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The Crystal Structure of an Actinolite

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The x and y atomic coordinates of an actinolite have been determined by Fourier synthesis, and the z coordinates deduced from packing considerations. Structural detail is seen to be very similar to that in crocidolite, reproducing features in which the latter's structure differs from the approximate structure described by Warren for tremolite. The Si_4O_{11} chains are nearer the plane of the Y metal ions than in the 'Warren' case; they are slightly bent about their central c axis away from this plane and are in other respects more distorted. There is no segregation of Fe ions at any one of the Y sites and it appears most likely that of the excess Y ions magnesium rather than iron enters the X position. The A site at $(\frac{1}{2}, 0, \frac{1}{2})$ is certainly not occupied by a water molecule nor by any ion. The approximate nature of the z coordinates derived does not allow a conclusive description of the environment of the X ions, but average Y–O and Si–O distances and certain other features are nevertheless deemed noteworthy.

Using a re-determined estimation of water content and a more direct method of formula derivation it is shown that extra hydrogen is present in the structure, compensated electrically by a deficit of positive charge elsewhere rather than by additional oxygen ions. It is suggested that $(OH)^-$ ions may be replacing some O^{--} in the Si_4O_{11} chains.

Introduction

The first crystal-structure analysis of an amphibole mineral was undertaken on tremolite (Warren, 1930*a*), and following this it was shown (Warren, 1930*b*) that several other members of the amphibole group gave X-ray diffraction patterns similar to that obtained in the previous investigation.

Warren showed that a somewhat idealized structure (Fig. 1(*a*)) gave fairly close agreement between calculated and observed intensities. Tremolite itself has the formula $Ca_2Mg_5Si_8O_{22}(OH)_2$, and most amphiboles are represented by the general formula $X_{2-3}Y_5Z_8O_{22}(OH, F)_2$, where X is Na, K or Ca; Y is Mg, Fe'', Fe''', Al, Mn, Ti etc., and Z is Si or Al.* The extent of such replacements is in some cases limited, and they are in any case regulated by conditions of ionic size and electrostatic neutrality. The X, Y and Z positions and also the A site at $(\frac{1}{2}, 0, \frac{1}{2})$, which is sometimes occupied by an additional X cation, are indicated in Fig. 1(*a*).

Today the basic structures of the principal mineral groups are well known, and attention is being given to points of detail which are nevertheless providing information of great interest and value to the mineralogist. The amphiboles, however, have been neglected in this respect although they possess many general features and relationships which are not completely understood. Knowledge of structural detail would no doubt help in the understanding and prediction of the extents and limits of solid solution between the various amphibole sub-groups, e.g. cummingtonite–actinolite, tremolite–riebeckite. Some examples of questions of detail in amphibole structures, which it is felt would be worthy of investigation, are:

1. To what extent are the atomic coordinates of other members of the group different from those of tremolite?
2. How do the atomic coordinates in tremolite itself differ from those of Warren's 'approximate structure'?
3. When several different Y-type ions are present, do they occupy the three different Y sites at random?
4. Under what conditions can Y ions occupy X sites, and to what extent, if at all, can X ions occupy Y sites?
5. Is the 'vacant space' at $(\frac{1}{2}, 0, \frac{1}{2})$ (in future referred to as the A site) occupied only after all others are filled? Can it be occupied by cations of other than X type, or by the anions (OH) and (F), or even by a water molecule?
6. How are physical properties, including that of fibrosity, related to chemical composition and structural detail?
7. What is the explanation of the high percentage of H_2O^+ found in some amphibole analyses (Hallimond, 1943; Buddington & Leonard, 1953; Frankel, 1953)?

Preliminary discussion

The answers to questions such as these would no doubt be obtained by subjecting very many different amphi-

