

The crystal structure of some chamosite minerals.

(With Plate XII.)

By G. W. BRINDLEY, Ph.D., F.Inst.P.

Reader in X-ray Physics, The University, Leeds.

With an appendix: *Geological and petrographical notes.*

By Prof. K. C. DUNHAM, Mr. V. A. EYLES, and Prof. J. H. TAYLOR.

[Read in part at the Clay Minerals Group meeting, April 9, 1949.]

1. *Introduction.*

CHAMOSITE is a commonly occurring hydrous ferrous silicate frequently found in close association with chalybite in marine mudstone deposits, the composition of different beds ranging from almost pure chamosite to pure chalybite. In oolitic ironstones chamosite is found both in the ooliths themselves and also in the groundmass. It occurs as a constituent in shales, as a cementing mineral in sandstones, and is occasionally found in lateritic and other deposits. Mineralogically it is usually regarded as a chlorite, or akin to the chlorites, but evidence has been accumulating which tends to show that some varieties may not be chlorites at all, but are probably closely related to the kaolin group of minerals (Brindley, 1949).

Following a preliminary announcement of these results by the present writer at the Clay Minerals Group meeting, April 1949, Orcel, Hénin, and Caillère (1949)¹ examined a number of micaceous minerals in oolitic iron ores both by X-ray and by thermal methods. Out of fifteen specimens they found three with a kaolin- or antigorite-type structure and nine with a chlorite-type structure. Independently, Brindley and Youell have also applied thermal methods and obtained confirmatory evidence that the chamosites previously studied by the writer had indeed a kaolin-type rather than chlorite-type of structure. Commenting on their results, Orcel, Hénin, and Caillère remarked (1949, p. 135): 'On désigne donc sous le nom de chamosite des minéraux cristallographiquement différents.' This clearly indicates that there is a problem of nomenclature to be solved. The writer considers, however, that this question

¹ References, p. 521.

can best be solved by agreement between those who have worked on the structure and identification of this mineral (or these minerals), and in the present paper the term 'chamosite' will continue to be used for minerals which will be shown to have a kaolin-type of structure.

2. *Survey of previous work.*

The earlier classification of chlorites rested largely on chemical analyses (cf. Tschermak, 1891; Orceel, 1927; Hallimond, 1939). Hallimond has discussed the relation of chamosite to the chlorites from the chemical standpoint and has shown how difficult it is to arrive at any firm conclusion. Physical data, however, such as dehydration curves, thermal curves, and more particularly X-ray diagrams, show distinctive differences between chamosites and chlorites. It seems, therefore, not unlikely that differences of structure may exist which are not accompanied by any clearly marked differences of composition.

Hallimond's paper contains a detailed report by Bannister of an X-ray comparison of several chamosites with a number of iron-bearing chlorites. His powder diagrams for six chamosites 'are very similar to each other, but are distinct from those of thuringite, daphnite, &c.' (Hallimond, 1939), which give typical chlorite diagrams. Bannister considered that the chamosite diagrams, though differing among themselves, were sufficiently distinctive to enable this mineral to be recognized from its X-ray diagram, and that the individual differences may have originated from variations in the size and degree of orientation of the crystallites, in their chemical composition, in the unit-cell dimensions, or in their crystal structures. He also noted that other minerals, namely amesite and cronstedtite, at that time regarded as chlorites, gave distinct powder diagrams and both of these have since been shown (amesite by Gruner, 1944, and cronstedtite by Hendricks, 1939) to be closely allied as regards their structures to the kaolin group of minerals.

It was unfortunate that Bannister did not, in this investigation, record the 14 kX line which is very characteristic of chlorite structures. This spacing corresponds to the thickness of one layer of the chlorite structure, and the observation of a 14 kX reflection (if it is not due to an impurity) shows at once that the mineral has essentially a chlorite-type rather than kaolin-type of structure. For reasons given in detail later, it cannot immediately be inferred that a mineral is of kaolin-type if a 14 kX reflection is not observed and a strong line at 7 kX is obtained. In a subsequent investigation (Bannister and Whittard, 1945) of a magnesian

chamosite, so called because of its 'mode of occurrence and physical properties', a strong 14 kX line was observed together with its second, third, and fourth orders. This is typical of chlorite powder diagrams and there are no grounds for doubting that this magnesian chamosite has a chlorite-type of structure. In this paper Bannister also gives X-ray data for an iron-ore chamosite from Frodingham and records the absence of an observable reflection at 14 kX, but (as stated above) this alone provides no certain proof of the nature of the structure.

