two glide planes and fairly minor violations of the first glide plane, the opposite of a *P*4*nc* model.

This study and another by the authors (Fitzgerald et al., 1986) also show "weak" and "strong" violators, as described by Arem and Burnham (1969). It is further suggested by these studies that a gradation from a few violations to many violations exists. These gradations in glide-plane violations produce a gradation in space-group symmetry. Vesuvianites exist that are strictly *P*4/*nnc* with disorder among the fourfold axes. With increasing order, strong violations of *P*4/*nnc* occur, and the symmetry reduces to *P*4/*n*. These order-disorder relationships do not appear to depend on the chemistry of the B and C atomic

Table 5. Interatomic distances (Å) in cation coordination polyhedra

Si(1)–O(1)	1.639(3)	Ca(3)–O(3)	2.443(3)
	1.635(3)		2.477(3)
Mean	1.637	–O(6)	2.613(3)
Si(2)–O(2)	1.649(3)		2.378(3)
	1.645(3)	–O(7)	2.340(3)
–O(3)	1.635(3)		2.480(3)
	1.633(3)	–O(7)	2.504(3)
–O(4)	1.679(3)		2.402(3)
	1.684(3)	–O(7)	2.629(3)
–O(7)	1.610(3)		2.507(3)
	1.617(3)	–O(8)	2.612(3)
Mean	1.644	–O(10)	2.516(6)
Si(3)–O(5)	1.632(3)		2.585(6)
	1.628(3)	–O(11)	2.546(3)
–O(6)	1.590(3)		2.466(3)
	1.608(3)	Mean	2.507
–O(8)	1.619(3)	C–O(6)	2.196(3)*
	1.625(3)		2.378(3)
–O(9)	1.663(3)	–O(9)	2.584(3)*
	1.652(3)		2.593(3)
Mean	1.627	Mean	2.438
Ca(1)–O(1)	2.324(3)	B–O(6)	1.935(3)
	2.333(3)		2.165(3)*
–O(2)	2.501(3)	–O(10)	1.810(6)
	2.518(3)		2.102(6)*
Mean	2.419	Mean	1.910
Ca(2)–O(1)	2.522(3)	Al-Fe–O(1)	1.921(3)
	2.444(3)		1.890(3)
–O(2)	2.399(3)	–O(2)	1.867(3)
	2.447(3)		1.931(3)
–O(3)	2.370(3)	–O(3)	1.964(3)
	2.389(3)		1.914(3)
–O(4)	2.459(3)	–O(4)	2.072(3)
	2.408(3)		2.036(3)
–O(5)	2.464(3)	–O(5)	2.035(3)
	2.335(3)		1.939(3)
–O(5)	2.327(3)	–O(11)	1.898(3)
	2.434(3)		1.925(3)
–O(6)	3.091(3)	Mean	1.950
	2.804(3)	A–O(4)	1.937(3)
–O(8)	2.308(3)		1.946(3)
	2.322(3)	–O(8)	1.865(3)
Mean	2.471		1.885(3)
		–O(11)	1.880(3)
			1.860(3)
		Mean	1.896

Note: Esd's are in parentheses.
* Distances to vacancies.

sites, as Giuseppetti and Mazzi (1983) refined a vesuvianite in *P*4/*n* that contains Fe in the B site.

Deviations from centrosymmetry

The Asbestos vesuvianite and one from Franklin, New Jersey, previously analyzed by Fitzgerald et al. (1986) were found to be acentric, although the degree of acentricity differs. Two other vesuvianites were also analyzed using SHG method at North American Philips Corporation. A vesuvianite from Sanford, Maine, was analyzed because it has long been thought to be a "typical" *P*4/*nnc* vesuvianite. The analysis showed this sample to be centrosymmetric. A vesuvianite from Crestmore, California, was analyzed, giving a signal 0.002 times that of quartz. This was the same signal intensity as the Franklin sample. The Asbestos vesuvianite gave a signal 0.014 times that of quartz, about seven times the intensity of the Crestmore and Franklin samples. These results show that vesuvianite can be centric or acentric and that acentric vesuvianites show varying degrees of acentricity.

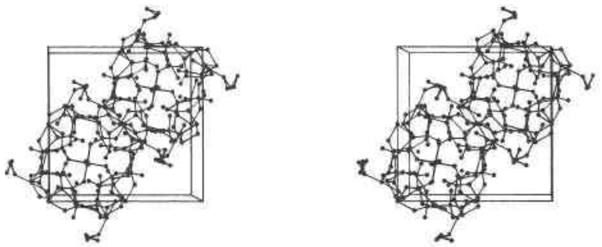

Fig. 1. Stereo view looking down the c axis.