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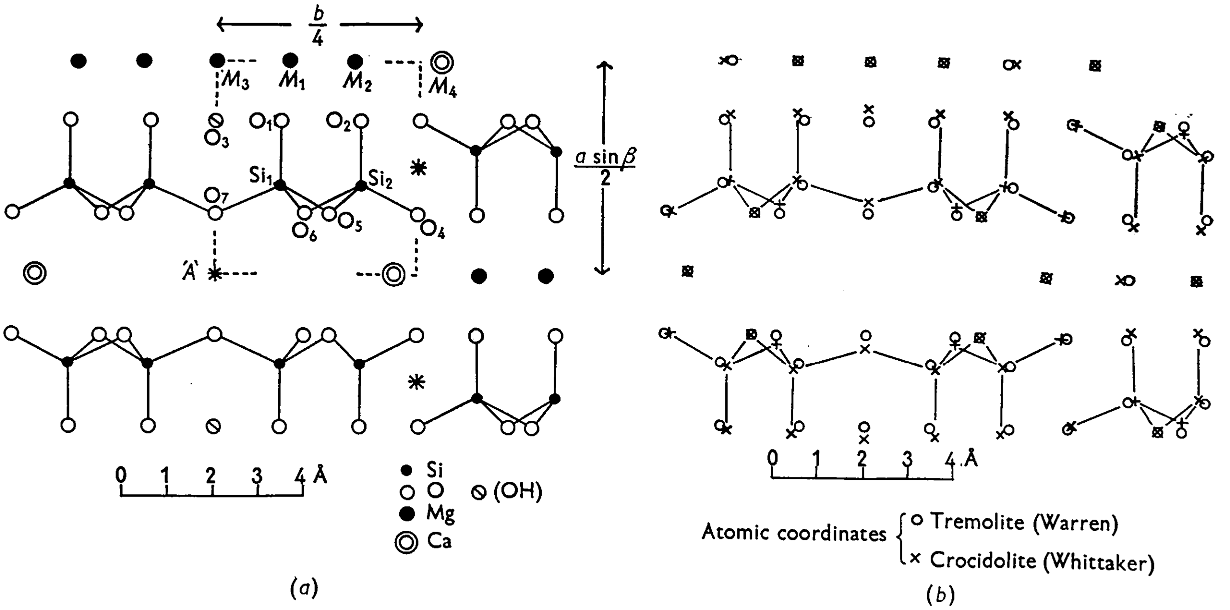
* The notation adopted here is that used by Warren (1930*a*, *b*) and many other authors, and not that adopted by Berman (1937), where X and Y have a different significance and W = Ca, Na, K. The latter notation is used frequently in American publications.



(a) (b)

Fig. 1. (a) The c-axis projection of the tremolite structure. Coordinates given by Warren (1930a). (b) Comparison between coordinates found for crocidolite (Whittaker) and those from Warren's approximate structure determination.

boles to detailed two- and/or three-dimensional structural analysis, but it is felt that the examination of comparatively few well chosen examples may yield some important guiding principles. Since 1930 only one investigation of this sort has been made,* namely that by Whittaker (1949) on a fibrous Bolivian crocidolite. This appears to be a strategic example as far as the question of fibrosity is concerned since Whittaker was able to split the fibre down and work with one approaching closely to a single crystal; but his results are likely to be most valuable only when other structures are available as a basis for comparison. Chemical analysis gave the formula for crocidolite as

$$\underbrace{(Ca_{0\cdot17}Na_{1\cdot38}K_{0\cdot13}Mg_{0\cdot25})}_{1\cdot93}\ \underbrace{(Mg_{2\cdot81}Fe'''_{1\cdot66}Fe''_{0\cdot48}Al_{0\cdot05})}_{5\cdot00}$$

$$\underbrace{(Si_{7\cdot94}Al_{0\cdot06})}_{8\cdot00}O_{22}(OH)_2\ ,$$

the principal differences from tremolite being a high replacement of calcium by sodium and of magnesium by iron, particularly ferric iron. From an electron-density map of the c axis projection (see cell dimensions, Table 1), the x and y coordinates of all except two oxygen atoms were determined. The z coordinates were deduced assuming maximum regularity of environment and minimizing as far as possible distortion from normal bond lengths and angles.

Table 1. *Cell dimensions*

	Tremolite	Crocidolite	Actinolite
a (Å)	9·78	9·89	9·89
b (Å)	17·80	17·95	18·14
c (Å)	5·26	5·31	5·31
β	106° 2′	107° 30′	105° 48′
a sin β (Å)	9·40	9·42	9·52

Table 2. *Atomic coordinates in tremolite (Warren), crocidolite (Whittaker) and actinolite*

	x/a			y/b		
	T	C	A	T	C	A
O_1	0·14	0·117	0·117	0·08	0·089	0·087
O_1	0·14	0·120	0·120	0·18	0·173	0·176
O_3	0·14	0·110	0·112	0·00	0·000	0·000
O_4	0·36	0·354	0·362	0·25	0·246	0·249
O_5	0·36	0·353	0·350	0·14	0·140	0·137
O_6	0·36	0·337	0·340	0·11	0·110	0·114
O_7	0·36	0·326	0·335	0·00	0·000	0·000
M_1	0·00	0·000	0·000	0·09	0·090	0·088
M_2	0·00	0·000	0·000	0·17	0·181	0·178
M_3	0·00	0·000	0·000	0·00	0·000	0·000
M_4	0·00	0·000	0·000	0·28	0·277	0·277
Si_1	0·29	0·280	0·280	0·08	0·088	0·086
Si_2	0·29	0·287	0·288	0·18	0·170	0·172

The electron-density map showed that the Y sites are not uniformly occupied but that the site M_2 (Whittaker's notation) is preferentially occupied by iron. It was also stated by Whittaker that of the excess Y ions, magnesium rather than iron entered the X positions. Other features of Whittaker's results which it is well to recall here concern the atomic coordinates, which are compared with those of Warren in Table 2 and Fig. 1(b). In crocidolite O_1, O_2, O_3 approach closer to the plane of Y ions and at the same time there is a bending of the double chain about its central c axis away from this plane. The only significant difference

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* A preliminary note (Garrod & Rann, 1952) reported that structural analysis of an amosite was in progress.

in coordinate of an X or Y ion lies in that of M_2, which is appreciably closer to M_4. These and other details are discussed more fully by Whittaker and also in a later part of this paper. The question arises as to whether they are to be interpreted as unusual divergences from a norm, or whether they are in fact possessed by other amphiboles (tremolite itself not excepted).