An investigation of thuringite, bavalite, and chamosite by Engelhardt (1942) showed that the first two are practically identical with each other and closely similar to sheridanite, a typical iron-bearing chlorite; Bannister (see Hallimond, 1939, p. 461) had previously arrived at the same conclusion. Engelhardt also finds that chamosite gives an X-ray diagram different from those of well-authenticated chlorites. He interpreted his chamosite data in terms of a structure closely resembling that of normal chlorites, consisting of layers of the same type, but arranged according to orthorhombic instead of monoclinic axes. Engelhardt's data agree generally with the spacings and intensities to be expected from this structure, but the total number of recorded reflections is not large and the structure cannot therefore be tested very critically.

Engelhardt observed a 14 kX line of weak intensity which is characteristic of chlorites rich in iron. Apart from this line, the evidence for a chlorite structure is rather slender. As regards other basal reflections, the lines indexed as (002) and (004) could be the usual strong lines (001) and (002) of a kaolin-type structure, the existence of (003) is doubtful because it coincides with (020), the (005) line is confused by a chalybite line, and higher orders are not observed. As regards other reflections, nine altogether, their l indices are *even* numbers, which suggests that a cell of half the height may be correct, while their h and k indices correspond to reflections which always tend to be prominent from both chlorite- and kaolin-type structures. The available data, therefore, do not permit a very detailed analysis to be made. Nevertheless, the existence of the 14 kX line points clearly to a chlorite-type of structure and the solution given by Engelhardt is very probably correct for the variety of chamosite which he examined.

Sudo (1943) has given X-ray and other data for a number of low-temperature hydrous silicates found in Japan. He confirms that chamosite has a powder diagram essentially different from that of chlorites and that it is a variable material, but he obtains no further information regarding the structure of this mineral.

3. *The present experiments.*

These have been carried out using chamosites from a variety of sources. They were all microcrystalline materials which could be investigated only by the powder method. In order that the X-ray data should be as complete as possible a 20-cm. diameter semi-focusing type of camera was employed, with filtered Co- $K\alpha$ radiation. The experimental arrangement entails packing the powder into a flat, shallow cavity (about $4 \times 2 \times 0.5$ mm.) in a glass plate. When fine powders of 'clay-like' materials are used, no adhesive is required to retain the powder in the holder, and provided the cavity is filled without unnecessary pressure and without smoothing the surface repeatedly, the preferential orientation of the particles is not very marked.

The method requires rather more powder than the minimum necessary to coat a fibre, and in the present experiments the material investigated was carefully selected under a powerful hand-lens and only apparently homogeneous green-coloured material was used. This is not by any means an infallible method for choosing material, but reliance was placed mainly, indeed almost entirely, on the X-ray powder diagrams themselves. From the six most satisfactory materials examined, which came from a wide range of localities, it was clear that the chamosite minerals in all of them yielded very similar patterns of lines (pl. XII). Some differences were noted, which will be discussed later, but they were not of such a kind as to suggest that essentially different minerals were being examined.

Other tests consisted in treating the material with hot, dilute HCl and examining any residue. This served to identify, for example, the presence of several per cent. of anatase and some rutile in one specimen (no. 874, see below) and a large proportion of kaolinite in another specimen, which was therefore discarded. Quartz and any other coarse material present after crushing or light grinding was largely removed by sedimentation.

