

*Gyrolite.*

(With Plate XII.)

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THE mineral gyrolite was discovered in Skye by T. Anderson<sup>1</sup> in 1851. He showed it to be a hydrated calcium silicate of approximate composition  $2\text{CaO} \cdot 3\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ . Subsequently gyrolite has been found in other localities, and has been prepared hydrothermally by Flint, McMurdie, and Wells.<sup>2</sup> The ratio of lime to silica found by Anderson appears well established, but various values of the water content have been reported and more recent analyses approximate to  $2\text{CaO} \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . X-ray powder measurements were given by McMurdie and Flint,<sup>3</sup> but no crystallographic or other investigations of a detailed character have been reported.

## A. THE PRESENT INVESTIGATION.

1. *Material.*

A sample of natural gyrolite from Bombay (B.M. 1925, 1044) was made available by the Trustees of the British Museum. The material was colourless and exhibited a pronounced basal cleavage in agreement with earlier descriptions. Relatively poor hexagonal prism cleavages were also observed. Calcite was present in contact with the gyrolite, but no other minerals were found.

2. *Chemical analysis.*

The results of an analysis, carried out by Mr. F. J. McConnell (Building Research Station, Watford) are given in table I. Before this analysis the material was examined microscopically to select a sample as free from calcite as possible. Nevertheless, 0.95 %  $\text{CO}_2$  was found; assuming this to be in the form of calcite, the ratios  $\text{CaO} : \text{SiO}_2 : \text{H}_2\text{O}$  for gyrolite given by the analysis are 0.70:1:0.79. The discrepancy between these and the theoretical ratios 0.67:1:0.67 may be partly due to the presence of other

<sup>1</sup> T. Anderson, *Phil. Mag.*, 1851, ser. 4, vol. 1, p. 111.

<sup>2</sup> E. P. Flint, H. F. McMurdie, and L. S. Wells, *Journ. Res. Nat. Bur. Standards U.S.A.*, 1938, vol. 21, p. 617. [M.A. 7-283.]

<sup>3</sup> H. F. McMurdie and E. P. Flint, *ibid.*, 1943, vol. 31, p. 225. [M.A. 9-45.]

oxides, particularly  $\text{Al}_2\text{O}_3$ . If it is assumed that Al replaces Si, the ratios  $\text{CaO}:(\text{Si},\text{Al})\text{O}_2:\text{H}_2\text{O}$  become 0.67:1:0.76.

TABLE I. Chemical analyses of gyrolite from Bombay.

			Mol. ratios.	A.
$\text{SiO}_2$	...	50.23	1.000	52.09
$\text{Al}_2\text{O}_3$	...	2.19	0.026	0.49
$\text{Fe}_2\text{O}_3$	...	0.20	0.015	—
MgO	...	$\leq 0.13$	$\leq 0.004$	0.29
CaO ...	...	34.04	0.700*	33.07
$\text{Na}_2\text{O}+\text{K}_2\text{O}$	...	$\leq 0.14$	$\leq 0.002$	0.52
$\text{CO}_2$ ...	...	$0.95 \pm 0.10$	—	—
$\text{H}_2\text{O}$	...	$11.98 \pm 0.15^\dagger$	0.795	13.35
		99.86		99.86

\* After deduction of calcite. † Loss on ignition at  $1250^\circ\text{C}$ ., after deduction of  $\text{CO}_2$ .  
 A.—W. A. K. Christie, Rec. Geol. Surv. India, 1925, vol. 56, p. 199 [M.A. 3-287]. Also SrO 0.05; sp. gr. 2.388–2.390,  $\omega$  1.549,  $\epsilon$  1.536. 2.99% water lost below  $107^\circ\text{C}$ .  $\text{Na}_2\text{O}$  0.51,  $\text{K}_2\text{O}$  0.01.

### 3. Optical examination.

Cleavage flakes gave a uniaxial negative optic axial figure. Some crystals appeared slightly biaxial, possibly due to bending of the flakes. Refractive indices for white light were  $\omega$   $1.545 \pm 0.01$  and  $\epsilon$   $1.535 \pm 0.01$ , agreeing well with the previously published values.

### 4. X-ray investigation of single crystals.

(a) *Diffraction Symmetry.*—A stationary crystal photograph (pl. XII, fig. 1) using copper radiation filtered through nickel foil, and taken with the incident beam perpendicular to the basal cleavage, showed the diffraction symmetry of the corresponding axis to be 6. A precession photograph confirmed the absence of symmetry planes parallel to this axis. The existence of a sixfold axis in the diffraction symmetry necessarily implies that of a symmetry plane perpendicular to it. Gyrolite thus appears to be hexagonal, with diffraction symmetry  $6/m$ .