The amphibole whose structure analysis is to be described here is an actinolite, three features of which are particularly noteworthy. First, that the variety occurs in small thin laths which very readily split into finer ones; it may therefore be regarded as approaching the fibrous condition although not as closely as does crocidolite. Secondly, the chemical analysis shows that, like crocidolite, it has more than five ions of the type which normally occupy Y sites (see Table 5, column (4)), and thirdly that an unusually high percentage of H_2O^+ appears in its chemical analysis, the significance of which had not been conclusively explained.

The mineral was described by Hutton (1940) and the results of chemical analysis are reproduced in Table 5.* The figure for H_2O^+ in an amphibole does not generally exceed 2% but in this case it is as high as 4·05%. Two possible explanations were considered by Hutton. One, that the water figure was in error, part of it referring to strongly adsorbed extra-structural water which had not been driven off at 105° C. The other, that the structure may have housed an extra (OH) ion or a water molecule in the otherwise vacant A site. These alternatives, and another, are discussed later.

X-ray investigation

Cell dimensions of the actinolite were obtained from single-crystal photographs and are listed in Table 1 along with those of tremolite and of crocidolite. The order of increasing cell volume, tremolite–crocidolite–actinolite, is somewhat surprising since the atomic replacements involved would certainly not place tremolite as the smallest of the three. The apparent anomaly is not easily explained without knowledge of structural detail in all three minerals, but it does suggest that some significent differences in atomic configuration may be involved.

Zero-layer Weissenberg photographs, using nickel-filtered Cu radiation, gave $hk0$ reflexions up to θ values limited by the Cu wavelength (absent reflexions were consistent with the space group $I2/m$). The intensities, which were measured by visual comparison with a prepared scale, were empirically corrected for absorption by comparing intensities on different parts of the film, and Lorentz and polarization factors were applied. A set of structure factors was calculated assuming random occupation of the Y sites by the available cations, using the Bragg & West (1928) atomic f values and the atomic coordinates given by Warren for tremolite. Another set was calculated using the coordinates found for crocidolite, and when the observed values had been suitably scaled these were seen to agree more closely with the latter set. The first electron-density map obtained, using an artificial temperature factor, showed relative peak heights roughly compatible with the chemical composition of the crystal, although M_1 appeared slightly lower than M_2 and M_3, which were equal, and it persisted in this manner after later refinements. F_o and (F_o-F_c) syntheses were used to indicate changes in atomic coordinates until these no longer produced appreciable improvement in the R index, the final value of which was left at 17%. (Observed and calculated structure factors are listed in Table 6.) The difference synthesis also indicated that some alteration in certain atomic f curves would improve structure-factor agreement, in that X and Y ions have greater thermal motion than the others. The final electron-density map is shown in Fig. 2, and the x and y coordinates of each atom are included in Table 2. The standard deviation in electron density, estimated from the 'difference' syntheses, is approximately 0·7 e.Å^{-2}, and the standard deviation in coordinates is 0·015 Å for the X and Y ions and 0·04 Å for the oxygens. The accuracy of the silicon coordinates is difficult to estimate since they are somewhat affected by the poor resolution among the four atoms Si_1, Si_2, O_5 and O_6, but it probably lies between the two values given above.

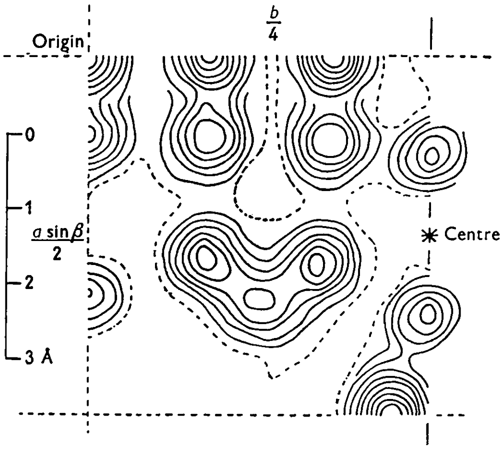

Fig. 2. Actinolite: electron-density map of c projection. Contours at intervals of 1 e.Å^{-2} for $O_1O_2O_3O_4O_7$, and at 2 e.Å^{-2} for other atoms. Lowest contour, at 2 e.Å^{-2}, is indicated by broken line.