The writer now places considerable reliance on a combined thermal and X-ray examination of these materials. This will be reported more fully in a separate note by Brindley and Youell, but it may be briefly described here because it has now been applied to three of the chamosites discussed in the present paper and fully confirms the X-ray conclusion, viz. that these chamosites have a structure similar to that of kaolinite. The principle of the method depends on the fact that in a kaolin- or antigorite-type of structure, the (OH)'s are associated with a *single* octahedral layer in the structure, whereas in a chlorite-type of structure

they are associated with two layers, a brucite-type layer and a talc-type layer. In all the cases yet examined, the dehydration of the brucite layer precedes that of the talc layer and the intermediate stage yields a characteristic X-ray pattern (Brindley and Ali, 1950; since this paper was published other chlorites including iron-bearing chlorites have been examined and they give similar results). This does not happen with kaolin-type structures, which appear to dehydrate and decompose in a single process. This method has been used by OrceI, Hénin, and Caillère (1949) and independently by Brindley and Youell.

TABLE I. Chemical analyses of some chamosites.

	No. 874 Ayrshire.	Wabana, Newfoundland.	Frodingham, Lincolnshire.	Schmiedefeld, Thuringia.
SiO ₂	22.03	21.40	24.9	26.65
Al ₂ O ₃	22.91	25.40	15.6	16.14
Fe ₂ O ₃	0.46	0.25	7.2	6.69
FeO	36.68	37.60	35.0	34.43
MgO	1.91	2.04	4.6	4.47
CaO	0.07	0.13	—	—
Na ₂ O	0.08	—	—	—
K ₂ O	0.03	—	—	—
H ₂ O +	10.65	} 12.02	(12.3) {	11.42
H ₂ O -	0.63			0.08
TiO ₂	3.63	0.89	—	trace
P ₂ O ₅	0.18	—	—	—
MnO	0.04	0.05	0.4	—
CO ₂	0.40	0.22	—	—
SO ₃	0.27	—	—	—
Cr ₂ O ₃	0.05	—	—	—
Organic	0.03	—	—	—
	100.05	100.00	100.00	99.88

No. 874. Geol. Survey Lab. (Analyst, B. E. Dixon.) Data from Mem. Geol. Survey, Scotland, 1930, Economic geol. Ayrshire coalfields, area III.

Wabana, Newfoundland. Analysis and material supplied by Dr. K. W. Andrews, United Steels Ltd., Stocksbridge. Figures given are obtained after deducting free quartz from total SiO₂ and recalculating to 100.

Frodingham, Lincolnshire. Geol. Survey Lab. no. 1015. (Analyst, C. O. Harvey.) After deducting carbonates, &c., and calculating to 100, assuming 12.3% H₂O. (A. F. Hallimond, Min. Mag., 1939, vol. 25, p. 445.)

Schmiedefeld, Thuringia. Data from H. Jung, Chem. Erde, 1931, vol. 6, p. 275. [M.A. 5-40.]

4. *The chamosites used in the present investigation.*

Results will be reported for materials from the following localities:

1. Ayrshire, Scotland. (No. 874, Geol. Surv. Lab.)
2. Knowehead, Co. Antrim, Ireland. (C/1 from Mr. V. A. Eyles, Geol. Surv. Lab.)

3. Carnlough, Co. Antrim, Ireland. (B/O, Mr. V. A. Eyles.)
4. Wabana, Newfoundland. (Wabana, Dr. K. W. Andrews, United Steels Ltd.)
5. Kongsberg, Norway. (B.M. 34121, Dr. F. A. Bannister.)
6. Finedon, Northamptonshire, England. (E. 20568, Prof. J. H. Taylor. Geol. Surv. Lab.)

Geological and petrographical notes on these materials are given in the Appendix (p. 522).

Two only have been chemically analysed and these data are given in table I, together with data for two other chamosites which have been taken from the literature. The analyses of the no. 874 and Wabana materials are very similar to those of other chamosites; they show relatively little Fe_2O_3 and correspondingly more Al_2O_3 . The FeO content remains almost constant in these materials.

5. Powder data for six chamosites.

Table II records the measured spacings, estimated intensities, and a few details concerning the line profiles of the observed X-ray reflections. The results are contained in columns 1-6; column 7 gives data by Engelhardt (1942) and columns 8 and 9 data by Bannister (Bannister and Whittard, 1945).

The information summarized in this table, together with the powder photographs reproduced in pl. XII, show that, while differences exist between the results for different specimens, there is an overall similarity between them. These minerals have rather imperfect crystal-line structures which is indicated by the occurrence of diffuse bands of a type characteristic of irregular layer structures.

