

The Structure of Bolivian Crocidolite

By E. J. W. WHITTAKER

Research Department, Ferodo Limited, Chapel-en-le-Frith, Stockport, England

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Bolivian crocidolite, a fibrous amphibole, is shown to contain fibres approximating to single crystals. The structure, which is determined by standard methods leading to a Fourier projection on (001), is shown to be generally similar to that of tremolite. The more precise determination reveals certain departures from that structure however. The silicate chain is found to bend away from the plane of the metal ions in a lateral direction. The Si-O bond length when the oxygen atom is bonded to one silicon atom only is found to be less than that when the oxygen atom is bonded to two silicon atoms. The distribution of the magnesium and iron atoms among the available atomic sites is found to be non-uniform and is discussed with reference to the charge distribution.

Introduction

The structure of a typical amphibole mineral, tremolite, was determined by Warren (1930*a*). The structure, which was obtained by trial, was shown to be in qualitative agreement with the observed intensities of the X-ray reflexions, and it was subsequently shown (Warren, 1930*b*) that four other monoclinic amphiboles gave rotation photographs so similar to that of tremolite that they could be assumed to have a closely analogous structure. No redetermination of the finer details of the amphibole structure such as is possible with modern techniques has hitherto been made, however, and apart from measurements of unit-cell dimensions, the minor structural variations among the different members of the series have not been investigated.

Description of the material

Bolivian crocidolite is a fibrous asbestiform variety of amphibole found in mass fibre deposits in the Cochabamba province of Bolivia. The fibres are very silky, pale blue in colour, and occur in lengths up to 12 in. In some samples the fibres lie straight and parallel, and in others they are curiously matted and twisted. The Bolivian variety differs somewhat in colour and considerably in physical properties from South African crocidolite, the blue asbestos of commerce, but X-ray fibre photographs of the two minerals show a greater resemblance to one another than to fibre photographs of other amphibole varieties. It is thus confirmed that the mineralogical classification of the Bolivian material as crocidolite is correct, in spite of some considerable differences in properties from South African crocidolite.

There is, however, one feature of the X-ray fibre photograph of Bolivian crocidolite which is distinctive and has not so far been observed on the photographs of other fibrous amphiboles. Owing to the difficulty of ensuring parallel alignment of all the fibres in a specimen,

the spots on a fibre photograph are normally spread somewhat along the Debye-Scherrer arcs. On the photograph of Bolivian crocidolite the intensity is not continuous over these short arcs, which are dotted with very small, intense, sharply defined spots resembling those observed on Debye-Scherrer photographs of powders containing large crystallites. In view of the silky texture and great flexibility of the fibres a similar explanation in terms of large crystallites seemed unlikely, but was in fact shown to be correct. One of the thickest fibres visible under the microscope was mounted alone and found by X-ray diffraction to approximate to a single crystal, actually somewhat twinned. The existence of such fibres makes Bolivian crocidolite a particularly favourable variety for the structural investigation of a fibrous amphibole.

The fibres are in the form of very thin laths, the largest having a cross-section of about 0.1 mm. wide \times 0.01 mm. thick. The extinction directions in polarized light are straight with the fibre length on the extended face, and no other faces are discernible. It is found from the diffraction work that the extended face is (100) and that this is also the twinning plane.

Crocidolite is classified mineralogically as a fibrous variety of riebeckite, a mineral the axial ratios of which are given as $a : b : c = 0.5475 : 1 : 0.2295$, $\beta = 76^\circ 10'$ (Dana, 1932). This $b : c$ ratio is abnormal for the monoclinic amphiboles and is not in accordance with the present X-ray measurements. It therefore seems that either the classification of crocidolite, or the $b : c$ ratio of riebeckite, is in error.

