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A Re-Examination of the Structure of Tremolite

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Improved values of the x and y atomic coordinates have been obtained for the structure of tremolite $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$, and accurate lattice parameters have been derived for tremolite and actinolite from X-ray powder patterns. Tremolite has $a = 9.840$, $b = 18.052$, $c = 5.275$ Å, $\beta = 104.7^\circ$ and actinolite $a = 9.861$, $b = 18.111$, $c = 5.336$ Å, $\beta = 105.0^\circ$. Cell parameters of hydroxy-tremolite are larger than those of fluor-tremolite.

Introduction

The essential features of the atomic structure of amphibole minerals have been known since the work on tremolite by Warren (1930). In more recent years some attention has been given to matters of structural detail, and (x, y) electron-density projections have been derived for a magnesian crocidolite (Whittaker, 1949), an actinolite (Zussman, 1955), and for the hornblendes karinthine and barroisite (Heritsch, Paulitsch & Walitzi, 1957). Differences between each of these and the tremolite structure might be expected on various grounds, in the case of crocidolite because it is a fibrous asbestos variety, and in the case of the hornblendes because they contain additional cations in the site A ($\frac{1}{2}, 0, \frac{1}{2}$). Actinolite displays neither of these features and is different from tremolite principally in the replacement of some magnesium by iron and of silicon by aluminium. Other chemical differences are illustrated below by the approximate formulae of the minerals studied.

Tremolite	Ca_2	Mg_5	Si_8	$\text{O}_{22}(\text{OH})_2$
Magnesian crocidolite	$(\text{Na}, \text{Ca})_2$	$\text{Mg}_3\text{Fe}_2^{3+}$	Si_8	$\text{O}_{22}(\text{OH})_2$
Actinolite	Ca_2	$\text{Mg}_{3.5}^+\text{Fe}_{1.5}^{2+}$	Si_7, Al	$\text{O}_{22}(\text{OH})_2$ (plus extra hydrogen)
Barroisite	Na ($\text{Ca}, \text{Na})_2$	$\text{Mg}_{2.5}\text{Fe}_{1.5}^{2+}\text{Al}_{1.0}$	$\text{Si}_{6.5}\text{Al}_{1.5}$	$\text{O}_{22}(\text{OH})_2$
Karinthine	Na ($\text{Ca}, \text{Na})_2$	$\text{Mg}_{3.5}\text{Fe}_{0.5}^{2+}\text{Al}_{1.0}$	$\text{Si}_{6.5}\text{Al}_{1.5}$	$\text{O}_{22}(\text{OH})_2$

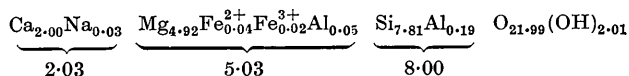
Atomic coordinates and cell parameters of the four amphiboles recently studied do indeed differ from those given by Warren (1930) for tremolite, and valid comparison between the four sets of results may be

Table 1. *Tremolite: Chemical analysis**

SiO_2	57.66	CaO	13.79
TiO_2	0.01	Na_2O	0.12
Al_2O_3	1.51	K_2O	0.02
Fe_2O_3	0.23	H_2O^+	2.22
FeO	0.33	F	nil
MnO	0.01	H_2O^-	0.04
MgO	24.34	Total	100.28%

* By R. A. Howie.

Formula on basis of 24 (O, OH):



Calculated density = 2.99 g.cm.⁻³.

made (Heritsch *et al.*, 1957). Comparison with tremolite however is of little value unless results of similar accuracy are available for it. The present paper presents such results in the form of accurate x and y coordinates and accurate lattice parameters.

Experimental results

Chemical analysis of the tremolite specimen studied is presented in Table 1. A single crystal was obtained

from a compact mass of very small needle-like white crystals of tremolite arranged in sheaf-like clusters. Intensities of $hk0$ X-ray reflections were measured visually on zero layer Weissenberg photographs obtained with nickel-filtered Cu K radiation. Appropriate geometric and polarization factors were applied to yield a set of $|F_{\text{obs}}|$ values, and the atomic coordinates previously determined for actinolite were used to initiate a sequence of 'least squares' refinements. The atomic scattering factors used were those given by Berghuis *et al.* (1955), initially modified by a temperature factor $\exp(-2.0 \sin^2 \theta / \lambda^2)$. Refinements were carried out on the Manchester University Mark I digital computer according to a programme prepared by A. R. Curtis and O. S. Mills (Mills, 1958). Atomic coordinates, an isotropic temperature factor for each atom, and an overall scaling factor were obtained by a converging series of refinements which was continued until changes in coordinates were less than 0.01 Å, and changes in the R index were negligible. The R index of agreement between F_o and F_c was 24% initially, 21% after re-scaling, and in successive cycles of refinement was 11.5, 9.5 and finally 8.0%. The final atomic coordinates are presented in Table 2 where they are compared with those for the idealized structure (Warren, 1930). The small variations in temperature factors for different atoms which emerged were not regarded as significant; the average value for all thirteen atoms is $B = 0.9 \text{ Å}^2$. Observed and

