

## COMPARISON OF THE CRYSTAL STRUCTURES OF WOLLASTONITE AND PECTOLITE

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### ABSTRACT

Wollastonite,  $\text{CaSiO}_3$ , and pectolite,  $\text{CaNaHSi}_3\text{O}_9$ , have similar triclinic cells; because of this and their analogous chemical compositions they have long been regarded as belonging to the same mineral family. An examination of the results of least-squares refinement reveals that although the structures contain similar metasilicate chains, they are not as closely isotypic as had been supposed. The principal differences are in the location of the large cations between layers of oxygen atoms parallel to (101) and in the relative orientations of the metasilicate chains.

The structures of both wollastonite and pectolite contain pseudomonoclinic subcells which are joined together on (100) to give an overall symmetry different from that of the subcell. The geometries of these subcells and the possibility of their being joined in different ways are important in explaining the types of twinning which occur in wollastonite and pectolite.

### INTRODUCTION

Pectolite and wollastonite belong to the same mineral family and have distinct but related crystal structures. Buerger and Prewitt (1961) have shown that the crystal structures proposed by Buerger (1956) for pectolite and by Mamedov and Belov (1956) for wollastonite are correct. The present paper describes in detail the similarities and differences between the two structures and attempts to explain some of the puzzling features of these minerals which have been observed in the past.

### CONFIRMATION OF THE STRUCTURES

Unit cell information for pectolite, wollastonite, and  $\text{NaAsO}_3$  is given in Table 1. The similarity of the triclinic cells (space group  $P\bar{1}$ ) and the analogous chemical compositions indicate that these substances might have the same structure. A comparison of the results given by Mamedov and Belov (1956) for wollastonite and Liebau (1956) for  $\text{NaAsO}_3$  shows that these two structures are identical. If either of these is compared to the pectolite structure given by Buerger (1956) certain discrepancies are noted. For example, while in both structures the silicate chains have re-

peat units of three tetrahedra, they do not have the same orientation in the two structures, and the large cations all lie in a sheet parallel to (101), but do not have the same distribution in the sheet.

In order to determine whether these differences were real, Buerger and Prewitt (1961) collected three-dimensional  $x$ -ray intensities for wollastonite and refined the structure by least-squares. In addition, they refined pectolite using relatively crude intensity data originally obtained by Buerger (1956). The final  $R$  factors for wollastonite and pectolite, respectively, were 8.9% and 17%. When the structures and  $x$ -ray data were interchanged, the wollastonite data could not be refined below 26% and the pectolite data not below 52%. Therefore, the structures as proposed must be correct but different.

### COMPARISON OF STRUCTURES

Figures 1 and 2 are projections along  $b$  of the wollastonite and pectolite structures, respectively. Coordinates for the figures in this paper were given originally by Buerger and Prewitt (1961) and are reproduced in Table 2 with a few changes so that all coordinates refer to atoms in or near the same silicate chain. Unless otherwise noted, the origin for the figures is that of the coordinates of Table 2.

Figures 1 and 2 reveal that the structures are topologically different. For example, the bends between the superposed  $\text{Si}_1$  and  $\text{Si}_2$  tetrahedra and the  $\text{Si}_3$  tetrahedron are reversed. The large cations, however, occupy approximately the same positions in the two structures. One immediately wonders whether the misfit is merely a result of identical structures being oriented in different ways. The authors spent some time in considering this possibility and found that the structures can be oriented so that the silicate

TABLE 1. UNIT CELLS OF WOLLASTONITE,  $\text{NaAsO}_3$ , AND PECTOLITE

	Wollastonite $\text{Ca}_3\text{Si}_3\text{O}_9$	$\text{Na}_3\text{As}_3\text{O}_9$	Pectolite $\text{Ca}_2\text{NaHSi}_3\text{O}_9$
$a$	7.94 Å	8.07 Å	7.99 Å
$b$	7.32 Å	7.44 Å	7.04 Å
$c$	7.70 Å	7.32 Å	7.02 Å
$\alpha$	90°02'	90°	90°31'
$\beta$	95°22'	91°30'	95°11'
$\gamma$	103°26'	104°	102°28'