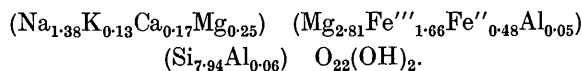
Chemical composition

There exist a number of published analyses of South African crocidolite, but none of the Bolivian variety. The material was therefore analysed with the following results:

	%
SiO ₂	56.1
Fe ₂ O ₃	15.6
FeO	4.06
Al ₂ O ₃	0.66
TiO ₂	Trace
MnO	Nil
CaO	1.11
MgO	14.5
Na ₂ O	5.05
K ₂ O	0.71
Loss at 105° C.	0.03
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	97.82
Water (theoretical 2 (OH)/mole)	2.21
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	100.03

The figures given are all means of repeated results in very good agreement, except in the case of the alkali metals. For these the highest result obtained was used, as there was reason to believe some lower values to be erroneous. Difficulty was experienced in obtaining a satisfactory water analysis, and the theoretical value for two hydroxyl groups per chemical molecule was used. No analysis was made for fluorine.

The ferrous iron present in the South African variety is thus found to be largely replaced in Bolivian crocidolite by magnesium. The formula corresponding to the above analysis is



Structure determination

A complete set of 15° oscillation photographs about the *c* axis was taken with cobalt radiation filtered through iron foil. Exposures of 6 hr. were required, using a crystal 0.1 mm. × 0.01 mm. in cross-section and several millimetres in length, with a ½ mm. diameter collimator. The intensities of the *hk0* reflexions were estimated visually with a calibration scale prepared by the use of a beam reflected from the crystal itself. A few photographs were taken about the other axes, but they were unsatisfactory on account of (a) the excessively anisotropic shape of the crystal; (b) fragmentation of the ends resulting from the fibrous cleavage when the crystal was cut down; and (c) the twinning. They were not used for intensity measurements.

The best unit-cell dimensions derived from the photographs were

$$a = 9.89, \quad b = 17.95, \quad c = 5.31 \text{ \AA.}, \quad \beta = 72\frac{1}{2}^\circ.$$

The choice of axes is the same as that used for tremolite by Warren (1930*a*). Absent reflexions are in accordance with the space-group symmetry given by Warren for tremolite, which for this choice of axes is in the orientation *I2/m*, and not in the standard orientation *C2/m* as given by Bragg (1937) with the same choice of axes.

In spite of the very small size of the crystal it was found that the absorption factor was appreciable. It was determined graphically for the *hk0* reflexions and found to be fairly constant at about 0.8 for most orientations of the crystal with respect to the incident

and diffracted rays, but to drop to a minimum of about 0.42 when either of these rays was parallel to the (100) face. An approximate relative absorption factor of 0.75 was therefore assumed for those reflexions for which the incident or diffracted ray made an angle of less than 10° with the (100) face. The polarization and Lorentz corrections were applied in the usual way. No account was taken of possible extinction effects. The values of $|F_{hk0}|$ on an arbitrary scale were then calculated from the corrected values of the intensities.

A set of structure factors F_{hk0} was calculated for an assumed structure having the atomic parameters given by Warren for tremolite and with random isomorphous replacement of the cations in accordance with the chemical composition. Semi-empirical temperature-corrected *f* values for use in silicates (Bragg & West, 1928) were used in the calculations, and appropriate weighted means were taken in calculating the contributions from the atomic sites assumed to be occupied randomly by several different atomic species. The results were in fair agreement with the observed values of $|F_{hk0}|$, and the calculated signs of the structure factors were used in evaluating a Fourier projection on (001). An artificial temperature factor, $\exp[-2 \sin^2 \theta]$, was employed in the Fourier synthesis. Appreciable changes in some of the atomic parameters were indicated by the projection. From the electron-density distribution it was also deduced that the three crystallographically non-equivalent positions available were not occupied entirely at random by the magnesium, aluminium and iron. The structure factors were recalculated in accordance with these findings, and after several further stages of refinement no further significant structural changes resulted from a recalculation. The structure factors of two planes, which calculated low, had signs sensitive to the exact co-ordinates of the silicon atoms. These were among the less accurately determinable of the atomic parameters, but as the observed structure factors for these two planes were small, the omission of the corresponding terms from the final Fourier synthesis did not have any significant effect.

The observed structure factors were scaled by the factor $\Sigma |F_{\text{calc.}}| \div \Sigma |F_{\text{obs.}}|$ in order to make them directly comparable with the calculated values and to enable the electron-density map to be put on an absolute scale. Table I shows the scaled values of $|F_{\text{obs.}}|$, and the values of $F_{\text{calc.}}$ obtained for the structure which was finally adopted. The factor of reliability $\Sigma ||F_{\text{calc.}}| - |F_{\text{obs.}}|| \div \Sigma |F_{\text{obs.}}|$ has the respective values 0.27, 0.23 or 0.19, according as the values of $|F_{\text{obs.}}|$ for those reflexions which are too weak to be observed are taken to be zero, half the minimum observable value, or are excluded, together with their calculated counterparts, from the summations.