Table 2. Tremolite: Atomic coordinates

	x/a		y/b	
	Warren (1930)	Present text	Warren (1930)	Present text
O ₁	0.14	0.1134	0.08	0.0873
O ₂	0.14	0.1195	0.18	0.1710
O ₃ *	0.14	0.1130	0.00	0.0000
O ₄	0.36	0.3651	0.25	0.2481
O ₅	0.36	0.3463	0.14	0.1340
O ₆	0.36	0.3434	0.11	0.1179
O ₇	0.36	0.3376	0.00	0.0000
M ₁	0.00	0.0000	0.09	0.0877
M ₂	0.00	0.0000	0.17	0.1761
M ₃	0.00	0.0000	0.00	0.0000
M ₄	0.00	0.0000	0.28	0.2783
Si ₁	0.29	0.2791	0.08	0.0838
Si ₂	0.29	0.2880	0.18	0.1707

* O₃ is the oxygen of an (OH)⁻ ion.

calculated structure amplitudes are listed in Table 3, and electron-density and $(F_o - F_c)$ maps are shown in Figs. 1(a), (b) respectively. The standard deviation in atomic coordinate is estimated as $\sigma = 0.02 \text{ Å}$ for oxygens and $\sigma = 0.01 \text{ Å}$ for heavier atoms.

Accurate cell parameters were determined for tremolite using a Philips X-ray diffractometer and nickel-filtered Cu K radiation. The positions of reflections were estimated with respect to those from a quartz internal standard which itself had been checked against an internal standard of silicon. Two of the important

Table 3. Observed and calculated structure amplitudes

hk	F_o	F_c	hk	F_o	F_c	hk	F_o	F_c	hk	F_o	F_c
02	53	-68	16	14	-13	7	48	44	4	26	22
4	87	-87	18	35	31	9	6	5	6	36	-33
6	10	-9	20	16	16	11	34	-32	8	0	6
8	25	21	22	21	19	13	68	-64	10	28	25
10	77	75				15	48	44	12	45	46
12	191	208	31	130	152	17	0	-4	14	9	11
14	4	-4	3	65	-62	19	9	8	16	13	-14
16	14	-14	5	72	-73	21	32	37			
18	21	19	7	80	89	60	110	121	91	30	26
20	72	-71	9	27	-25	2	45	-42	3	26	24
22	67	70	11	97	93	4	16	17	5	9	-8
			13	3	2	6	17	16	7	62	66
11	49	56	15	9	11	8	64	64	9	21	21
3	44	41	17	25	24	10	15	13	11	22	20
5	5	-7	19	36	-34	12	30	-27	13	27	-24
7	13	11	21	7	6	14	15	14	15	33	35
9	82	-77				16	19	18			
11	134	146	40	14	14	18	34	32	10,0	82	77
13	14	12	2	22	-21	20	13	-13	2	18	-17
15	11	-11	4	13	9				4	6	7
17	4	-5	6	22	-17	71	81	84	6	15	13
19	4	-2	8	113	-116	3	39	-36	8	55	-57
21	24	27	10	54	49	5	15	-12	10	30	30
23	12	11	12	50	44	7	31	-24	12	57	61
			14	23	24	9	96	-105	11,1	58	52
20	40	-24	16	70	-71	11	150	158	3	15	-13
2	44	-46	18	22	22	13	43	44	5	34	-34
4	107	112	20	46	-49	15	49	-51	7	3	1
6	20	-13	22	30	33	17	4	-6	9	25	-26
8	21	20				19	22	-22			
10	34	31	51	94	-100				12,0	10	-10
12	54	-54	3	78	82	80	120	128	2	4	4
14	36	30	5	18	-18	2	30	-24	4	18	21