In order to provide a more sensitive test of the diffraction symmetry, oscillation photographs were taken about the sixfold axis. For reasons given in the next paragraph, certain difficulties had to be overcome before the crystal could be set accurately about this axis. The crystal was, however, set to within  $\pm 5$  minutes on each goniometer arc and  $15^\circ$  oscillation photographs taken at exactly  $120^\circ$  intervals. These showed very slight differences from each other, as regards the intensities of corresponding reflections. They, and other oscillation and Laue photographs, also showed similar very slight deviations from a plane of symmetry perpendicular to the sixfold axis. It is thus possible that the true

diffraction symmetry is lower than  $6/m$ . The discrepancies are, however, so slight that the diffraction symmetry must in that case be to a high degree of accuracy pseudo- $6/m$ .

(b) *Cell size*.—In a complete rotation photograph about the  $c$ -axis (pl. XII, fig. 5), all row-lines could be indexed on hexagonal axes having  $a = 9.72 \pm 0.01$  Å. From the row of  $000l$  reflections in a Weissenberg photograph a value of  $22.13 \pm 0.05$  Å. was found for the spacing in the  $c$ -direction. The layer-lines in rotation photographs about the  $c$ -axis show that the true repeat distance is six times this, namely,  $132.8 \pm 0.3$  Å. Owing to the very long  $c$ -axis and the relatively short  $a$ -axis the layer-lines are difficult to pick out, but row-lines are evident even if there is considerable mis-setting. A special X-ray method of setting, described elsewhere (Mackay),<sup>1</sup> based on the row-lines, had to be developed.

(c) *Production of characteristic reflections in a stationary crystal photograph*.—The stationary crystal photograph along the  $c$ -axis (pl. XII, fig. 1), using Cu- $K$  radiation filtered through Ni foil, exhibits a regular hexagonal array of spots. The use of unfiltered, as distinct from filtered, copper radiation did not affect the relative intensities, but introduced additional reflections due to the  $K\beta$  component. Symmetrical oscillation through  $15^\circ$  about the mean position (pl. XII, fig. 2) affected the intensities, but not the positions of the spots. The latter are therefore due to the characteristic, and not the white, radiation, and for this reason the result has not been described as a Laue photograph.

It was at first thought that the effect was caused by imperfections in the crystal, giving rise to a reciprocal lattice consisting of  $h$ ,  $k$  rods. The row-lines in  $c$ -rotation photographs of good crystals (pl. XII, fig. 5) consisted, however, of quite distinct spots. The reciprocal lattice points are, nevertheless, so closely packed along the  $h$ ,  $k$  lines that characteristic reflections always occur in stationary crystal photographs along the  $c$ -axis. This is probably due mainly to finite divergence of the beam together with slight bending of the specimen.

(d) *Extinctions and space-group*.—As has been mentioned above, the  $000l$  reflections are only present when  $l = 6n$ . Other complicated regularities are visible but are not relevant to the space-group determination.

The diffraction symbol for gyrolite is thus found to be  $6/m-C6_1$ , which is characteristic for the enantiomorphous pair of space-groups  $C6_1$  and  $C6_5$ . These groups are non-centrosymmetrical and every atom occurs in multiples of six. The  $hki0$  zone is centrosymmetrical but no others.

<sup>1</sup> A. L. Mackay, *Acta Cryst.*, 1952, vol. 5, p. 691.

(e) *The contents of the unit cell.*—The space-group symmetry demands that the number of molecules in the unit cell be divisible by six. The

TABLE II. Powder data for natural gyrolite.