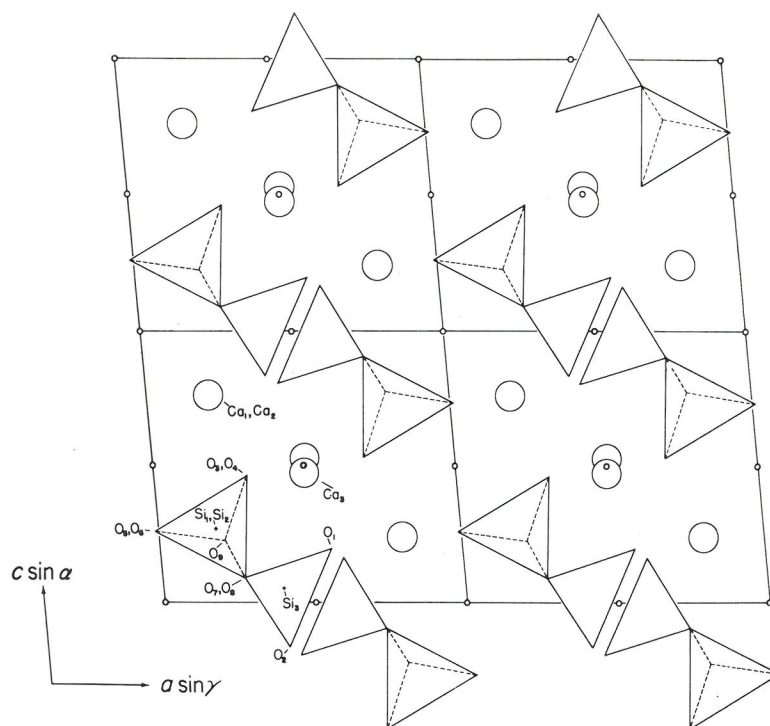
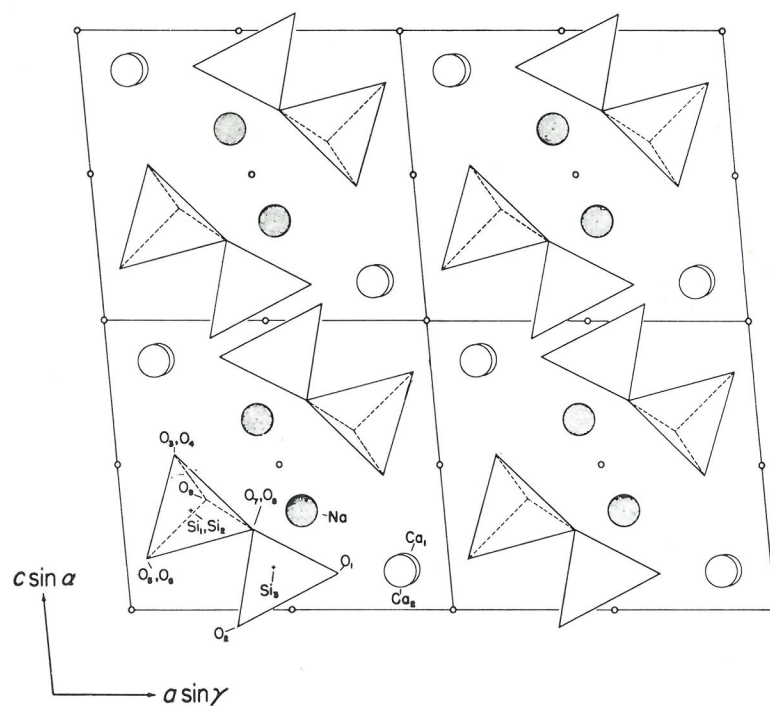
FIG. 1. Projection of the wollastonite structure along  $b$ .FIG. 2. Projection of the pectolite structure along  $b$ . Although the  $Si_1$  and  $Si_2$  tetrahedra should not be exactly superimposed, they are presented this way to simplify the drawing.

TABLE 2. ATOM COORDINATES FOR WOLLASTONITE AND PECTOLITE

Atom	Wollastonite			Pectolite			
	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>
Ca <sub>1</sub>	.1985	.4228	.7608	Ca <sub>1</sub>	.857	.596	.146
Ca <sub>2</sub>	.2027	.9293	.7640	Ca <sub>2</sub>	.843	.074	.139
Ca <sub>3</sub>	.5034	.7505	.5280	Na	.552	.265	.344
Si <sub>1</sub>	.1852	.3870	.2687	Si <sub>1</sub>	.221	.402	.337
Si <sub>2</sub>	.1849	.9545	.2692	Si <sub>2</sub>	.210	.954	.344
Si <sub>3</sub>	.3970	.7235	.0560	Si <sub>3</sub>	.451	.735	.148
O <sub>1</sub>	.5709	.7686	.1981	O <sub>1</sub>	.652	.788	.125
O <sub>2</sub>	.4008	.7259	-.1698	O <sub>2</sub>	.322	.702	-.057
O <sub>3</sub>	.3037	.4635	.4641	O <sub>3</sub>	.185	.496	.538
O <sub>4</sub>	.3017	.9374	.4655	O <sub>4</sub>	.171	.839	.541
O <sub>5</sub>	-.0154	.3746	.2657	O <sub>5</sub>	.070	.393	.171
O <sub>6</sub>	-.0175	.8681	.2647	O <sub>6</sub>	.053	.896	.179
O <sub>7</sub>	.2732	.5118	.0919	O <sub>7</sub>	.396	.533	.275
O <sub>8</sub>	.2713	.8717	.0940	O <sub>8</sub>	.402	.906	.275
O <sub>9</sub>	.2188	.1784	.2228	O <sub>9</sub>	.260	.182	.381

chains are nearly superposed. This is accomplished by interchanging the *a* and *c* axes and shifting the origin of one of the structures. Figure 3 shows projections along *b* of wollastonite and pectolite in which the silicate chains are oriented to correspond with one another. The *y* coordinates of the atoms in the respective chains are about as close to each other as are the *x* and *z* coordinates. The locations of the large cations, however, are not similar. In fact, the large cations occupy completely different interstices between oxygens when the structures are oriented in

this way. The structures must then be different even though the packing of oxygens is roughly similar. The authors originally thought that this kind of comparison might be more useful than the conventional one, but further investigation as reported below showed that the conventional orientations should be retained.

#### PSEUDOMONOCLINIC SYMMETRY

A number of investigators have commented on the unusual features which are observed in *x*-ray diffraction photographs of wollastonite and pectolite. Among these features are a mirror symmetry between relative even-numbered reciprocal lattice levels normal to *b*<sup>\*</sup>, and the presence of a substructure along *b* with a period of *b*/2 as indicated by the average spot intensity in even-numbered reciprocal lattice levels normal to *b*<sup>\*</sup> being greater than in the odd-numbered levels. Ito (1950) discussed these effects and proposed that triclinic wollastonite could be constructed by starting with a hypothetical monoclinic cell and shifting successive cells along (100) in increments of  $\pm \frac{1}{4}b$ . To this pseudomonoclinic cell he attributed a symmetry of *P2*/*m* or *P2*<sub>1</sub>/*m*. Figures 4 and 5 show that both wollastonite and pectolite can indeed be so regarded, and that the space group of this unit, which is infinite in the *b* and *c* directions and one unit cell thick along *a*, is *P2*<sub>1</sub>/*m*. Liebau (1956) also noticed that NaAsO<sub>3</sub> can be so regarded.