Discussion of projection

If the height of a peak is taken as proportional to the weighted mean electron content of atoms occupying a particular site, it should be possible to determine the manner in which the various atoms are distributed.

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* A specimen of actinolite schist No. 2662 (Hutton, 1940) was kindly provided by the Department of Mineralogy and Petrology, Cambridge, by courtesy of Prof. C. E. Tilley.

Unlike the case of crocidolite there is no significant difference of height among the three Y peaks, which indicates that there is no tendency for the Fe ions to segregate.

The number of X and Y ions is known to be less than 7 and the number of Y type is greater than 5. In Table 3 four possible distributions of ions between X and Y sites are considered and the estimated ratio of X to Y peak height is calculated for each. The table explores the possibilities that either magnesium or iron accompanies calcium in the X position, and that either the X or the Y site is deficient. The ratio of X to average Y peak height observed on the final electron-density map is 1·13:1. Clearly many simplifying assumptions have been made, so that it can only be said that (1) is the most likely of the four simple alternatives, perhaps only (4) being ruled out completely.

Table 3. *Actinolite: relative heights of X and Y peaks*

	In Y site	In X site	Theoretical estimate of peak ratio X/Y
1	$\mathrm{Mg}_{3\cdot58}\mathrm{Fe, etc.}_{1\cdot42}$	$\mathrm{Ca, etc.}_{1\cdot62}\mathrm{Mg}_{0\cdot20}$	1·11
2	$\mathrm{Mg}_{3\cdot40}\mathrm{Fe, etc.}_{1\cdot42}$	$\mathrm{Ca, etc.}_{1\cdot62}\mathrm{Mg}_{0\cdot38}$	1·20
3	$\mathrm{Mg}_{3\cdot78}\mathrm{Fe, etc.}_{1\cdot22}$	$\mathrm{Ca, etc.}_{1\cdot62}\mathrm{Fe}_{0\cdot20}$	1·25
4	$\mathrm{Mg}_{3\cdot78}\mathrm{Fe, etc.}_{1\cdot04}$	$\mathrm{Ca, etc.}_{1\cdot62}\mathrm{Fe}_{0\cdot38}$	1·45

Whilst the electron-density map is somewhat inconclusive as far as this point is concerned it certainly does show that the A site is not occupied by a water molecule, nor by anything else.

Table 2 shows how the x and y coordinates of actinolite compare with those of crocidolite.* It is clear that the two structures are very similar, most of the differences between Whittaker's coordinates and those of Warren being reproduced in the present case. In most cases where a coordinate differs it does so in the sense which brings it slightly closer to the Warren value. The result is again a closer approach of the double chains to the plane of Y ions and a bending of the SiO_4 bonds about their central longitudinal axis away from this plane. As Whittaker has commented, the bending of the tetrahedral chain appears similar to that encountered in silicate polar sheet structures, occurring for the same reason, i.e. that the repeat distances in a free tetrahedral and a free octahedral layer or strip do not match. Since the octahedral section here lies between two tetrahedral ones, no bending of the sandwich as a whole can occur, but, unlike in the micas, the 'sandwich' is here not continuous and so the tetrahedral strips are free to bend away from the octahedral cations between them. If no other feature has overriding influence, this effect should occur also in tremolite to approximately the same extent, and in fact the only amphiboles in which it ought to be less marked are those with high aluminium and/or ferric iron content.

In crocidolite M_2 is closer to M_4 (by about 0·25 Å) than in the Warren structure, and it was suggested that this is a result of charge distribution, M_1 carrying less and M_2 more than the normal positive charge. In the present case there can be little departure from the ideal charge distribution yet M_2 remains as much as 0·2 Å nearer to M_4, so that it seems doubtful that the above explanation is valid. It may be that the approximate coordinate of M_2 given by Warren is itself too small by about 0·2 Å. One would expect that the distances M_1-M_2 and M_1-M_3 should be approximately equal, and in fact they are so in both crocidolite and actinolite.

The z coordinates

These were deduced in a manner similar to that described by Whittaker (1949) and are listed in Table 4.

Table 4. *z coordinates*

	Actinolite	Crocidolite	Tremolite
	z/c	z/c	z/c
O_1	0·10	0·09	0·10
O_2	0·60	0·62	0·60
O_3	0·60	0·60	0·60
O_4	0·43	0·45	0·40
O_5	0·79	0·82	0·75
O_6	0·30	0·34	0·25
O_7	−0·01	0·02	−0·10
M_1	0·50	0·50	0·50
M_2	0	0	0
M_3	0	0	0
M_4	0·50	0·50	0·50
Si_1	0·06	0·08	0·01
Si_2	0·55	0·59	0·51

The X and Y ions are fixed through lying in crystallographically special positions, whilst the possible configurations of the 'backbone' Si_1–O_5–Si_2–O_6–Si_1 etc. are restricted by the known x and y coordinates and the c repeat distance. The additional assumption of equal Si–O distances fixes its configuration completely. This chain of atoms can then be translated as a whole in the [001] direction, and it has been positioned to make O_5 and O_6 equidistant from M_4. The sites of O_1 and O_2 were deduced by compromising between two considerations: (a) regularity of environment with respect to M_1, M_2 and M_3, and (b) near-normal values for the resulting Si–O bond lengths and bond angles in the Si_4O_{11} chain. For O_3 only the first, and for O_7 only the second consideration was relevant. Finally, when O_4 had been placed so that M_4–O_4 = M_4–O_2 it was seen that the distance Si–O and the associated bond angles were close to accepted values and also that O_4 lay approximately equidistant from the O_2 atoms above and below it in the neighbouring chain.