Spacing (Å.).	Intensity.	Principal reflections contributing.	Calculated spacing (Å.) where applicable.	
22	vs	0006 only	0006	22.13
11.0	s	000.12 only	000.12	11.07
8.4-7.4	m, d	10 $\bar{1}l$	10 $\bar{1}0$	8.42
7.4-5.4	w, d			
4.75	w	11 $\bar{2}l$	11 $\bar{2}0$	4.86
4.20	s	20 $\bar{2}l$	20 $\bar{2}0$	4.21
3.72-3.45	w, d	20 $\bar{2}l$	000.36	3.69
3.65	ms			
3.21-3.02	m, d	21 $\bar{3}l$	21 $\bar{3}0$	3.18
3.12	vs			
2.80-2.61	m, d	21 $\bar{3}l$	000.42	3.16
2.80	ms			
2.42	w	22 $\bar{4}l$	22 $\bar{4}0$	2.43
		20 $\bar{2}l$		
2.31-2.03	vw, d	21 $\bar{3}l$	31 $\bar{4}0$	2.33
2.31	w			
2.17	w			
2.06	w			
1.90	w	32 $\bar{5}l$	32 $\bar{5}0$	1.93
1.82-1.73	vw, d	41 $\bar{5}l$	41 $\bar{5}0$	1.83
1.82	s			
1.57	mw	42 $\bar{6}l$	42 $\bar{6}0$	1.59
1.52-1.50	vw, d	42 $\bar{6}l$	51 $\bar{6}0$	1.51
1.50	w			
1.41-1.37	vw, d	51 $\bar{6}l$	43 $\bar{7}0$	1.38
1.37	w			
1.34	mw	52 $\bar{7}l$	52 $\bar{7}0$	1.35
1.28	vw	61 $\bar{7}l$	61 $\bar{7}0$	1.28
1.195	mw	53 $\bar{8}l$	53 $\bar{8}0$	1.203
		and 70 $\bar{7}l$		
1.168-1.154	w, d; band	53 $\bar{8}l$	and 70 $\bar{7}0$	
		and 70 $\bar{7}l$		
1.060	w	63 $\bar{9}l$	6390	1.061
1.040	w	63 $\bar{9}l$		
0.965 approx.	vwv, d; band	63 $\bar{9}l$ (?)		
0.934 approx.	vwv, d; band	?		
0.908	w	8.2. $\bar{1}0.l$	8.2. $\bar{1}0.0$	0.918
0.882	w	6.5. $\bar{1}1.l$	6.5. $\bar{1}1.0$	0.882
		and 9.1. $\bar{1}0.l$		
0.868 approx.	vwv, d	7.4. $\bar{1}1.l$	and 9.1. $\bar{1}0.0$	0.873

s = strong, m = moderate, w = weak, v = very, d = diffuse.

most likely number of molecules of composition  $2\text{CaO} \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  is 48, which gives a calculated density of 2.40. Observed values, reported in

the literature, vary between 2.342 and 2.446. Alteration in the postulated number of molecules to 42 or 54 gives calculated densities of 2.10 and 2.70 respectively. The assumption of 48 molecules of composition  $2\text{CaO}\cdot 3\text{SiO}_2\cdot 3\text{H}_2\text{O}$  would make the density 2.53. In each case the result is well outside the observed limits. The X-ray results therefore support the view that the unit cell contains 48 molecules of formula  $2\text{CaO}\cdot 3\text{SiO}_2\cdot 2\text{H}_2\text{O}$ . This gives a volume per O atom of  $22.7 \text{ \AA}^3$ .

### 5. X-ray powder photographs.

The X-ray powder data (table II) for the natural mineral were obtained using copper  $K\alpha$  radiation, with cameras of 6 cm. and 19 cm. diameter. The laboratory preparation (p. 87) gave results indistinguishable from the natural mineral.

The indexing was carried out by direct comparison of 6 cm. powder photographs with single-crystal photographs. Except for a few strong 000*l* reflections, the powder photographs consist entirely of *hk* bands. An attempt has been made in the table to indicate the apparent limits of each band and also any pronounced maxima within them. The limits were estimated visually and are therefore to a small extent arbitrary, but it appears unlikely that any uncertainties could arise on this account in regard to identification of the mineral.

The data are in fair agreement with those of McMurdie and Flint (1943, loc. cit.), whose data are, however, incomplete at both high and low angle ends, and no mention is made of the widely varying breadths of the lines. They also include, as the strongest spacing, one of  $3.36 \text{ \AA}$ . This cannot have been due to gyrolite.

### 6. Dehydration.

(a) *The dehydration curve.*—A dehydration curve is shown in text-fig. 1. At temperatures up to  $520^\circ \text{C}$ ., isobaric conditions were maintained, the partial pressure of water-vapour being 6 mm. The apparatus used has been described elsewhere.<sup>1</sup> For the determination of the next three points the material was transferred to a platinum crucible, which was heated in an electric furnace without control of the humidity. The final point was obtained by ignition with a large Meker burner, and the temperature quoted ( $1250^\circ$ ) is only approximate.