This shift between successive pseudomonoclinic units not only determines the triclinic symmetry in

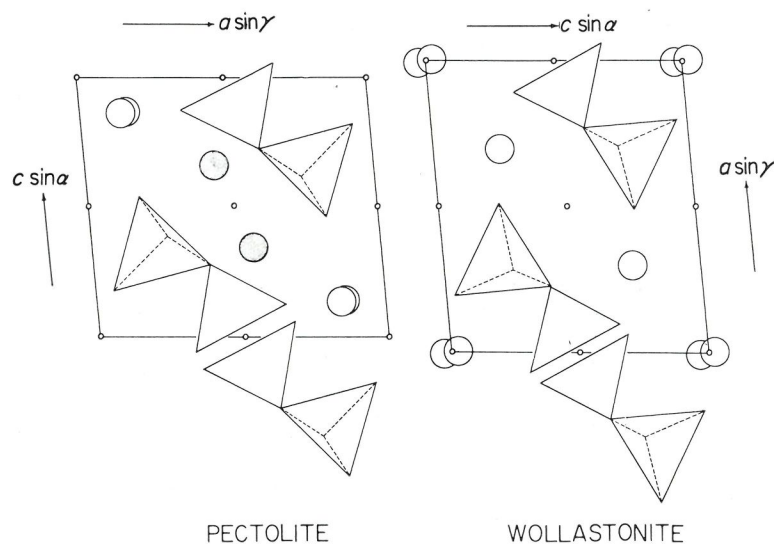


FIG. 3. Projections of the pectolite and wollastonite structures along *b*. The origin and orientation of wollastonite has been changed from that of Fig. 1 so that the silicate chains in wollastonite have the same orientation as in pectolite.

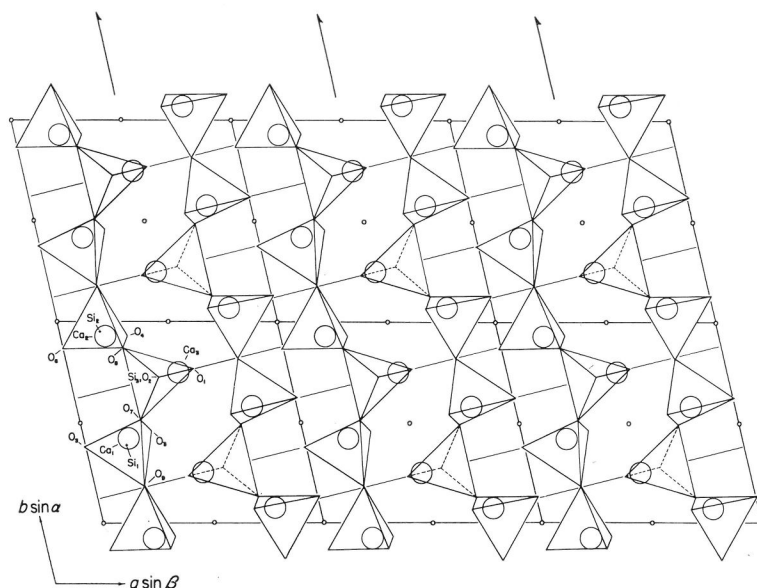


FIG. 4. Projection of the wollastonite structure along  $c$ . The mirror planes and screw axes are elements of the pseudomonoclinic unit.

pectolite and wollastonite, but also is the key to twinning in these minerals and probably will be found to be significant in other triclinic metasilicates as well. The results of the different shifts which can be made are discussed in another section of this paper.

It is interesting to note how closely the refined atom coordinates conform to the monoclinic symmetry. The coordinates were refined in the space group  $P\bar{1}$  so that all atoms were in the general position with no restrictions on  $x$ ,  $y$  or  $z$ . Table 3 gives the wollastonite and pectolite coordinates transformed to the pseudomonoclinic cell using the cell transformation<sup>1</sup>

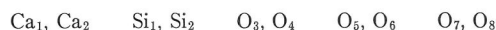
	Pseudomonoclinic		
Triclinic	1	$-\frac{1}{2}$	0
	0	1	0
	0	0	1

and adding 0.125 to the transformed  $y$  coordinates.

For the atoms  $Ca_3$ ,  $Si_3$ ,  $O_1$ ,  $O_2$  and  $O_9$  in wollastonite, which would be on the mirror plane in  $P2_1/m$ , the  $y$  coordinates should be .250 or .750. The very small deviations of about .001 (or .007 Å) are within the expected accuracy of the measurements. The other atoms which are related by the mirror planes also show little deviation from the positions they would occupy if the monoclinic symmetry held. If the space group  $P2_1/m$  is assumed, then the following

<sup>1</sup> This transformation is not exact when there is a departure of  $\alpha$  (triclinic) from  $90^\circ$ ;  $\alpha$  in wollastonite is nearly  $90^\circ$  and departs from  $90^\circ$  by only  $31'$  in pectolite.

paired atoms are equivalent and occupy the general position:



$Ca_3$ ,  $Si_3$ ,  $O_1$ ,  $O_2$  and  $O_9$  are each in the special positions  $m$ .

Although the atoms in pectolite have the same pseudoequipoint distributions as do those in wollastonite, the refined coordinates for the pectolite atoms do not conform as closely to the monoclinic symmetry. For example, the  $y$  coordinate of  $O_9$  is .242 as compared with .250 if  $O_9$  were on the mirror plane. This is a deviation of about 0.06 Å. A detailed refinement of pectolite now being carried out in this laboratory has shown that these deviations in the pectolite coordinates are real.

The pseudosymmetry gives rise to the strong substructure along  $b$ , since all the atoms except  $O_7$  and  $O_8$  in both wollastonite and pectolite and Na in pectolite have  $x$  and  $z$  coordinates similar to another atom of the same type located  $\frac{1}{2}b$  away. It is interesting that  $Ca_3$  and its inversion equivalent in wollastonite have similar  $x$  and  $z$  coordinates and are approximately  $\frac{1}{2}b$  apart, while Na and its inversion equivalent in pectolite do not have similar  $x$  and  $z$  coordinates even though they are separated by  $\frac{1}{2}b$ . This is one of the major differences between these minerals.