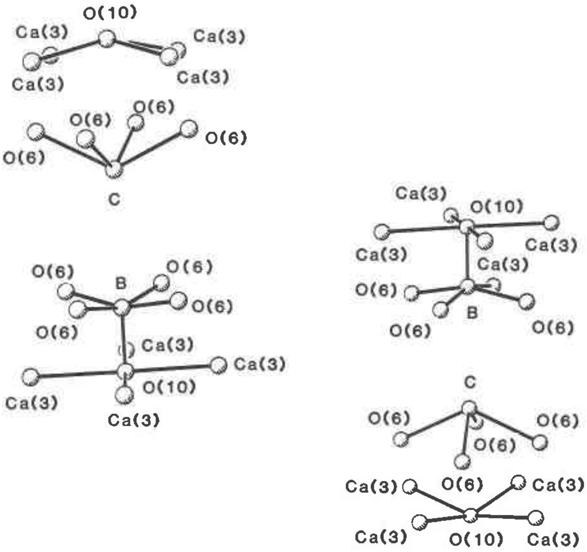

Fig. 2. Atomic positions along the fourfold axes and coordinating atoms in *P*4/*n* vesuvianite.

Violations of *n*-glide symmetry perpendicular to the c axis are another indication of this acentricity. The Franklin vesuvianite is very weakly acentric and has only three exceptions to the *n*-glide extinction rule that are greater than 3σ, whereas the Asbestos vesuvianite has 31 violations greater than 3σ. The Asbestos sample has about ten times more violations than the Franklin sample and tests about seven times more acentric than the Franklin samples. The glide-plane violations along the c axis and the intensity of the SHG signal are roughly proportional, and violations of the first glide plane should be a reliable predictor of acentricity in vesuvianites.

It must be emphasized that even the most acentric vesuvianite tested is only weakly noncentrosymmetric. Extremely sensitive SHG tests are necessary to determine acentricity. Unless these tests are done, vesuvianite will appear centric. This phenomenon is illustrated by both of our intensity data sets, which yielded values of $|E^2 - 1|$ near 1.0, suggesting centrosymmetric structures.

Structural patterns in vesuvianite

The majority of the space-group variations and anomalies observed in vesuvianites can be explained by vari-

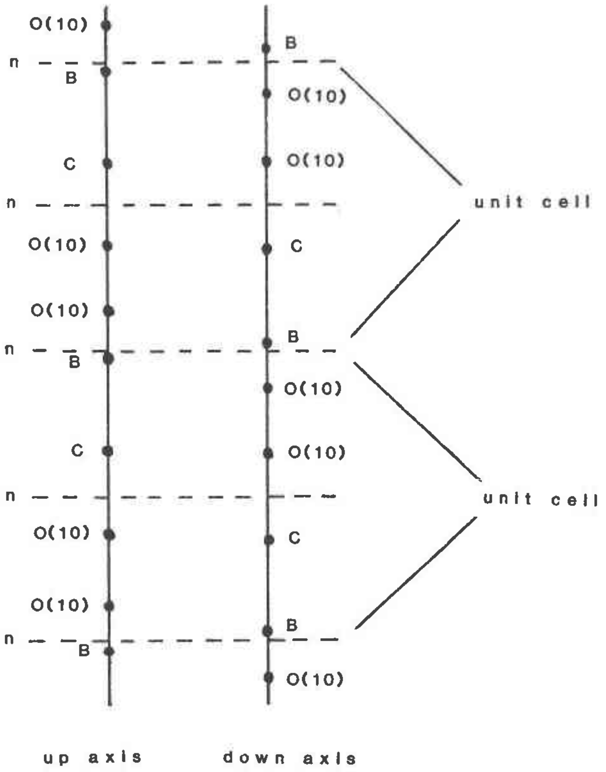

Fig. 3. Arrangement of atoms along the fourfold axes in *P*4/*n* vesuvianite [O(10) adjacent to C = OH(10)].