The result shows clearly that the water is lost in two stages. The first is complete at about  $450^\circ$ , and entails a loss of  $9.0 \pm 0.2 \%$ . The second begins at about  $500^\circ$  and is complete by  $850^\circ$ . After correction for the

<sup>1</sup> H. F. W. Taylor, Journ. Chem. Soc. London, 1953, p. 163.

$\text{CO}_2$  present ( $0.95 \pm 0.1\%$ ), the loss in the second step amounts to  $3.0 \pm 0.3\%$  of the initial weight.

The loss at  $100^\circ$ ,  $4.15\%$ , is in fair agreement with that found by Anderson, for his original sample, of  $4.42\%$ . The total water loss, at  $1250^\circ$ , of  $11.98 \pm 0.15\%$ , is higher than that ( $10.95\%$ ) required by the

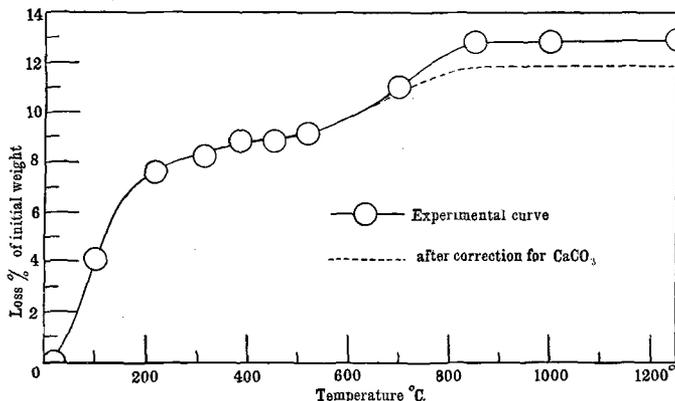


FIG. 1. Dehydration curve of natural gyrolite.

formula  $2\text{CaO} \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , but much lower than that ( $15.6\%$ ) corresponding to  $2\text{CaO} \cdot 3\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ . The first formula would thus appear the more probable, especially in view of the X-ray results described in the previous section. The possibility that gyrolite has some intermediate composition, such as  $4\text{CaO} \cdot 6\text{SiO}_2 \cdot 5\text{H}_2\text{O}$ , cannot be altogether excluded, although the density calculated for this formula ( $2.47$ ) is outside the range of observed values.

(b) *X-ray single-crystal investigation of heated material.*—Cleavage flakes of natural gyrolite were heated to various temperatures, X-ray single-crystal photographs being taken before and after the treatment. In this way the nature of the products formed at various points on the dehydration curve was established, and the orientation relative to that of the original gyrolite crystal determined in each case.

(i) Heating to  $450^\circ$ , i.e. to the end of the first step in the dehydration curve.—A rotation photograph about the  $c$ -axis showed the positions of the row-lines to be unchanged. Within each individual row-line, however, a marked simplification was observed, almost all the spots lying on the  $22.13 \text{ \AA}$ . layer-lines. Stationary crystal photographs with the incident beam parallel to the  $c$ -axis showed no appreciable change in the positions of the spots, but the intensities suggested a reduction in the

symmetry to trigonal. A zero-layer Weissenberg photograph about an  $a$ -axis showed no significant changes in the spacing or intensities of the  $00l$  reflections, but certain 'extra' reflections appeared in this row in non-integral positions.

While the full significance of these effects has yet to be determined, it is clear that heating gyrolite to  $450^\circ$  produces certain alterations in the structure, but leaves it basically unchanged. The layers of thickness  $22.13 \text{ \AA}$ . appear to be stacked in a less complicated way, in the direction of the  $c$ -axis, than in the unheated material.

A crystal, which had been heated to  $450^\circ$ , was exposed to water-vapour in a vacuum desiccator for four days at room-temperature. This treatment caused no further change in the X-ray pattern. Hence, if rehydration takes place at all under these conditions, it does not fully reverse the structural changes occurring on dehydration.

(ii) Heating to  $550$ – $750^\circ$ , i.e. to points on the second step in the dehydration curve.—At  $550^\circ$  the product gave X-ray patterns very similar to those obtained at  $450^\circ$ . Certain additional minor changes were observed, but the structure evidently remained basically that of gyrolite. At  $700^\circ$  and  $750^\circ$  the gyrolite reflections could still be observed, but many more additional spots were also present. The most prominent of these could be attributed to the formation of  $\alpha$ -wollastonite; this is discussed in the next paragraph. Some of the spots, however, could not easily be accounted for by the presence of gyrolite or of  $\alpha$ - or  $\beta$ -wollastonite, and it is possible that some intermediate phase may be formed over a small range of temperature.