The similarities and differences between wollastonite and pectolite brought out in this section seem to be more useful in describing the structures than do those in the last section where a special orientation of one of the structures was used to show how the sili-

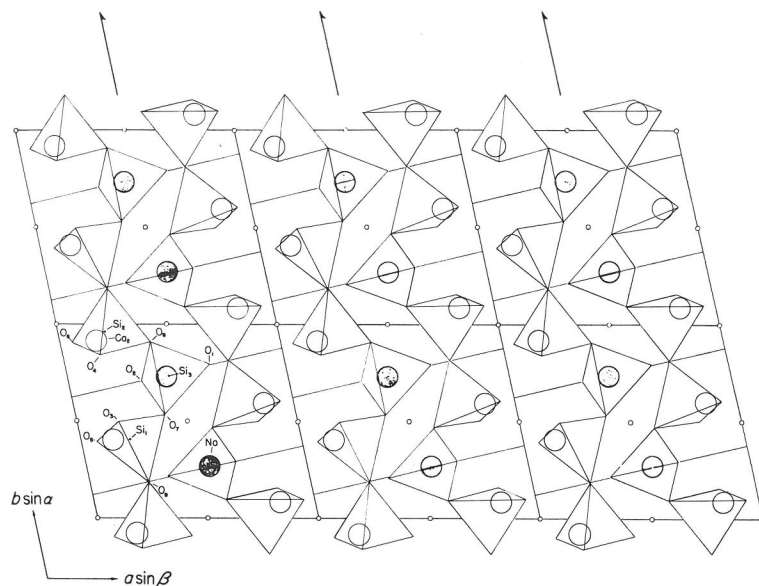


FIG. 5. Projection of pectolite along  $c$  corresponding to that of wollastonite of Fig. 4. Note that the orientations of the silicate chains are different in the two structures.

cate chains could be superposed. Because of this, the authors feel that the conventional orientation should be retained and that while the other aspect is interesting, it will not be useful except, for example, in a classification of metasilicates based on oxygen packing.

TABLE 3. ATOM COORDINATES OF WOLLASTONITE AND PECTOLITE REFERRED TO A PSEUDOMONOCLINIC CELL  $P2_1/m$  (ORIGIN AT  $\bar{1}$ )

Pseudo-equipoint	Wollastonite				Pectolite			
	Atom	$x$	$y$	$z$	Atom	$x$	$y$	$z$
4f	2Ca <sub>1</sub>	.1985	.4982	.7608	2Ca <sub>1</sub>	.857	.507	.146
	2Ca <sub>2</sub>	.2027	.0038	.7440	2Ca <sub>2</sub>	.843	-.002	.139
2e	2Ca <sub>3</sub>	.5034	.7496	.5280	2Na	.552	.252	.344
4f	2Si <sub>1</sub>	.1852	.4657	.2687	2Si <sub>1</sub>	.221	.472	.337
	2Si <sub>2</sub>	.1849	.0333	.2692	2Si <sub>2</sub>	.210	1.026	.344
2c	2Si <sub>3</sub>	.3970	.7492	.0560	2Si <sub>3</sub>	.451	.747	.148
2e	2O <sub>1</sub>	.5709	.7509	.1981	2O <sub>1</sub>	.652	.750	.125
2e	2O <sub>2</sub>	.4008	.7507	-.1698	2O <sub>2</sub>	.322	.746	-.057
4f	2O <sub>3</sub>	.3037	.5126	.4641	2O <sub>3</sub>	.185	.575	.538
	2O <sub>4</sub>	.3017	.4870	.4655	2O <sub>4</sub>	.171	.921	.541
4f	2O <sub>5</sub>	-.0039	.5035	.2657	2O <sub>5</sub>	.070	.500	.175
	2O <sub>6</sub>	-.0044	.9975	.2647	2O <sub>6</sub>	.053	1.008	.179
4f	2O <sub>7</sub>	.2732	.5685	.0919	2O <sub>7</sub>	.396	.559	.275
	2O <sub>8</sub>	.2713	.9287	.0940	2O <sub>8</sub>	.402	.930	.275
2e	2O <sub>9</sub>	.2188	.2487	.2228	2O <sub>9</sub>	.260	.242	.381

#### DISTRIBUTION OF Ca AND Na

The main difference in the wollastonite and pectolite structures is in the way the large cations are distributed in the sheet parallel to (101). Figures 6 and 7 show parts of the wollastonite and pectolite structures projected onto (101) of the pseudomonoclinic cell. Only the silicate chains on the upper side of (101) are shown.

The Ca in wollastonite are arranged in a nearly planar hexagonal pattern which is separated into bands 3 Ca columns wide running in the  $b$  direction and parallel to the silicate chains. The Na and Ca in pectolite are also arranged in a hexagonal pattern with bands consisting of 2 Ca columns bounded on either side by a half-filled Na column. Because each of these bands is translated by  $\frac{1}{4}b$  with respect to neighboring bands, every other Na in a particular Na column is missing. This is necessary because otherwise the Na-Na distances between neighboring Na columns would be much too small.