Before proceeding to discuss interatomic distances it would be well to consider in which respects the deriva-

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* Nomenclature of atoms is the same as Whittaker's except that labels O_2 and O_3 have been interchanged so as to achieve correspondence between Si_2, O_2 and M_2.

tion of z coordinates described above differs from that employed by Whittaker which led to a slightly different set. Some minor differences doubtless ensue through the small differences in x and y coordinates. Others occur through a different location of the Si–O–Si–O– 'backbone' with respect to the fixed cations. In the present case the main criterion used to locate its position was the equality of distances M_4–O_5, M_4–O_6. In the crocidolite investigation it was to make bond lengths Si_1–O_1 and Si_2–O_2 and the associated angles as near as possible to accepted values. This gave a 'backbone' position with coordinates approximately 0·16 Å greater, and resulted in a different environment for M_4. In both cases M_4 has eight neighbouring oxygen atoms: in the former case four at 2·3 Å and four at 2·7 Å; in the latter case four at 2·4 Å, two at 2·5 Å and two at 2·9 Å. Since both types of coordination are known to occur for calcium ions it does not seem possible to decide which is correct in actinolite without resorting to three-dimensional or generalized projection X-ray techniques. It does seem likely, however, that the alternatives of approximately eightfold or sixfold coordination for ions in the X position are related to the different β angles observed in the tremolite–common hornblende series on the one hand (106°) and those of the cummingtonite series on the other ($109\frac{1}{2}$°). The octahedral 'brucite-like' strip may be regarded as common to all amphiboles, with comparatively minor variations occurring through replacements such as (Mg, Fe″, Fe‴, Al), thus fixing the Si_4O_{11} chain. The position adopted by the X ions will then determine the β angle of the cell.

Interatomic distances

A diagram showing approximate interatomic distances is shown in Fig. 3. Whilst no great significance may be attached to the value of individual bond lengths, certain qualitative features and some average values are nevertheless noteworthy. For example, any errors in the coordinates of O_5 and O_6, or in the z coordinates of Si atoms, can have only a minor effect on the average Si–O distance, which is seen to be 1·67 Å. The distance between silicon and the peripheral oxygen atoms appears to be shorter (approximately 1·60 Å), and the latter value is in accordance with the majority of Si–O distances found in other minerals. However, a lengthening of the bond where oxygen is linked to two silicon atoms was also found in crocidolite by Whittaker, and a similar feature was noted in the Si_2O_7 groupings of tilleyite (Smith, 1953).

The average distances from Y-type ions to oxygens are:

$$M_1\text{–O} = 2{\cdot}12\ \text{Å},\quad M_2\text{–O} = 2{\cdot}11\ \text{Å},\quad M_3\text{–O} = 2{\cdot}11\ \text{Å}.$$

M_4 is coordinated by eight oxygens; four (which are associated with one silicon each) are at an average distance of 2·33 Å, and the average distance of the other four (attached to two silicons each) is 2·7 Å. Distances for Y–O and X–O, calculated on the basis of ionic radii given by Ahrens (1952), are 2·07 and 2·34 Å respectively. (Goldschmidt radii give 2·11 and 2·36 Å.)

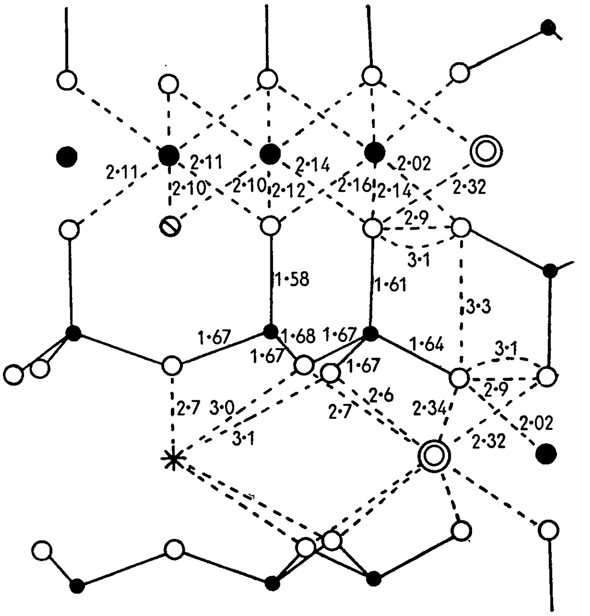

Fig. 3. Actinolite: diagram showing interatomic distances and coordination of cations. Key to atoms as for Fig. 1.