(iii) Heating to  $1000^\circ$ , i.e. to the end of the second step in the dehydration curve.—The photograph obtained by oscillation, through  $15^\circ$ , symmetrically about a position with the cleavage plane perpendicular to the incident beam, is shown in pl. XII, fig. 4. Together with oscillation photographs about the original  $c$ -axis, this showed that the gyrolite had been converted into almost a single crystal of  $\alpha$ -wollastonite. This compound is pseudo-hexagonal, with  $a$   $6.85$ ,  $c$   $19.65 \text{ \AA}$ . (Heller, unpublished work). The product was oriented with its  $c$ -axis coinciding with that of the original gyrolite, and its  $\{11\bar{2}0\}$  directions coinciding with the  $\{21\bar{3}0\}$  directions of the gyrolite. This is shown most clearly by the series of photographs in pl. XII. Figs. 1 and 2, given by the unheated material, are of gyrolite. Fig. 3, given by a crystal heated to  $700^\circ$ , shows just inside the ring of strong  $\{21\bar{3}0\}$  reflections of the gyrolite, a ring of  $\{11\bar{2}0\}$  reflections of the  $\alpha$ -wollastonite. The two sets of spots are scarcely resolved in the reproduction. Gyrolite and  $\alpha$ -wollastonite are

thus present together in this product. In pl. XII, fig. 4, given by the crystal heated to 1000°, the gyrolite spots have disappeared and the pattern of  $\alpha$ -wollastonite can be seen. The  $\alpha$ -wollastonite crystal obtained by the heating of gyrolite is imperfect. The  $c$ -oscillation photograph showed that the directions of the  $c$ -axes of the crystallites of  $\alpha$ -wollastonite deviated by up to 10 degrees in all directions from the normal to the cleavage plane of the flake.

### 7. *Synthesis.*

The laboratory preparation of gyrolite by Flint, McMurdie, and Wells (1938, loc. cit.) was confirmed in the present investigation. Calcium hydroxide and moist silica gel (20 %  $\text{SiO}_2$ ), in the approximate molar proportions 2:3, were treated with water in a closed bomb at 150° for 76 days. The experimental technique has been described elsewhere.<sup>1</sup> Optical investigation of the product showed it to consist of sub-microscopic particles of mean refractive index 1.54. X-ray powder photographs showed excellent agreement with those of natural gyrolite (table II) over the whole range of spacings from 22 Å. to less than 1 Å.

## B. DISCUSSION.

### 1. *The existence of layers.*

The marked basal cleavage strongly suggests that gyrolite resembles the micas and clay minerals in having a layer structure. This is supported by the character of the 000 $l$  reflections, which are always thin, sharp arcs of closely defined spacing. This is true even in the case of very poor crystals; when these are mounted with the  $c$ -axis perpendicular to the X-ray beam, the  $hkil$  reflections are very weak and indefinite, but the 000 $l$ 's are still sharp and of approximately their usual intensities. Whatever type of disorder may occur does not, therefore, affect the spacings in the direction of the  $c$ -axis. This would be accounted for by a layer structure, in which the chemically discrete layers could readily be displaced parallel to each other.

### 2. *Composition of the layers.*

The observed space-group,  $C6_1$ , indicates that the unit of pattern is a layer 22.13 Å. thick, and containing one-sixth of the cell contents. The layer thus contains 8 molecules of approximate composition



The fact that a product, giving a powder photograph identical with that

<sup>1</sup> L. Heller and H. F. W. Taylor, Journ. Chem. Soc. London, 1951, p. 2397. [M.A. 11-471.]

of natural gyrolite, can be made artificially from pure materials, shows that the alumina and other minor constituents in the natural mineral are not essential to the structure.

### 3. *Nature of the layers.*

The results of the dehydration experiments show that three-quarters of the water is lost in the first stage of the dehydration, and that this does not cause any fundamental change in the structure. Loss of the remaining water, on the other hand, brings about transformation to a different compound. This suggests that three-quarters of the water is present as molecules, and one-quarter probably as hydroxyl groups, which would be in accordance with the formula  $\text{Ca}_4(\text{Si}_6\text{O}_{15})(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ , assigned by Betekhtin,<sup>1</sup> but he does not state on what grounds his view was based. It is, of course, not certain that some or all of the hydroxyl is not attached to silicon. However, the lamellar nature of the material suggests that the anion probably has the empirical formula  $\text{Si}_2\text{O}_5$ , giving rise to infinite sheets of linked  $\text{SiO}_4$  tetrahedra, rather than a more basic composition which would produce a chain or ring type anion.