#### INTERATOMIC DISTANCES AND INTERBOND ANGLES

Interatomic distances and angles given in Table 4 were calculated for wollastonite and pectolite using a computer program written by Busing and Levy (1959). The Si-O distances in both wollastonite and pectolite show a considerable variation, the lengths apparently being determined by the coordinations of the oxygens. Table 5 gives the coordination and dis-



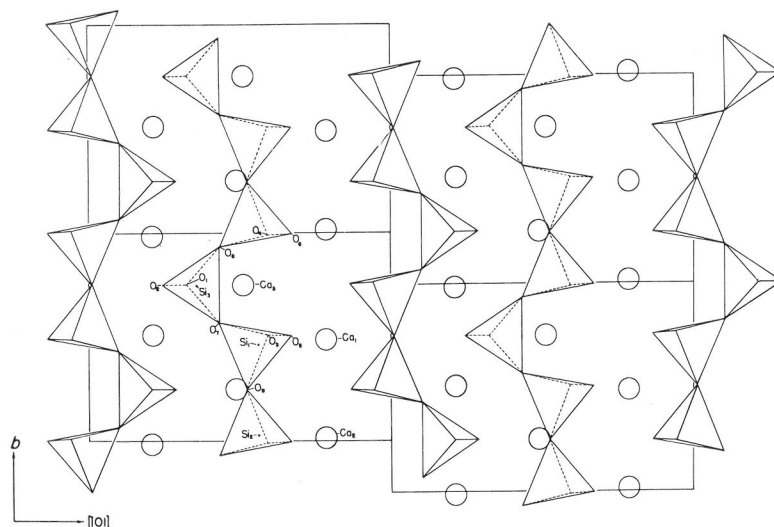


FIG. 6. Structure of wollastonite projected onto (101) of four adjacent pseudomonoclinic cells. Only the silicate chains on the near side of (101) are shown. The axial directions are for the pseudomonoclinic cell.

tances of cations around the oxygens. It can be seen that, for  $O_1$  through  $O_6$  in wollastonite, the Si-O distances are longer when an oxygen is coordinated by 3 Ca than when coordinated by 2 Ca. The situation is different for  $O_7$  through  $O_9$  because these oxygens are coordinated by 2 Si as well as Ca, showing that Pauling's electrostatic valence rule does not hold. The Si-O distances here are larger than in either of the examples above. The coordination of oxygens in wollastonite can thus be divided into three classes:

1. Oxygen ( $O_1, O_2, O_3, O_4$ ) coordinated by 1 Si and 3 Ca;
2. Oxygen ( $O_5, O_6$ ) coordinated by 1 Si and 2 Ca;
3. Oxygen ( $O_7, O_8, O_9$ ) coordinated by 2 Si and 1 Ca.

It is felt that an analysis of the pectolite interatomic distances before a detailed refinement is completed would be premature, particularly since the range in Si-O distances is so great, varying from 1.58 Å for  $Si_2-O_9$  to 1.75 Å for  $Si_2-O_8$ . This may be a real variation, however, since Morimoto *et al.* (1960) reported a range of 1.58–1.74 Å for Si-O in clinoenstatite.

$Ca_1$  and  $Ca_2$  in wollastonite are octahedrally coordinated by six oxygen atoms at average distances of 2.38<sub>3</sub>Å for  $Ca_1$  and 2.38<sub>8</sub>Å for  $Ca_2$ .  $Ca_3$  is surrounded by six oxygen atoms at an average distance of 2.39<sub>0</sub>Å and by an additional oxygen ( $O_9$ ) at 2.64<sub>2</sub>Å. The

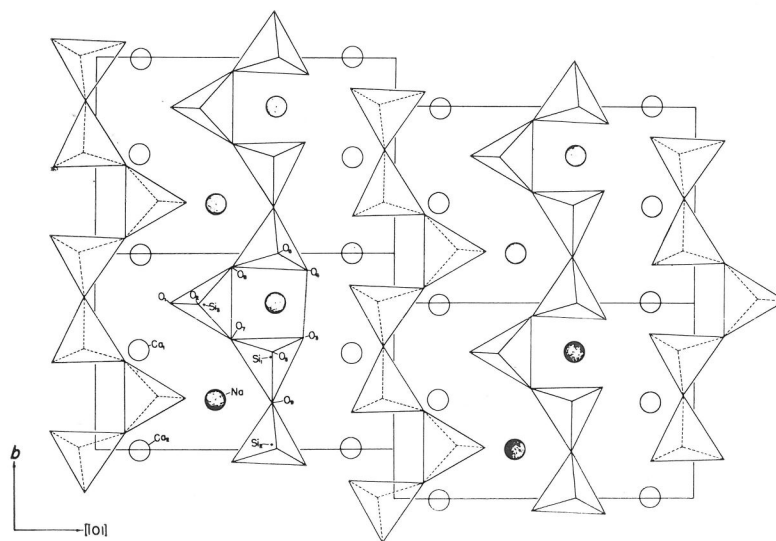


FIG. 7. Structure of pectolite projected onto (101) of the four adjacent pseudomonoclinic cells. Only the silicate chains on the near side of (101) are shown. The most likely location for the hydrogen bond is indicated by the line between the labeled  $O_3$  and  $O_4$ .