Of the twelve O–Si–O bond angles eight lie between 105° and 115°, two are approximately 103°, and two 117°.

Si–O–Si angles are:

$$Si_1\text{–}O_5\text{–}Si_2 = 132°,$$
$$Si_1\text{–}O_6\text{–}Si_2 = 135°,$$
$$Si_1\text{–}O_7\text{–}Si_1 = 138°.$$

Oxygens of neighbouring chains are 'in contact' at several places as shown by the following distances:

$$\left.\begin{matrix}O_5\text{–}O_6'\\O_6\text{–}O_5'\end{matrix}\right\} = 3{\cdot}0\ \text{Å},\quad \left.\begin{matrix}O_4\text{–}O_4'\\O_7\text{–}O_7'\end{matrix}\right\} = 3{\cdot}3\ \text{Å},\quad \begin{matrix}O_4\text{–}O_2'(a) = 2{\cdot}9\ \text{Å},\\O_4\text{–}O_2'(b) = 3{\cdot}1\ \text{Å}.\end{matrix}$$

$O_2'(a)$ and $O_2'(b)$ are in one Si_4O_{11} chain but are separated by one cell translation parallel to c.

The environment of the A position, like that of X, is affected by the alternative locations of the Si–O–Si 'backbone', but to a lesser extent since the distances from A to O_5 and O_6 in the plane of the projection are greater. With the coordinates assumed here the nearest approach to A is by O_7 at 2·7 Å, O_5 and O_6 lying at 3·1 and 3·0 Å respectively. In Whittaker's structure the nearest approaches are by O_7 at 2·8 Å and by O_6 at 2·9 Å. In either case these distances are surprisingly large if the A site is to accommodate a cation other than potassium, unless the binding forces are more nearly of the van der Waals type than ionic. It may be, of course, that in amphiboles where A is occupied the configuration of the Si_4O_{11} band and environment of A is somewhat different. It is hoped to make this the subject of a future investigation. The possibility of a water molecule sometimes occupying this site, perhaps involved in the formation of hydrogen bonds to O_7, cannot be dismissed.

Concerning extra water in chemical analysis

The chemical analysis (Hutton, 1943) is given in Table 5, together with formulae calculated by different methods. Columns (1) and (2) were given by Hutton and were derived in the usual manner on the basis of 24 (O, OH, F) per formula unit. The first uses the figure 4·05% for H_2O^+ whilst the second assumes that, of this, only 2% is really structural water. Hutton remarked on the poor agreement of column (1) with the ideal amphibole formula and suggested that the better agreement of column (2) supports the idea that the excess water is merely adsorbed owing to the finely divided state of the mineral.

Column (3) has now been calculated, using all of the H_2O^+, and on the basis of 25 (O, OH, F) per formula unit, in order to test the possibility that an extra H_2O molecule fills the A position. It is seen that this gives no less good agreement with the ideal formula than does column (2). Moreover, as is shown later, neither of the assumptions for column (2) and (3) is correct!

If cell dimensions and density of a mineral are known its formula may be derived from the analysis with no assumption as to the total (O, OH, F) (Hey, 1939). Before using this method, however, it was felt that a redetermination of the water figure was desirable, and this was kindly carried out by G. D. Nicholls in this Department, first on an air-dried sample using a silica Penfield tube. After the water had been determined it was ascertained that the sample had undergone fusion to a glass. A second sample, after air drying, was kept successively at 100, 200, 300 and 400° C. for several hours and no appreciable loss of weight was observed at any stage. 0·44 g. of this were used for an H_2O^+ determination, and the results for the two samples were 3·03 and 3·06% respectively.

The density of the mineral (3·07 g.cm.$^{-3}$) was determined by flotation in a mixture of bromoform and methylene iodide, and was used to determine the 'molecular weight' of a formula unit. With this, and the redetermined water content, the formula of column (4) was obtained. This shows (*a*) that the total (O, OH, F) is 24 (not 25), i.e. that there is *no* excess oxygen in the structure, (*b*) that there *is* excess hydrogen in the structure, and (*c*) that there is a deficiency below 15 for the number of $(X+Y+Z)$ ions.