The final Fourier projection on (001) is shown in Fig. 1 (a), together with a diagram of the atomic arrangement in Fig. 1 (b). It will be seen that the oxygen atoms O₁, O₂ and O₃ are imperfectly resolved from the adjacent

Table 1. Observed and calculated structure factors

hkl	$F_{\text{obs.}}$	$F_{\text{calc.}}$	hkl	$F_{\text{obs.}}$	$F_{\text{calc.}}$	hkl	$F_{\text{obs.}}$	$F_{\text{calc.}}$	hkl	$F_{\text{obs.}}$	$F_{\text{calc.}}$
020	56	- 54	280	18	- 4	4.14.0	0	- 16	730	67	- 63
040	146	-129	2.10.0	51	+ 47	4.16.0	49	- 43	750	0	+ 1
060	26	+ 10	2.12.0	44	- 48	4.18.0	0	+ 10	770	46	- 32
080	23	0	2.14.0	0	+ 18				790	92	- 79
0.10.0	112	+120	2.16.0	26	+ 32	510	94	- 80	7.11.0	166	+186
0.12.0	176	+246	2.18.0	0	+ 9	530	56	+ 49	7.13.0	41	+ 31
0.14.0	54	- 62				550	25	+ 7	7.15.0	0	- 63
0.16.0	26	- 2	310	196	+191	570	21	+ 20			
0.18.0	0	+ 10	330	102	-100	590	0	+ 3	800	104	+138
			350	44	- 42	5.11.0	36	- 16	820	0	- 22
110	77	+103	370	61	+ 57	5.13.0	69	- 66	840	0	- 3
130	0	- 1	390	0	- 6	5.15.0	54	+ 55	860	0	- 12
150	46	+ 34	3.11.0	130	+133	5.17.0	0	+ 5	880	44	- 20
170	28	- 16	3.13.0	0	+ 5				8.10.0	33	+ 46
190	69	- 50	3.15.0	0	- 25	600	158	+148	8.12.0	39	+ 54
1.11.0	163	+171	3.17.0	30	+ 17	620	38	- 43			
1.13.0	0	- 10	3.19.0	20	- 24	640	0	+ 15	910	35	+ 31
1.15.0	0	- 3				660	35	+ 13	930	48	+ 19
1.17.0	0	+ 13	400	23	+ 39	680	46	+ 41	950	13	+ 21
1.19.0	0	- 24	420	0	- 9	6.10.0	26	+ 33	970	51	+ 48
			440	0	- 11	6.12.0	0	+ 10	990	35	+ 25
200	23	- 22	460	0	+ 2	6.14.0	0	- 19			
220	33	- 23	480	122	-111	6.16.0	33	+ 42	10.0.0	79	+103
240	105	+ 94	4.10.0	74	+ 79				10.2.0	0	- 8
260	16	+ 19	4.12.0	64	+ 66	710	100	-116	10.4.0	15	- 10

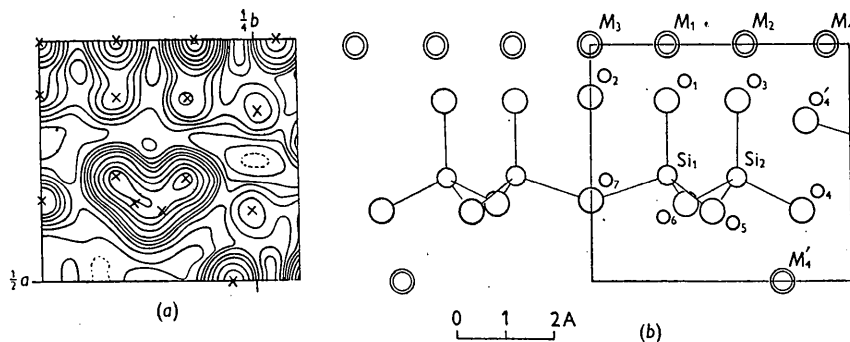


Fig. 1. (a) Electron-density projection along the c axis on (001). Contours at intervals of 1 e.A.^{-2} up to the 8th and then at intervals of 2 e.A.^{-2} . Zero contour dotted. (b) Arrangement of the atoms in the projection on (001) showing the complete double silicate chain.