TABLE 4. INTERATOMIC DISTANCES AND INTERBOND ANGLES IN WOLLASTONITE AND PECTOLITE

Interatomic Distances			
Atoms	Wollastonite	Pectolite	
Si <sub>1</sub>	O <sub>3</sub>	1.61 <sub>8</sub> Å	1.63 Å
	O <sub>5</sub>	1.57 <sub>2</sub>	1.59
	O <sub>7</sub>	1.65 <sub>9</sub>	1.60
	O <sub>9</sub>	1.64 <sub>7</sub>	1.67
	O <sub>av</sub>	1.62 <sub>4</sub>	1.62
Si <sub>2</sub>	O <sub>4</sub>	1.61 <sub>7</sub>	1.63
	O <sub>6</sub>	1.58 <sub>1</sub>	1.61
	O <sub>8</sub>	1.65 <sub>0</sub>	1.75
	O <sub>9</sub>	1.63 <sub>7</sub>	1.58
	O <sub>av</sub>	1.62 <sub>1</sub>	1.64
Si <sub>3</sub>	O <sub>1</sub>	1.59 <sub>9</sub>	1.59
	O <sub>2</sub>	1.59 <sub>9</sub>	1.68
	O <sub>7</sub>	1.66 <sub>5</sub>	1.68
	O <sub>8</sub>	1.67 <sub>3</sub>	1.63
	O <sub>av</sub>	1.63 <sub>4</sub>	1.65
Ca <sub>1</sub>	O <sub>1</sub>	2.54 <sub>8</sub>	2.33
	O <sub>2</sub>	2.43 <sub>7</sub>	2.31
	O <sub>3</sub>	2.32 <sub>4</sub>	2.35
	O <sub>5</sub>	2.30 <sub>2</sub>	2.35
	O <sub>5</sub> '	—	2.44
	O <sub>6</sub>	2.27 <sub>2</sub>	2.34
	O <sub>7</sub>	2.41 <sub>2</sub>	—
	O <sub>av</sub>	2.38 <sub>3</sub>	2.35
Ca <sub>2</sub>	O <sub>1</sub>	2.50 <sub>1</sub>	2.30
	O <sub>2</sub>	2.42 <sub>1</sub>	2.25
	O <sub>4</sub>	2.31 <sub>6</sub>	2.32
	O <sub>5</sub>	2.36 <sub>8</sub>	2.51
	O <sub>6</sub>	2.31 <sub>6</sub>	2.35
	O <sub>6</sub> '	—	2.45
	O <sub>8</sub>	2.40 <sub>6</sub>	—
	O <sub>av</sub>	2.38 <sub>8</sub>	2.36
Ca <sub>3</sub>	O <sub>1</sub>	2.43 <sub>9</sub>	
	O <sub>2</sub>	2.34 <sub>9</sub>	
	O <sub>3</sub>	2.42 <sub>9</sub>	
	O <sub>3</sub> '	2.33 <sub>5</sub>	
	O <sub>4</sub>	2.44 <sub>1</sub>	
	O <sub>4</sub> '	2.34 <sub>9</sub>	
	O <sub>9</sub>	2.64 <sub>2</sub>	
	O <sub>av</sub>	2.39 <sub>0</sub> (excluding Ca <sub>3</sub> -O <sub>9</sub> )	
Na	O <sub>2</sub>		2.32
	O <sub>3</sub>		2.46
	O <sub>4</sub>		2.54
	O <sub>7</sub>		2.50
	O <sub>7</sub> '		2.97
	O <sub>8</sub>		2.57
	O <sub>8</sub> '		2.97
	O <sub>9</sub>		2.32
	O <sub>av</sub>		2.45 (excluding Na-O <sub>7</sub> ', Na-O <sub>8</sub> ')

Interatomic Distances		
Atoms	Wollastonite	Pectolite
Si <sub>1</sub> Si <sub>2</sub>	3.16 <sub>5</sub>	3.10
	3.11 <sub>6</sub>	3.04
Si <sub>2</sub> Si <sub>3</sub>	3.12 <sub>5</sub>	3.11
Interbond Angles		
	Wollastonite	Pectolite
Si <sub>1</sub> -O <sub>9</sub> -Si <sub>2</sub>	149°	150°
Si <sub>2</sub> -O <sub>8</sub> -Si <sub>3</sub>	140°	135°
Si <sub>3</sub> -O <sub>7</sub> -Si <sub>1</sub>	139°	136°

Ca-O sheet is similar to a brucite sheet separated into slabs running along *b* and distorted by the presence of O<sub>9</sub>.

The coordination of Ca<sub>1</sub> and Ca<sub>2</sub> in pectolite is similar to that of Ca<sub>1</sub> and Ca<sub>2</sub> in wollastonite with an average Ca<sub>1</sub>-O distance of 2.35 Å and an average Ca<sub>2</sub>-O distance of 2.36 Å. Na is surrounded by 6 oxygen atoms at an average distance of 2.45 Å and two further oxygen atoms, both at 2.97 Å.

The most probable location for the hydrogen bond in pectolite is between O<sub>3</sub> and O<sub>4</sub>. These atoms are separated by 2.44 Å which is short even for a hydrogen bond. This is represented by a line between the labelled O<sub>3</sub> and O<sub>4</sub> in Fig. 7. This separation is much less than that between similar atoms in the wollastonite chain as seen in Fig. 6. Buerger (1956) attributed the presence of a shorter *b* axis in pectolite than in wollastonite to the hydrogen bond.

In both structures, the silicon-oxygen-silicon angles have the same distribution, with Si<sub>1</sub>-O<sub>9</sub>-Si<sub>2</sub> being larger than Si<sub>2</sub>-O<sub>8</sub>-Si<sub>3</sub> and Si<sub>3</sub>-O<sub>7</sub>-Si<sub>1</sub>, which are approximately equal. This difference results from the somewhat abnormal location of O<sub>9</sub> in the oxygen sheet.

#### TWINNING

One of the most interesting aspects of the pectolite and wollastonite structures is the way in which twinning can occur. Mention has already been made of the way in which pseudomonoclinic subcells are fitted together to give a triclinic structure. This is shown schematically in Fig. 8b. It is also possible to reverse the shift between successive pseudomonoclinic subcells to give the sequence shown in Fig. 8a, which corresponds to a twinned structure. If, however, the shift is reversed in each successive cell, the effect is as shown in Fig. 8c. This latter sequence was