Table 5. *Actinolite: derivation of formula from analysis**

	Chemical analysis	Ions	(1)	(2)		(3)		(4)	
SiO_2	50·21	Si	6·99	7·28		7·28		7·13	
Al_2O_3	4·55	Al	0·75	0·78	0·72 0·06	0·78	0·72 0·06	0·76	
TiO_2	1·20	Ti	0·13	0·13		0·13		0·13	0·11 0·02
Fe_2O_3	2·77	Fe'''	0·29	0·30		0·30		0·30	
Cr_2O_3	0·10	Cr	0·01	0·01		0·01		0·01	
NiO	n. d.	Ni	—	—		—		—	
MgO	17·85	Mg	3·70	3·85		3·85		3·78	
FeO	9·03	Fe	1·05	1·09		1·10		1·07	
MnO	0·19	Mn	0·02	0·02		0·02		0·02	
Na_2O	0·40	Na	0·11	0·11		0·11		0·11	
CaO	9·69	Ca	1·45	1·50		1·51		1·47	
K_2O	0·23	K	0·04	0·04		0·04		0·04	
H_2O^+	4·05	H	3·76	1·93		3·92		2·84	
H_2O^-	0·02								
F_2	0·15	F	0·07	0·07		0·07		0·07	
Total	100·44								
$-O{=}F_2$	0·06								
	100·38								

Structural formulae

(1) $\underbrace{X_{1\cdot60}Y_{5\cdot07}}_{6\cdot67}Z_{7\cdot87}O_{22\cdot0}(OH, F)_{2\cdot0}H_{1\cdot83}$ (on basis of 24(O, F)).

(2) $\underbrace{X_{1\cdot65}Y_{5\cdot46}}_{7\cdot11}Z_{8\cdot00}O_{22\cdot0}(OH, F)_{2\cdot0}$ (on basis of 24(O, F), and only 2% H_2O^+).

(3) $\underbrace{X_{1\cdot66}Y_{5\cdot47}}_{7\cdot12}Z_{8\cdot00}O_{22\cdot0}(OH, F)_{2\cdot0}H_2O$ (on basis of 25(O, F)).

(4) $\underbrace{X_{1\cdot62}Y_{5\cdot20}}_{6\cdot82}Z_{8\cdot00}O_{22\cdot0}(OH, F)_{1\cdot99}H_{0\cdot92}$ (on basis of experimentally determined 'molecular weight', and redetermined $(H_2O)^+$ value (3·05%)).

* Analysis by Hutton (1940, Table 4, p. 15).

Table 6. *Observed and calculated hk*0 *structure factors*

hk	$\|F_o\|$	F_c	*hk*	$\|F_o\|$	F_c	*hk*	$\|F_o\|$	F_c
02	63	−60	3,11	107	119	71	89	102
04	104	−92	3,13	0	16	73	43	−49
06	0	−10	3,15	0	−11	75	5	− 6
08	22	− 7	3,17	27	16	77	32	−32
0,10	96	103	3,19	38	−22	79	84	−93
0,12	227	232	3,21	12	10	7,11	135	168
0,14	22	−21				7,13	42	38
0,16	13	−16	40	33	29	7,15	46	−42
0,18	17	11	42	16	−11	7,17	16	8
0,20	67	−66	44	9	− 1	7,19	28	−43
0,22	82	87	46	14	−13			
			48	95	−108	80	119	138
11	85	88	4,10	59	56	82	26	−20
13	38	31	4,12	56	52	84	24	13
15	9	11	4,14	19	13	86	31	−32
17	4	− 1	4,16	60	−54	88	11	− 6
19	76	−59	4,18	20	20	8,10	35	34
1,11	177	150	4,20	58	−68	8,12	45	56
1,13	11	1	4,22	42	48	8,14	0	14
1,15	11	7				8,16	0	−10
1,17	0	7	51	72	−90			
1,19	6	−19	53	70	68	91	35	23
1,21	36	27	55	10	−16	93	21	28
1,23	21	27	57	38	44	95	0	− 3
			59	5	4	97	55	55
20	19	−21	5,11	25	−28	99	23	27
22	38	−40	5,13	56	−47	9,11	29	28
24	110	108	5,15	44	48	9,13	32	−29
26	17	3	5,17	0	−10	9,15	36	31
28	16	20	5,19	0	9			
2,10	44	37	5,21	43	37	10,0	74	84
2,12	44	−54				10,2	14	−16
2,14	31	30	60	118	129	10,4	0	3
2,16	0	3	62	41	−40	10,6	17	24
2,18	29	28	64	8	16	10,8	54	−48
2,20	19	13	66	22	10	10,10	38	34
2,22	33	32	68	49	58	10,12	73	56
			6,10	24	23			
31	149	177	6,12	15	− 3	11,1	51	62
33	69	−70	6,14	10	− 1	11,3	16	−23
35	67	−58	6,16	23	11	11,5	32	−27
37	80	80	6,18	29	35	11,7	0	− 1
39	23	−28	6,20	15	2	11,9	22	−34

Thus the true explanation of Hutton's figure of 4·03% H_2O^+ is that only part of the excess above 2% is non-structural water. The amount of adsorbed water which remains, and may be recorded as H_2O^+, is no doubt influenced by the condition and treatment of the powder prior to H_2O^+ determination.