metal atoms, and that the oxygen atoms O_5 and O_6 are not resolved from the silicon atoms. Resolution of O_1 , O_2 and O_3 was effected as follows. The structure factors corresponding to a hypothetical structure consisting only of the atoms M_1 , M_2 , M_3 and M_4 were calculated and multiplied by the artificial temperature factor. A Fourier synthesis was then performed, using these values but subject to the same conditions of termination of series as are imposed in the Fourier synthesis of the true structure from the observed structure factors. The resulting projected electron-density distribution was then subtracted point by point from the experimentally determined one, thereby giving a projection free from the effects of the metal atoms. This procedure was carried out at each stage of the refinement of the structure, and the final metal-free projection is shown in Fig. 2. The silicon atoms were resolved by assigning reasonable co-ordinates to the O_5 and O_6 atoms in accordance with (a) the observed electron-density distribution, (b) their co-ordinates in the tremolite structure, and (c) considerations of the structure of the silicate

chain discussed in a subsequent section. These atoms were then assumed to have circular symmetry in the projection, with a radial distribution of electron density

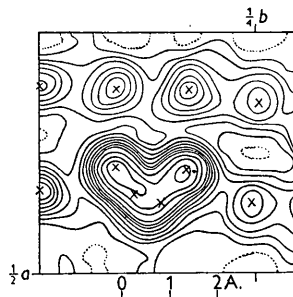


Fig. 2. Electron-density projection along the c axis on (001) after subtraction of the contribution of the metal ions. Contours at intervals of 1 e.A.^{-2} up to the 8th and then at intervals of 2 e.A.^{-2} . Zero contour dotted.

similar to that of O_7 along the line $y=0$; the atom O_7 being chosen on account of its satisfactory resolution and the fact that it is similarly situated to O_5 and O_6 .

The distribution of electron density due to O_5 and O_6 on these assumptions was then subtracted from the projection point by point in the vicinity of the silicon atoms. The resulting contours are shown in Fig. 3, and their shape, which is more sensitive to the assumed positions of O_5 and O_6 than are the derived silicon coordinates, provides some justification of the procedure.

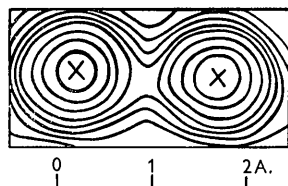


Fig. 3. Electron density in the neighbourhood of the silicon atoms in the projection of Fig. 2, after subtraction of the contribution of the oxygen atoms at O_5 and O_6 .

Derivation of the z -parameters

In view of the difficulty of obtaining satisfactory intensities for reflexions from planes of types other than $hk0$ the z parameters were not derived directly from diffraction data. It was possible, however, to derive fairly reliable values of the z co-ordinates of the atoms from the known x and y co-ordinates and the general principle that distances between similar atoms should be as regular as possible throughout the structure and in satisfactory agreement with generally accepted bond lengths and ionic radii. This is conveniently done by graphical construction on an orthogonal projection on (100).

The metal atoms all lie in special positions with known z co-ordinates. The oxygen atoms O_1 , O_2 and O_3 were therefore considered first and assigned z co-ordinates designed to make the co-ordination of the metal ions at M_1 , M_2 and M_3 as regular as possible. It was also possible to derive the z co-ordinates of the oxygen atoms O_5 , O_6 and O_7 relative to those of the silicon atoms without invoking any considerations other than that of regularity. Assignment of the silicon positions depends on the precise lengths of the Si_1-O_1 and Si_2-O_3 bonds, and it appeared necessary to compromise at this stage between unduly short bonds and unduly great distortion of the tetrahedral co-ordination of the silicon atoms. The position of the oxygen atom at O_4 could then be derived satisfactorily from consideration of its distances from Si_2 and from M_2 .

The complete set of atomic co-ordinates is given in Table 2.