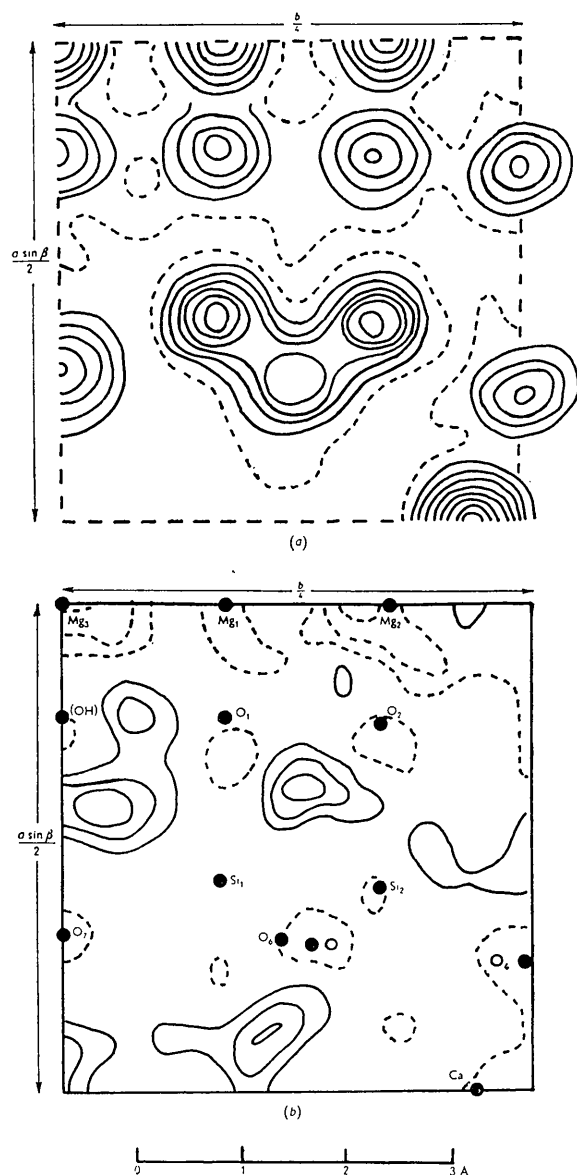


Fig. 1. (a) Tremolite. Electron-density map from $hk0$ synthesis. Contour intervals for single oxygen atom $2 \text{ e.}\text{\AA}^{-2}$, elsewhere $3 \text{ e.}\text{\AA}^{-2}$. Lowest contour at $2 \text{ e.}\text{\AA}^{-2}$ indicated by broken line. (b) $hk0$ difference synthesis, ($F_o - F_c$). Negative contours indicated by broken line. Lowest contour at $-1\frac{1}{2} \text{ e.}\text{\AA}^{-2}$; interval $\frac{1}{2} \text{ e.}\text{\AA}^{-2}$; zero contour omitted.

Table 4. Cell parameters of tremolite and of other amphiboles

	(C-centred cell)					Reference
	a (Å)	b (Å)	c (Å)	β (°)	$a \sin \beta$ (Å)	
Actinolite*	9.861	18.111	5.336	105.0	9.524	Present text
Tremolite*	9.840	18.052	5.275	104.7	9.517	Present text
Fluor-tremolite	9.781	18.007	5.267	104.5	9.469	Comeforo & Kohn (1954)
Crocidolite	9.74	17.95	5.30	103.9	9.45	Present text
Tremolite†	9.76	17.8	5.27	105.2	9.42	Warren (1930)

* a and $b \pm 0.05\%$; c and $\beta \pm 0.1\%$.

† These values for tremolite are derived from Warren's after conversion of kX. to Å and recalculation to refer to the C-centred cell.

peaks of silicon would have been overlapped by tremolite peaks if silicon had been used directly, and it was found that no consistent results could be obtained using silicon in a separate mount. The specimen was well ground and packed in a cavity $1 \times 1.5 \text{ cm}$. Instrument settings were: time constant 4; scanning speed $\frac{1}{2}^\circ/\text{min}$.; chart speed 80 cm./hr .; divergence and scatter slits 1° ; receiving slit 0.1 mm . up to $2\theta = 50^\circ$, 0.2 mm . at higher angles. Chart measurements of 2θ were made with a vernier rule and have a standard deviation of 0.005° . Approximate cell parameters were used to index all lines up to $2\theta = 65^\circ$. The reflexion 600 gave d_{100} ; this together with 1, 11, 0 gave the value of b , and d_{001} and β were derived from 202 and $20\bar{2}$. Cell parameters of crocidolite and actinolite (specimens previously studied by Whittaker (1949) and Zussman (1955), respectively) were also redetermined by the powder method and are given with those of tremolite in Table 4.