Sheets of  $(\text{Si}_2\text{O}_5)_n$  composition, which are known to occur in silicate minerals, are of at least two kinds, which may be described as the mica type and the apophyllite type respectively. The hexagonal symmetry of gyrolite leads to a comparison with the first of these.<sup>2</sup> The unit cell of the mica-type sheet is hexagonal, with  $a$  5.2 Å., and contains a single  $\text{Si}_2\text{O}_5$  group. For comparison with gyrolite it is possible to select a larger hexagonal cell, with  $a$  9.0 Å. and containing three  $\text{Si}_2\text{O}_5$  groups. Assuming tentatively that sheets of this kind are present in gyrolite (which has  $a$  9.72 Å.), each 22.13 Å. layer would contain four such sheets. This appears not unreasonable, by comparison, for example, with talc and antigorite, which contain four sheets in thicknesses of 18.8 Å. and 28.6 Å. respectively (Brindley).<sup>3</sup> The observed volume per oxygen atom for gyrolite, of 22.7 Å.<sup>3</sup>, suggests a fairly open structure, which is also in agreement with this hypothesis.

The assumption of  $(\text{Si}_2\text{O}_5)_n$  sheets of the mica type nevertheless raises serious difficulties. The  $a$ -axis of such a sheet can be stretched from

<sup>1</sup> A. G. Betekhtin, *Mineralogia*, Moscow, 1950, p. 877. [M.A. 12-1.]

<sup>2</sup> The space-group shows that the layers do not necessarily possess any symmetry, but the fact that they are stacked on top of each other with successive angular displacements of 60° suggests that their essential framework at least approximates to hexagonal symmetry.

<sup>3</sup> G. W. Brindley (editor), *X-ray identification and structures of clay minerals*, Min. Soc., London, 1951, pp. 72, 311, &c. [M.A. 11-253.]

9.0 to 9.72 Å. only if the bond angles of the  $\text{SiO}_4$  tetrahedra are seriously distorted, or alternatively by stretching the Si-O bonds to over 1.7 Å. A similar problem arises in the case of cronstedtite, where this axis has a value of 9.49 Å., but this was accounted for by Hendricks<sup>1</sup> on the assumption that silicon was replaced by the larger  $\text{Fe}^{3+}$  ion. It is difficult to imagine that the  $\text{Ca}^{++}$  ion could replace silicon in this way. The structure of the gyrolite layers thus remains to be determined.

#### 4. Patterson projection.

The long series of 000*l* reflections (28 observed) invited an attempt to obtain information on the structure of the layers by carrying out a one-dimensional Patterson projection along the *c*-axis. The resulting synthesis showed strong interlayer vectors of lengths 1.5, 3.0, and 7.0 Å. This is little more than could be seen directly from the intensities, and no useful deductions could be drawn from it.

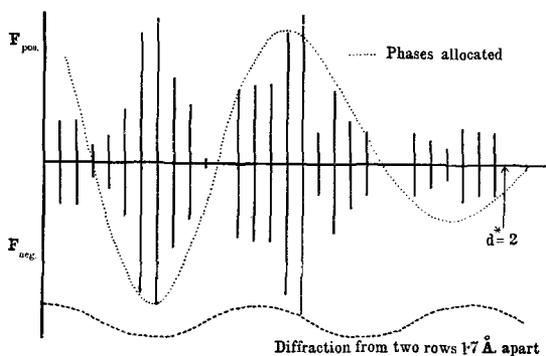


FIG. 2. Fourier synthesis, 000*l* reflections of natural gyrolite.  $F_{000l}$  plotted on an arbitrary scale both positively and negatively for allocation of signs.

#### 5. Fourier synthesis.

Inspection of the row of 000*l* reflections (fig. 2) shows that the variations in intensity occur smoothly from one reflection to another. This at once suggests, in spite of the absence of a centre of symmetry, a speculative attempt to allocate phases for a one-dimensional Fourier synthesis following the method of W. L. Bragg.<sup>2</sup>

On the whole, in layer minerals, interatomic distances projected on to a line perpendicular to the layers are of the order of 1.7 Å. The transform of this spacing is drawn out below the observed amplitudes to give

<sup>1</sup> S. B. Hendricks, *Amer. Min.*, 1939, vol. 24, p. 529. [M.A. 7-496.]