Discussion of the structure

The metal ions

As has already been stated, it was found to be necessary to postulate a non-random distribution of the available Mg, Fe^{++} , Fe^{+++} and Al ions among the three positions M_1 , M_2 and M_3 —the positions occupied by magnesium in tremolite. The electron-density peak at M_2 is considerably higher than that at M_1 or at M_3 , and

the latter two positions have about equal electron densities. Comparison of the peak values with those obtained in Fourier syntheses of the metal atoms alone showed that the peak value is very nearly proportional to the total number of electrons corresponding to the weighted mean of the atoms occupying a given position. More elaborate electron counts were therefore unnecessary, and it was possible to calculate the probability of occupation of each site by (Mg + Al) and by Fe ions from the peak values of the electron density. The proportions of the ions occupying these positions on the average are found to be:

$$M_1 = M_3 = 0.72 \text{ Mg} + 0.28 \text{ Fe},$$

and

$$M_2 = 0.33 \text{ Mg} + 0.02 \text{ Al} + 0.65 \text{ Fe}.$$

The small amount of aluminium is placed preferentially in M_2 for reasons to be considered later; it cannot be distinguished from the magnesium on the basis of electron density.

Table 2. Atomic co-ordinates (A.)

	x	y	z
M_1	0	1.62	2.66
M_2	0	3.25	0
M_3	0	0	0
M_4	0	4.97	2.66
O_1	1.16	1.60	0.50
O_2	1.09	0	3.16
O_3	1.19	3.10	3.31
O_4	3.50	4.42	2.37
O_5	3.49	2.51	4.35
O_6	3.33	1.98	1.78
O_7	3.23	0	0.13
Si_1	2.77	1.58	0.43
Si_2	2.84	3.05	3.11

The position at M_4 is occupied by calcium in tremolite and is believed to be usually occupied by the monovalent cations and by the larger divalent cations such as calcium and manganese. In the present structure it is evident from the composition that M_4 must be occupied to a small extent by iron or magnesium ions, which cannot all be accommodated in the M_1 , M_2 and M_3 positions. The existence of amphiboles with formulae approaching $Mg_7Si_4O_{22}(OH)_2$ and $Fe_7Si_4O_{22}(OH)_2$ indicates that it is possible for both magnesium and iron to occupy this position. In the present case, however, the electron density at M_4 is about equal to, or even a little lower than, that corresponding to the occupation of the position on the average by

$$0.69 \text{ Na} + 0.065 \text{ K} + 0.085 \text{ Ca} + 0.125 \text{ Mg},$$

whereas if any iron occurred in this position the electron density would be higher. It therefore seems that magnesium enters the M_4 position in preference to iron. It is also evident from the formula that the number of cations present is less than 7, the number of sites M_1 , M_2 , M_3 and M_4 in the doubled asymmetric unit. The low electron density at M_4 therefore also shows that it is here that a proportion of the sites are left vacant, and that the M_1 , M_2 and M_3 positions are completely filled.

It was pointed out by Warren that there is room in the amphibole structure for a cation at the twofold position $(\frac{1}{2}, 0, \frac{1}{2})$, and that it is presumably at this point that the additional alkali ion is accommodated in the aluminous amphiboles, but in absence of a detailed investigation of such varieties it is not known at what composition occupation of this position may begin—it might well occur at the expense of complete occupation of the M_4 position under some circumstances. The Fourier synthesis shows, however, that the $(\frac{1}{2}, 0, \frac{1}{2})$ position is certainly unoccupied in the present structure. It should also be mentioned that this position at $(\frac{1}{2}, 0, \frac{1}{2})$ has its nearest atomic neighbours at a distance of about 2.8 Å., and these nearest neighbours are oxygen atoms. There is therefore room in this position for a small molecule such as water. Such a molecule could not enter or leave the structure as in a zeolite, but could conceivably be enclosed if suitable conditions obtained during crystallization. It is therefore theoretically possible for water to be accommodated in the amphibole structure, additional to that corresponding to the hydroxyl groups.