The powder diagrams of the present materials differ most remarkably in the group of spacings between 2.7 and 2.3 kX. Specimens 1, 2, and 3 of table II give a trio of clearly defined lines at about 2.67, 2.51, and 2.40 kX; the 2.51 kX line is always the strongest, but the intensities of the two outer lines are variable. Specimens 4, 5, and 6 show the first two lines only, the 2.40 kX line having disappeared entirely, and for specimens 5 and 6 the strong 2.51 kX line has become noticeably weaker and very diffuse. Other lines also are present with specimens 1, 2, and 3, such as the line at 2.01 kX, which are absent from 4, 5, and 6.

The data obtained by Engelhardt and by Bannister, columns 7 and 8 of table II, show general agreement with the data in columns 1-6, especially for the more consistently occurring reflections, but as regards

TABLE II. X-ray spacings and estimated intensities of X-ray powder diagrams of some chamosites.

1 874 Ayrshire.	2 C/I Co. Antrim.	3 B/O Co. Antrim.	4 Wabana, Nfld.	5 B.M. 34121 Norway.	6 E. 20568 Finedon.	7 Schmiede- feld.	8 Froding- ham.	9 Wickwar, Glos.
7.04 10	7.06 10	7.05 10	7.07 10	7.15 9	7.17 9	6.93 10	7.1 10	7.1 10
4.66 2†	4.66 3	4.66 3‡	4.67 4‡	4.61 3‡	4.65 2‡	4.65 5	4.63 5	4.73 2; 4.69 7
4.57 2	4.56 3	4.59 3	—	—	4.58 ½	—	—	—
4.27 ½	—	—	—	—	—	—	—	—
3.891 1	3.882 3	3.888 2	3.89 ½	3.898 ½	—	—	—	—
3.513 10	3.513 10	3.514 10	3.524 10	3.553 9	3.547 9	3.50 9	3.53 9	3.53 10
2.796 ?	—	—	—	—	—	2.779 3 s	—	2.83 5
2.673 4	2.667 8	2.668 9	2.699 3	2.675 2	2.681 4	2.689 1	2.69 7	2.69 2; 2.61 2
2.514 9	2.510 10	2.508 10	2.516 7	2.574 5‡	2.516 6‡	2.507 7	2.53 7	2.52 1; 2.60 1
2.399 4	2.396 9	2.397 10	—	—	—	—	2.47 4	2.46 4
—	—	—	—	—	—	—	2.40 4	2.39 4
2.332 ½	2.346 1	2.340 ½	2.342 ½	—	2.330 ½	2.330 ½	—	—
2.269 ½	2.274 1	2.269 ½	2.274 ½	2.28 ?	2.28 ?	—	—	2.28 2
2.137 6	2.135 5	2.134 4	2.143 4 b	2.143 ½	2.140 1	2.134 3	2.16 2	2.14 1
2.007 1	2.007 5	2.006 3	—	—	1.991 ½	—	2.02 1	2.08 1; 2.01 5
1.890 1	1.888 ½	1.883 ½	—	—	1.88 ?	—	—	1.89 2; 1.83 1
1.765 4	1.764 3	1.764 2	1.765 2 b	1.778 ½ b	—	1.767 2	1.78 1	—
1.69 ? a	—	—	—	—	—	—	1.74 1	—
—	—	—	—	—	—	—	1.72 1	1.72 2
1.662 ½ a	1.661 1	1.659 1	1.656 ?	1.66 ?	1.65 ?	—	1.68 2	1.67 2; 1.63 1
—	—	—	—	—	—	—	—	1.573 3
1.552 7	1.553 7	1.550 8	1.558 6	1.549 2 b	1.554 5	1.556 5	1.557 8	1.552 6
1.518 3	1.519 3	1.515 2	1.522 3	1.515 ½	1.518 2	1.524 2	1.524 7	1.517 4
—	1.484 2 b	1.488 1 b	—	1.484 ½	1.49 ?	—	—	1.479 1
1.470 1	1.469 1	—	1.477 ½	—	—	1.473 1	—	—
1.422 1	—	—	1.422 ½	1.42 ?	1.421 ½	1.425 1	1.427 4	1.424 4
1.404 ½	—	—	—	—	—	—	—	1.395 4
1.358 ½	—	—	—	—	—	—	1.350 2	1.361 1
1.344 ½	—	—	—	—	—	—	—	—
1.323 ½	—	—	—	1.32 ?	—	—	1.328 2	1.333 1

(1) to (6), Brindley and Goodyear (not previously published). Filtered Co- K_{α} radiation; camera radius, 100 mm.