Discussion

A possible source of confusion which may arise when the cell parameters of amphiboles are compared lies in the choice of unit cell. The monoclinic lattice may be described by a body-centred or by a C -face-centred cell, and the lattice geometry is such that the parameters do not differ greatly for the two cases. Relationships between the C (subscript 1) and I (subscript 2) cells are given by

$$\left. \begin{aligned} a_2 &= c_1 + a_1 \\ b_2 &= b_1 \\ c_2 &= -c_1 \end{aligned} \right\} \text{ and } a_1 \sin \beta_1 = a_2 \sin \beta_2.$$

The cell parameters of tremolite are compared with those of other amphiboles (all with reference to the C -centred cell) in Table 4, and are seen to differ somewhat from those previously accepted for tremolite. Thus the implications of earlier comparisons of cell parameters must be re-examined.

Comeforo & Kohn (1954) compared accurately determined cell parameters of fluor-tremolite with the approximate values for hydroxy-tremolite and remarked that 'substitution of fluorine for hydroxyl causes virtually no change in the a and c dimensions; b_0 increases slightly (1+%) while β increases by 1.5° '

(2%).' This comparison needs revision in the light of new parameters for hydroxy-tremolite, but it is also invalidated because the parameters for fluor-tremolite refer to a *C*-centred cell whereas those given by Warren (1930) for hydroxy-tremolite refer to a body-centred cell. The effect of this is particularly marked in the case of the β angle. Table 4 shows that in fact all dimensions are slightly lowered by the substitution of *F* for (OH). The reductions are 0.6%, 0.2%, 0.2% and 0.2% for *a*, *b*, *c* and β respectively. [Reduction of cell parameters on substitution of *F* for (OH) occurs also for phlogopite. (Yoder & Eugster, 1954.)]

The apparent anomaly that the cell parameters of crocidolite were larger than those of tremolite was noted in a previous paper (Zussman, 1955). The new values for tremolite (with the exception of *c*) are seen however to lie between those of crocidolite and actinolite, as would be expected from the chemical relationship between the three minerals. The values obtained for crocidolite by the powder method agree very closely with those given by Whittaker (1949) when both sets are derived for the same choice of unit cell. Peaks in the crocidolite powder pattern were not as sharp as those for tremolite and actinolite, so that its parameters could not be determined with as high a degree of accuracy.

The atomic coordinates determined for tremolite show small differences from those of Warren's idealized structure (see Table 2 and Fig. 2). Comparison with results for other amphiboles shows that chemical and physical differences between these and tremolite cannot be associated with their deviations from the ideal structure since tremolite itself is now seen to possess similar deviations. When the data for actinolite and the new data for tremolite are compared, it is seen that the maximum difference in corresponding atomic coordinates is 0.09 Å, and in the comparison of crocidolite and tremolite it is 0.15 Å. There appears to be little structural difference between fibrous and non-fibrous varieties, and little change, even in the immediate environment of the *A* site, among amphiboles in which it is occupied and those in which it is vacant. Apart from the unlikely possibility that major variations are confined to *z* coordinates alone, it may be said that structural differences between the amphibole varieties studied are very small.

No attempt has been made to deduce inter-atomic distances at this stage, since it is hoped to derive *z*

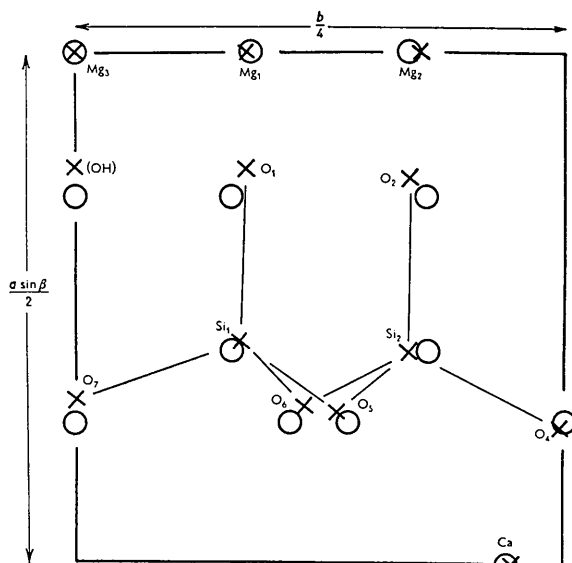


Fig. 2. Comparison between atomic positions in tremolite (X) and those in Warren's idealized structure (O).

coordinates for tremolite by three-dimensional analysis in due course.

In conclusion I would like to thank Dr R. A. Howie for the chemical analysis, Mr O. S. Mills for the refinement computations, and the Staff of the Computing Machine Laboratory for permission to use the machine. I am also grateful to Dr E. J. W. Whittaker of Ferodo Ltd. for supplying the specimen of crocidolite.

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