<sup>2</sup> W. L. Bragg, Guthrie Lecture. *Proc. Physical Soc., Sect. B*, 1952, vol. 65, p. 833.

a guide as to how quickly the latter can change sign. When a synthesis with the indicated signs was carried out, the result was unpromising, giving only a small peak at the origin with large peaks 1.5 Å. to each side of it. Other density deviations from the general level were small.

Patterson and Fourier syntheses may be useful in deciding between various hypotheses as to the nature of the layers, but are not really helpful in setting up a tentative structure in the present case. The hypothesis adopted for allocating the signs is only valid if the 22.13 Å. layers are centrosymmetrical in the projection, and there is no convincing reason to suppose that this is so.

#### 6. Conversion to $\alpha$ -wollastonite.<sup>1</sup>

The formation of  $\alpha$ -wollastonite on complete dehydration is of interest, since this compound is unstable relative to the  $\beta$ -form at temperatures below 1125° (Muan and Osborn).<sup>2</sup> Evidence of its formation from gyrolite was, however, obtained in the present investigation at temperatures as low as 700°. The explanation must lie in the fact that, on account of the close structural relationship between the two compounds, the energy of activation for the change from gyrolite to  $\alpha$ -wollastonite is much less than that from  $\alpha$ - to  $\beta$ -wollastonite. The latter transition, however slow, must nevertheless take place eventually, on sufficiently prolonged heating at any temperature below 1125°. Inspection of the photograph reproduced in pl. XII, fig. 4, shows the presence of certain pairs of spots, which are unlikely to be due to  $\alpha$ -wollastonite, and it appeared possible that these were due to  $\beta$ -wollastonite.

This was confirmed when a crystal of gyrolite was annealed at 1050° for four days. X-ray photographs showed complete conversion to  $\beta$ -wollastonite. Like the transition from gyrolite to  $\alpha$ -wollastonite, this further transition from the  $\alpha$ - to the  $\beta$ -form occurs in an ordered way, apparently six crystals of  $\beta$ -wollastonite being produced from the original crystal of gyrolite. The orientation of these relative to that of the original gyrolite crystal was not fully determined, but the pairs of reflections visible in pl. XII, fig. 4, were identified as the strong reflections (320,  $d$  2.97 Å.)<sup>3</sup> of the  $\beta$ -wollastonite crystals.

<sup>1</sup> Throughout this paper,  $\alpha$ -wollastonite denotes pseudo-hexagonal pseudo-wollastonite  $\alpha$ -CaSiO<sub>3</sub>;  $\beta$ -wollastonite may indicate either triclinic wollastonite or the very similar monoclinic parawollastonite, or an intimate intergrowth of the two.

<sup>2</sup> A. Muan and E. F. Osborn, preprint of paper read at the American Iron and Steel Institute, May 1951.

<sup>3</sup> Indices on M. Barnick's unit cell for the monoclinic form; Naturwiss., 1935, vol. 23, p. 770; Strukturber., 1936, vol. 4, p. 207. [M.A. 6-332.]

The structural similarity between gyrolite and  $\alpha$ -wollastonite is evidently very close, being shown:

- (a) by the relationship in symmetry, or pseudo-symmetry;
- (b) by the similarity in  $c$ -axial lengths; and especially,
- (c) by the relationship between the  $\{21\bar{3}0\}$  planes in gyrolite and the  $\{11\bar{2}0\}$  planes in  $\alpha$ -wollastonite. The reflections corresponding to these planes are strong in each case, the spacings are similar (3.18 and 3.42 Å. respectively), and when  $\alpha$ -wollastonite is formed by the dehydration of gyrolite, the orientations of its  $\{11\bar{2}0\}$  planes are identical with those of the  $\{21\bar{3}0\}$  planes of the gyrolite.