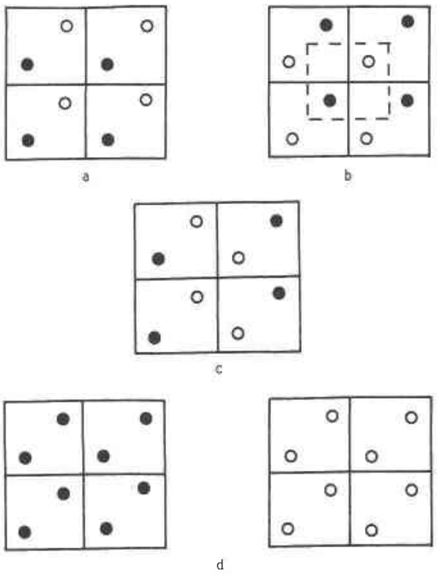

Fig. 4. Patterns of axial vectors in vesuvianite (circle = down axis, dot = up axis). (a) Pattern in *P*4/*n* vesuvianite (majority of unit cells). (b) Pattern in *P*4/*n* vesuvianite (minority of unit cells). (c) Twinned combination of axial vector patterns. (d) Patterns in *P*4*nc* vesuvianite.

ations in orientation of the atomic pattern along the fourfold axes. Figure 3 illustrates the axial configuration of the *P*4/*n* vesuvianite from Asbestos, Quebec. Other vesuvianites with *P*4/*n* symmetry will show the same relative pattern but may have minor bond-length differences.

The arrangement of atoms along each fourfold axis is ordered and periodic. This configuration is stable because the O(10)–O(10) distance is short enough to necessitate a H bond between OH(10) and O(10). The improved charge balance provided by this H bond assures that of ions in adjacent O(10) sites, one will be O^{2-} [O(10) ion] and one will be OH^- [OH(10) ion]. The relationship between O(10) and OH(10) is an important one, in that O(10) is always bonded to B, and OH(10) is always adjacent to but not bonded to C. These relationships determine the ordering of cations along the fourfold axes.

The arrangement of atoms along the fourfold axes is polar and acentric; each axis has a definite "up" or "down" direction. The two axes in one unit cell are identical in atomic order but reversed in polarity. Figure 4a illustrates the general pattern for a number of unit cells looking down the **c** axis. Axes that point up are represented by a solid dot, and axes that point down are represented by an open circle (as shown in Fig. 3).

The two B sites and the C sites are preferentially occupied in the Asbestos vesuvianite. Although Figure 3 shows the preferred pattern for this vesuvianite, the reverse pattern (Fig. 4b) exists in a minority of the unit cells in this vesuvianite. The two patterns of axial distribution can be considered the same, but with different origins for the unit cell, although in a given crystal they are distinct. The dotted unit cell in Figure 4b shows the unit cell as diagrammed in Figure 4a.

The two patterns shown in Figures 4a and b have another relationship to each other; i.e., they can be considered twins. These twins are related to each other by reflection across a diagonal mirror plane (Fig. 4c). Twinning of unexplained character has been a popular explanation for difficulties encountered in the refinement of vesuvianite structures. Although vesuvianite technically shows twinning, it is more useful to consider the pattern in terms of the orientations of the fourfold axes.

Another alternative exists: both fourfold axes may point in the same direction, both up or both down. Figure 4d shows this pattern, which has the overall symmetry of *P*4*nc*, a noncentric space group. The two patterns are twinned by reflection on a mirror plane that lies perpendicular to the **c** axis. No vesuvianite has yet been reported with this symmetry, but the presence of this pattern in small amounts in vesuvianite would cause the signal detected in SHG tests in the Franklin and Asbestos specimens. It would also cause the violations of the first glide-plane extinction rule that are found in all the analyzed samples. The weakness of these violations indicate that this pattern is less prevalent than the *P*4/*n* patterns that cause stronger violations of glide-plane extinction criteria.

The *P*4/*nnc* structure can be considered to be a random distribution on a unit-cell scale of any of the following: (1) combinations of both patterns with *P*4/*n* symmetry, (2) combinations of both patterns with *P*4*nc* symmetry, or (3) combinations of patterns with both *P*4/*n* and *P*4*nc* symmetry. Giuseppetti and Mazzi (1983) proposed a similar model for the *P*4/*nnc* structure. All of these combinations give interchangeable and indistinguishable patterns and result in the statistical half-occupancy of the B and C sites.

Violations of glide-plane extinction criteria are introduced when blocks of the same pattern, a number of unit cells across, occur in the structure. A positive piezoelectric test results if some blocks have *P*4*nc* symmetry. The larger the blocks or domains, the greater the violations. However, the overall structure can remain *P*4/*nnc* if blocks of different patterns are present. There is thus a gradation between strictly *P*4/*nnc* vesuvianites and those of other space groups.

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