Two possible ways in which extra hydrogen may enter the amphibole structure unaccompanied by extra oxygen are suggested: (*a*) Through replacement of some oxygens of the Si_4O_{11} bands by (OH) ions in a manner similar to that which occurs in afwillite (Megaw, 1952), where the presence of $\{SiO_3OH\}$ groups has been demonstrated. In the amphiboles such replacement might perhaps occur at O_4 to some extent, and the possibility of hydrogen bonding between O_4 and O_2 of a neighbouring chain also suggests itself. (*b*) Alternatively, some of the SiO_4 groups which link together to form bands might be replaced by $(OH)_4$ (see Hutton (1943) on hydrogrossular and McConnel (1952) on viséite).

(*a*) leads to a formula

$$\underbrace{Si_{7\cdot13}Al_{0\cdot76}Ti_{0\cdot11}}_{8\cdot00}\quad\underbrace{Mg_{3\cdot58}Fe_{1\cdot37}Cr,\text{ etc.}_{0\cdot05}}_{5\cdot00}$$

$$\underbrace{Ca,\text{ etc.}_{1\cdot62}Mg_{0\cdot20}}_{1\cdot82}\quad\underbrace{F_{0\cdot07}(OH)_{1\cdot93}}_{2\cdot00}\quad\underbrace{O_{21\cdot09}(OH)_{0\cdot91}}_{22\cdot00},$$

in which the extra hydrogens are approximately balanced by the replacement of Si by Al.

(*b*) gives a formula

$$\underbrace{Si_{7\cdot13}(H_4)_{0\cdot23}Al_{0\cdot64}}_{8\cdot00}\quad\underbrace{Mg_{3\cdot38}Fe_{1\cdot37}Cr,\text{ etc.}_{0\cdot03}Ti_{0\cdot13}Al_{0\cdot12}}_{5\cdot03}$$

$$\underbrace{Ca,\text{ etc.}_{1\cdot62}Mg_{0\cdot40}}_{2\cdot02}\quad\underbrace{F_{0\cdot07}(OH)_{1\cdot93}}_{2\cdot00}\quad O_{22\cdot00},$$

and it is tempting to associate the extra hydrogens with the appropriate deficit of other cations! The ratio of X to Y peak in this case should be approximately 1·17, a value not incompatible with that observed.

It is felt that alternative (*a*) is the more feasible in the amphibole structure, but no decision as to which is correct can be made in the present circumstances.

It may be that some of the structural features common to this actinolite and to crocidolite are characteristic of the more nearly fibrous members of the amphibole series. It is hoped that similar and in some cases more extensive studies of other amphiboles including a pure tremolite, to be made in due course, may throw light on this and other problems encountered in the course of the present and previous investigations.

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A Comparison of Optical Methods and Difference Synthesis in the Location of Hydrogen

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A comparison has been made between optical methods of testing possible positions of hydrogen atoms in a crystal and the more objective method of a difference synthesis. The (010) projection of diphenylene naphthacene was used in the investigation. The results show that the optical methods give a quick guide, but that the difference synthesis is more definite. Optical methods can, however, be used for non-centrosymmetrical projections, whereas the difference synthesis cannot. The inclusion of hydrogen in the structure-factor calculations for diphenylene naphthacene reduced the agreement residuals from 0·18 to 0·11 for the (*h*0*l*) zone and from 0·21 to 0·14 for the (0*kl*) zone. This has important implications concerning the lengths of C–C bonds.

Optical methods

Bennett & Hanson (1953) have published a structure for diphenylene naphthacene which included some apparently anomalous C–C bond distances. No great accuracy was claimed, however, the comparatively large values of $\Sigma(|F_o|-|F_c|)\div\Sigma|F_o|$ (0·18 for *h*0*l*, 0·21 for 0*kl*) being attributed to lack of accuracy in the visually observed X-ray intensities. The present work was undertaken to see if by optical methods the hydrogen atoms could be detected. The techniques used were essentially those described by Pinnock & Lipson (1954), in which the optical transform of a mask representing assumed positions of hydrogen atoms only is superimposed on the reciprocal-lattice net. The first trial indicated clearly that the signs and magnitudes of the transform peaks were such as to effect a considerable reduction in (F_o-F_c) for the majority of reflexions.

Since it is possible to deduce from the transform pattern the changes in atomic parameters most likely to produce an improvement in the agreement, an arrangement of the hydrogen atoms was arrived at which improved the agreement residual for the *h*0*l* zone from 0·18 to 0·13, structure-factor calculations being carried out only for those reflexions for which the transform indicated a significant contribution.

Further refinement was effected by punching two separate masks, each corresponding to half of the hydrogen atoms. Since their transforms are additive, this technique shows the contribution of each group of atoms to any particular reflexion. This, combined with some 'atom by atom' refinement by means of an instrument devised by Hughes & Taylor (to be published), reduced the *h*0*l* residual to 0·12.

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