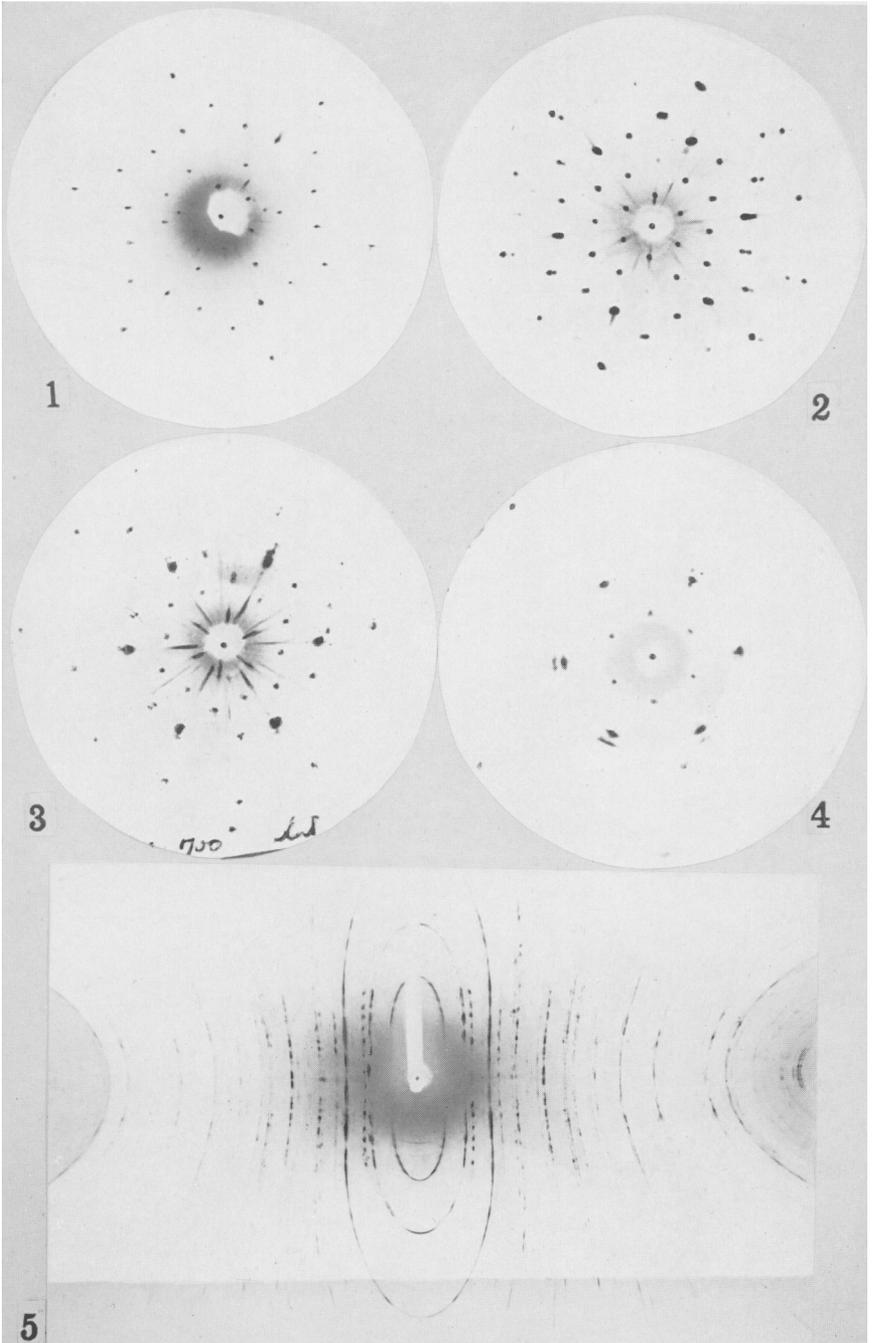
The co-existence of gyrolite and  $\alpha$ -wollastonite in the crystal heated to 700° shows in a particularly convincing way that a very high degree of order is maintained throughout the process of dehydration. There is no evidence of the formation of any intermediate, amorphous stage. It may, however, be noted that gyrolite is richer in silica than is  $\alpha$ -wollastonite. The absence of any evidence of crystalline silica in the X-ray photographs of the dehydrated material suggests that the excess of silica must be expelled from the structure in an amorphous condition.

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#### EXPLANATION OF PLATE XII.

X-ray photographs of gyrolite from Bombay.

- FIG. 1. X-ray stationary crystal photograph. Incident beam parallel to the sixfold axis. Filtered copper radiation.
- FIG. 2. As fig. 1, but crystal oscillated through 15° symmetrically about the stationary position.
- FIG. 3. X-ray stationary crystal photograph. After heating to 700°. Incident beam parallel to the original sixfold axis. Filtered copper radiation.
- FIG. 4. X-ray oscillation photograph. As for fig. 2, but after heating the crystal to 1000°.
- FIG. 5. X-ray rotation photograph about  $c$ -axis. Filtered copper radiation.



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