The distribution of charge in crocidolite among the positions M_1 , M_2 , M_3 and M_4 presents some interest. In the ideal tremolite structure there is a positive charge of two units on each of these positions, but in the present structure the average charge on M_4 is only 1.17 units. The electrostatic potential at M_2 due to the neighbouring ions will therefore be lower than that at M_1 and M_3 , and the probability of the ion being in a trivalent state will be greater at M_2 than at M_1 or M_3 . If all the iron at M_2 is assumed to be in the ferric state, and the small amount of aluminium is also assumed to be located there, then the average charge at M_2 is 2.67. The M_1 position will be similarly affected but to a lesser degree. The potential at the M_3 position would then be higher than in tremolite, and the probability of a trivalent ion in this position would be low. It is therefore suggested that the distribution of the iron atoms among the M_1 , M_2 and M_3 positions may be qualitatively explained as a compromise between entropy considerations which would tend to equalize the average distribution, and energy considerations which require a more unequal distribution of charge than this would permit. But when a sufficient proportion of the iron has been put in the M_2 position there is still sufficient iron in the M_1 position to satisfy the charge requirements without disturbing the equality of the average distribution of atoms at M_1 and M_3 .

The y co-ordinates are the only co-ordinates of the metal atoms M_1 , M_2 and M_4 which are not determined by the space group. Those of M_1 and M_4 are the same as in tremolite within the experimental error, but that of M_2 is about 0.2 Å. greater than in tremolite. This change is probably to be ascribed to the charge distribution discussed in the previous paragraph, which would be expected to produce a displacement of the equilibrium position of M_2 , in this sense, as compared with the more uniform charge distribution in tremolite.

The metal atoms M_1 , M_2 and M_3 are approximately octahedrally co-ordinated by oxygen atoms. The M -O distances are found to be

M_1 -O ₁	2.12 Å.	M_2 -O ₁	2.16 Å.	M_3 -O ₁	2.12 Å.
M_1 -O ₂	2.10 Å.	M_2 -O ₃	2.00 Å.	M_3 -O ₂	2.10 Å.
M_1 -O ₃	2.12 Å.	M_2 -O ₄	2.04 Å.		

The radius sums for magnesium, and ferric and ferrous iron are 2.10, 1.99 and 2.15 Å., respectively. The atom at M_4 is in a position of eightfold co-ordination, but two of the eight oxygen atoms are at greater distances than the other six. Four of the co-ordinating oxygen atoms are already bonded to two silicon atoms and, according to the electrostatic valency rules, should form no electrostatic bonds with the M_4 atom, apart from the effect of the small amount of replacement of silicon by aluminium. These four oxygen atoms all lie to one side of the M_4 position, and the corresponding interatomic distances are M_4 -O₅ = 2.48 Å. and M_4 -O₆ = 2.86 Å. The 'electrostatically bonded' oxygen atoms are at distances of 2.41 Å., which is slightly larger than the usual radius sum for the atoms concerned.

The silicate chains

The results of the present work show that the structure of crocidolite is built up from the double silicate chains shown by Warren to be characteristic of the amphiboles, but a number of differences in the details of the chain structure are revealed by the more exact analysis. It is possible, of course, that these details of the structure may vary in different amphibole varieties.

The Fourier projection (Fig. 1) shows directly that the oxygen atoms O₄, O₅, O₆ and O₇ are not coplanar as in Warren's structure. The double silicate chain is in fact slightly folded outwards, away from the metal ions, about its centre line, i.e. the line through the O₇ atoms indicated by AA' in Fig. 4 (c). Now the unit of structure in the amphiboles is essentially a narrow strip of the talc structure, which consists of a layer of metal ions arranged as in brucite and sandwiched between two silicate sheets extended indefinitely in two dimensions. Such silicate sheets are well known to have a natural repeat distance somewhat less than that of brucite (Pauling, 1930). In talc the layers are kept flat by the equal and opposite strain on the two sides, but it has been suggested that if the metal layer were attached to a silicate sheet at one side only a curvature of the layers would result, and this hypothesis has been used to interpret the structure of chrysotile and antigorite (Aruja, 1944, 1945). In the present structure the metal ions are coplanar, just as in talc, because of the similar environment on their two sides, but owing to their small extent laterally the chains are able to curve away from the plane of the metal atoms in the way described. Direct evidence is thus provided for the existence of a type of curvature closely related to that which has been postulated in the structure of chrysotile.