TABLE 5. COORDINATION OF OXYGENS IN WOLLASTONITE AND PECTOLITE

Wollastonite			Pectolite		
Atoms		Interatomic Distances	Atoms		Interatomic Distances
O <sub>1</sub>	Si <sub>3</sub>	1.59 <sub>9</sub> Å	O <sub>1</sub>	Si <sub>3</sub>	1.59 Å
	Ca <sub>1</sub>	2.54 <sub>8</sub>		Ca <sub>1</sub>	2.33
	Ca <sub>2</sub>	2.31 <sub>6</sub>		Ca <sub>2</sub>	2.30
	Ca <sub>3</sub>	2.43 <sub>9</sub>			
O <sub>2</sub>	Si <sub>3</sub>	1.59 <sub>9</sub>	O <sub>2</sub>	Si <sub>3</sub>	1.68
	Ca <sub>1</sub>	2.43 <sub>7</sub>		Ca <sub>1</sub>	2.31
	Ca <sub>2</sub>	2.36 <sub>9</sub>		Ca <sub>2</sub>	2.25
	Ca <sub>3</sub>	2.34 <sub>9</sub>		Na	2.32
O <sub>3</sub>	Si <sub>1</sub>	1.61 <sub>8</sub>	O <sub>3</sub>	Si <sub>1</sub>	1.63
	Ca <sub>1</sub>	2.32 <sub>4</sub>		Ca <sub>1</sub>	2.35
	Ca <sub>3</sub>	2.42 <sub>9</sub>		Na	2.46
	Ca <sub>3</sub> '	2.33 <sub>5</sub>			
O <sub>4</sub>	Si <sub>2</sub>	1.61 <sub>7</sub>	O <sub>4</sub>	Si <sub>2</sub>	1.63
	Ca <sub>2</sub>	2.42 <sub>1</sub>		Ca <sub>2</sub>	2.32
	Ca <sub>3</sub>	2.44 <sub>1</sub>		Na	2.54
	Ca <sub>3</sub> '	2.34 <sub>9</sub>			
O <sub>5</sub>	Si <sub>1</sub>	1.57 <sub>2</sub>	O <sub>5</sub>	Si <sub>1</sub>	1.59
	Ca <sub>1</sub>	2.30 <sub>2</sub>		Ca <sub>1</sub>	2.35
	Ca <sub>2</sub>	2.50 <sub>1</sub>		Ca <sub>1</sub> '	2.44
				Ca <sub>2</sub>	2.51
O <sub>6</sub>	Si <sub>2</sub>	1.58 <sub>1</sub>	O <sub>6</sub>	Si <sub>2</sub>	1.61
	Ca <sub>1</sub>	2.27 <sub>2</sub>		Ca <sub>1</sub>	2.34
	Ca <sub>2</sub>	2.50 <sub>1</sub>		Ca <sub>2</sub>	2.35
				Ca <sub>2</sub> '	2.45
O <sub>7</sub>	Si <sub>1</sub>	1.65 <sub>9</sub>	O <sub>7</sub>	Si <sub>1</sub>	1.60
	Si <sub>3</sub>	1.66 <sub>5</sub>		Si <sub>3</sub>	1.68
	Ca <sub>1</sub>	2.41 <sub>2</sub>		Na	2.50
				Na'	
O <sub>8</sub>	Si <sub>2</sub>	1.65 <sub>0</sub>	O <sub>8</sub>	Si <sub>2</sub>	1.75
	Si <sub>3</sub>	1.67 <sub>3</sub>		Si <sub>3</sub>	1.63
	Ca <sub>2</sub>	2.40 <sub>6</sub>		Na	2.57
				Na'	
O <sub>9</sub>	Si <sub>1</sub>	1.64 <sub>7</sub>	O <sub>9</sub>	Si <sub>1</sub>	1.67
	Si <sub>2</sub>	1.63 <sub>7</sub>		Si <sub>2</sub>	1.58
	Ca <sub>3</sub>	2.64 <sub>2</sub>		O <sub>9</sub>	2.39

suggested by Ito (1950) for parawollastonite<sup>1</sup> which was originally distinguished from wollastonite by Peacock (1935a).

<sup>1</sup> The Commission on Mineral Data recommended at the meeting of the International Mineralogical Association in Washington, D. C., April 17-20, 1962, that wollastonite and parawollastonite be redesignated wollastonite-1T and wollastonite-2M, respectively.

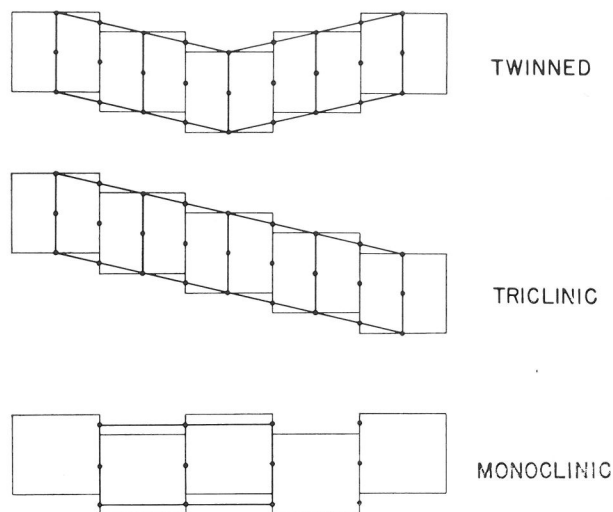


FIG. 8a (top), b (middle) and c (bottom). Three ways in which the pseudomonoclinic unit can be stacked on (100) to produce different overall diffraction effects.

Peacock (1935b) found that the twin law in pectolite is such that  $b$  is the twin axis with (100) as the composition plane. This is consistent with Fig. 8a since a rotation of  $180^\circ$  around  $b$  of one of the pseudomonoclinic units would be approximately equivalent to translating it by  $\frac{1}{2}b$  along a neighboring cell. This is not exactly true unless the cell is actually monoclinic, thus making  $\alpha$  (triclinic) equal to  $90^\circ$ . The authors have taken  $x$ -ray photographs of several twinned pectolite crystals from various localities and have found that the diffraction effects substantiate the above ideas. Fig. 9a represents part of the composite reciprocal lattice of twinned pectolite. When the members of the twin are present in equal amount, oscillating-crystal photographs around  $b$ , as well as  $c$ -axis precession photographs, show an apparent mirror plane normal to  $b$ . Close examination of the films reveals, however, that the registry of superposed spots is not perfect and that the registry is slightly different in different specimens.