The silicate chain is shown in plan in Fig. 4(c). The relative arrangement of the silicon atoms and the O₅, O₆ and O₇ oxygen atoms may be deduced without any assumptions other than approximate equality of the various Si-O bonds, as described in the section on the derivation of the *z* parameters. The positions of O₁, O₃ and O₄ relative to the silicon atoms are less unambiguously determinable, and their positions as shown all depend on assuming a compromise between improbably short Si-O bonds and improbably large distortions of the O-Si-O valency angles. The Si-O bond lengths within the silicon oxygen ring, assumed approximately equal, are found to be 1.65–1.66 Å., whereas it appears impossible to assign lengths greater than 1.59–1.60 Å. to the peripheral bonds Si₁-O₁, Si₂-O₃ and Si₂-O₄ without assuming very large angle strains. The peripheral bonds are, therefore, almost certainly significantly shorter than those within the chain.

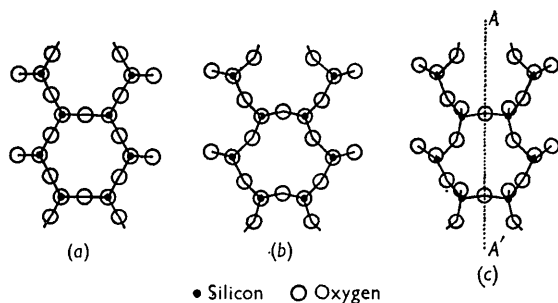


Fig. 4. Arrangement of the atoms of the double silicate chain in orthogonal projection on (100). (a) Regular arrangement commonly used as a diagrammatic representation of the amphibole structure. (b) Arrangement deduced for tremolite by Warren (1930a). (c) Arrangement deduced in the present work.

The shape of the silicon oxygen rings may be understood by comparison with Figs. 4(a, b). Fig. 4(a) shows the regular arrangement of the chain which is commonly used as a diagrammatic representation of the amphibole structure. A chain of this form could not be packed satisfactorily in the structure on account of an unduly short M_2 -O₄ distance which would result, but may be distorted to avoid this, without appreciable strain, to the form shown in Fig. 4(b), which is the form assumed by Warren. This distortion, however, results in a narrowing of the chain, which is undesirable on account of the greater lateral dimensions of the metal layer. The configuration which occurs (Fig. 4(c)) therefore seems to arise from a resistance to this lateral contraction, a resistance which is exhibited in the disposition of the Si₁-O₇-Si₁' atoms, and in a sharing of

the resulting angle strains at the two silicon atoms by appropriate adjustments of the O₅ and O₆ positions.

The angular displacements of the Si₁-O₁ and Si₂-O₃ bonds from the symmetrical positions, which must be assumed in order to avoid assigning unduly short lengths to these bonds, are in the same direction but of unequal magnitude. It seems likely that the valency-angle distortions at Si₁ and Si₂ will be equalized by appropriate displacements of O₅ and O₆ in the *x* direction, and *x* co-ordinates were assigned to these atoms in accordance with this consideration. The electron-density distribution (Fig. 1) suggests that the projected distance between Si₁ and O₆ is less than that between Si₂ and O₅, and therefore provides some experimental confirmation of the conclusions resulting from the assignment of *z* co-ordinates.

The oxygen valency angles which occur in the structure that has been deduced are

$$\begin{aligned} \angle \text{Si}_1\text{-O}_5\text{-Si}_2 &= 130^\circ, & \angle \text{Si}_1\text{-O}_5\text{-Si}_2 &= 136^\circ, \\ \angle \text{Si}_1\text{-O}_2\text{-Si}_1' &= 147^\circ. \end{aligned}$$

The silicon valency angles not involving bonds to O₁ and O₃ vary between 102° and 115°. Those involving bonds to these two atoms vary between 99° and 123°. The distance of closest approach between oxygen atoms in neighbouring chains is 2.97 Å. This value is rather low, but it could only be increased to a small extent even at the expense of postulating very improbable bond lengths in other positions. The corresponding distance in Warren's structure is only 2.78 Å. The larger value in the present structure results from the appreciably closer approach of the silicate chains to the plane of the metal ions that is shown directly in the Fourier projection.

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