If the pseudomonoclinic cells are joined as in Fig. 8c, the parawollastonite structure is formed having an overall monoclinic symmetry with a doubling of the cell along  $a$ . The symmetry of this monoclinic cell should be  $P2_1/a$  with extra centers of symmetry, not required by the space group,<sup>2</sup> being present. In an attempt to refine the structure of parawollastonite,

<sup>2</sup> Tolliday (1958) gives the systematic absences in the parawollastonite diffraction pattern as: for  $hkl$ ,  $2h+k=4n+2$ , and for  $0k0$  as  $k=2n+1$ .



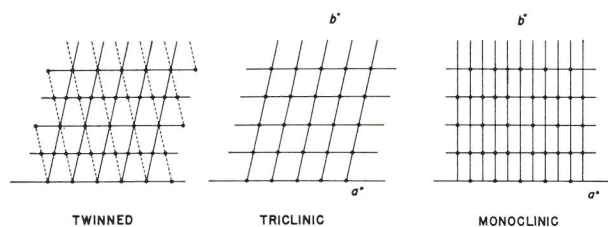


FIG. 9a (left), 9b (middle) and 9c (right). Reciprocal lattices corresponding to the geometries shown in Figs. 8a, 8b and 8c.

however, Tolliday (1958) found that the structure could not be refined using the centrosymmetric space group  $P2_1/a$  and that when the non-centrosymmetric space group  $P2_1$  was assumed, the refinement proceeded satisfactorily. Since no coordinates, structure factors or  $R$  factors were published, the validity of this assumption cannot be evaluated. This is an extremely important point in the crystal chemistry of  $\text{CaSiO}_3$  and one which should be resolved.

One of the interesting features of Figs. 9a, 9b and 9c is that the reciprocal-lattice levels with  $k$  even are identical (when  $\alpha = 90^\circ$ ) and that the differences between triclinic, monoclinic and twinned composite reciprocal lattices occur in only the odd levels. It is simpler for wollastonite than for pectolite to alternate to form the parawollastonite type because  $\alpha$  in wollastonite is  $90^\circ$  (within experimental error) and because the symmetry of the repeating unit in wollastonite is nearly monoclinic, *i.e.*, the  $\text{Si}_1$  and  $\text{Si}_2$  tetrahedra, as well as  $\text{Ca}_1$  and  $\text{Ca}_2$ , are symmetrically equivalent. The authors examined several wollastonite specimens from the Monte Somma, Italy, Csiklova, Romania, and Crestmore, California, localities before finding one which gave a parawollastonite diffraction pattern.<sup>3</sup> Continuous radiation streaks along reciprocal lattice rows parallel to  $a^*$  were observed in the  $b$ -axis Weissenberg photographs with  $k$  odd for the monoclinic as well as several triclinic specimens. This effect was interpreted by Jeffrey (1953) as a type of disorder due to the presence of regions of wollastonite and parawollastonite, but it could also be thought of as an irregular sequence of pseudomonoclinic subcells.

Peacock (1935a) was unable to find any twinned triclinic wollastonite in the material available to him. Spencer (1903), however, reported a twinned wollastonite crystal from Chiapas, Mexico, which

<sup>3</sup> The parawollastonite crystal (locality: Crestmore, California) was supplied by Professor A. Pabst from a specimen, 138-80, in the University of California collection.

would presumably give a diffraction pattern similar to our twinned pectolite. It is possible that some of the material reported in the literature as ordered parawollastonite is actually twinned wollastonite. One could be misled by diffraction photographs if the members of the twin were present in equal amounts.

One point which should be brought out here is that the way in which these pseudomonoclinic units fit together results in what Ito (1950) called "space-group twinning" and "structure twinning." The "space-group twinning" is seen in the joining of pseudomonoclinic cells to give an overall triclinic or a different monoclinic symmetry, while "structure twinning" corresponds to our twinned pectolite. Dornberger-Schiff (1956) has developed a general classification of order-disorder structures which includes the "space-group twinning" concept.

#### CONCLUSIONS

It has been established that wollastonite and pectolite have many structural similarities but yet must be classified as having different structures. Whether the pseudomonoclinic unit found in both wollastonite and pectolite will be of significance in an overall classification of the triclinic metasilicates will depend on the results of structural investigation of such minerals as bustamite, rhodonite and pyroxmangite. This pseudomonoclinic unit at present appears to be important in determining the relations between different modifications of a particular mineral in the wollastonite series. Its departure from actual monoclinic symmetry may also be a controlling factor in determining what forms of a particular triclinic metasilicate can occur. Certainly, any study of the stability relations of wollastonite and parawollastonite would have to be concerned with the details of the structures to a greater extent than is usual in such investigations, because the difference in energy between the two structures must be quite small.

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## DISCUSSION

HANS ADLER (Washington, D. C.): Why do you think the hydrogen bonding occurs within the chains rather than between the chains in pectolite?

AUTHORS' REPLY: The unusually short oxygen-oxygen distance of 2.44 Å is taken as evidence of the location of hydrogen between  $\text{O}_3$  and  $\text{O}_4$ . In recent work with new data, we found an anomaly in three-dimensional difference maps which would correspond to this hydrogen location.

J. D. H. DONNAY: (Baltimore, Md.): Does the wollastonite struc-

ture satisfactorily account for the cleavages parallel to the  $b$  axis? The cleavages were redetermined by Peacock.

AUTHORS' REPLY: Certainly the nature of the silicate chains does account for the fact that the good cleavages are parallel to the  $b$  axis in both wollastonite and pectolite. Peacock lists five cleavages for wollastonite, (100), (102), (001), (101), and (101), with the first three being perfect cleavages. While these can be qualitatively justified in an examination of the structure, no work has been done with regard to proving that these are the most likely cleavages.