(7), by v. Engelhardt (1942). Filtered Fe- K_{α} radiation, camera radius 57.5 mm.

(8), (9), Bannister and Whittard (1945). Unfiltered Fe- K radiation; camera radius 30 mm.

So far as is known specimens (1) to (8) are 'normal' chamosites; (9) is a magnesian chamosite.

a, lines wholly or partly due to anatase; b, unusually broad line; g, additional lines in this region probably due to goethite impurity; s, doubtful chalybite line; *, observed, but not measured; †, the head of a diffuse band shading to smaller spacings.

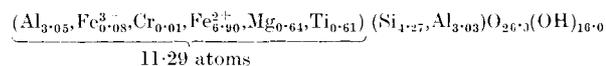
the 2·67, 2·51, 2·40 kX trio, Engelhardt finds only two lines and his material appears to resemble most closely the present no. 4. Bannister's data for the magnesian chamosite, column 9, contain many more lines than are ever found for 'normal' chamosites. Bannister's earlier data (Hallimond, 1939) also show general concurrence, but he gave consistently smaller spacings than those recorded in table II, especially for the lower orders.

The importance of determining whether a reflection occurs from a spacing of about 14 kX has already been stressed and has been studied with special care. No reflection which can be observed in powder diagrams occurs in this region from specimens 1, 2, 3, 5, and 6. Specimen no. 4 gave a very weak line at about 14 kX, which is probably due to a trace of chlorite impurity; this is also suggested by the thermal investigations by the writer and Youell (see section 11).

6. *Has chamosite a chlorite type of structure?*

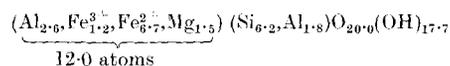
This question requires mainly a consideration of the intensities of the basal reflections. Chamosite does not give very well ordered aggregates, but specimens have been produced sufficiently well orientated to show that the strong reflections at 7·05 and 3·51 kX are basal reflections and from these the higher orders can be calculated and compared with recorded values. If the structure is of chlorite type, and if the thickness of a single chlorite layer, about 14 kX, is accepted as the basal spacing, then the 7·05 and 3·51 kX lines will be respectively (002) and (004). In what follows the data for specimen no. 1 (no. 874 from Ayrshire) will be mainly considered, since this was the only material for which a detailed chemical analysis was available when this work was begun. It also gives the clearest X-ray photograph. The analysis of this material (see table I) is very similar to that of other chamosites, especially as regards the iron content, and the calculation of the reflected X-ray intensities would be modified very slightly by using other chamosite analyses. The intensities depend very much more on the type of structure which is assumed than on *small* changes of composition.

In the ideal chlorite structure, the brucite layer has the composition $\text{Mg}_6(\text{OH})_{12}$, and the talc or mica layer $\text{Mg}_6(\text{Si}_8\text{O}_{20})(\text{OH})_4$; the combined formula is $\text{Mg}_{12}(\text{Si}_8\text{O}_{20})(\text{OH})_{16}$. The analysis in table I for the no. 874 material leads to the following chlorite-type formula:



k k

It is doubtful if the TiO_2 recorded in the analysis should be included in the chamosite composition, since X-ray examination reveals anatase and possibly rutile after dissolving out the chamosite with warm HCl. Since it is not certain that all the TiO_2 can thus be accounted for, the analytical figures have been accepted without corrections; in any case it makes little difference to the formula. It is satisfactory to find that the O/OH ratio works out to exactly 20:16. Engelhardt's formula for the material which he examined is as follows:



The main difference lies in the extent to which Si is replaced by Al; the 'octahedral atoms' are roughly the same.

TABLE III. Comparison of F_{001}^2 calculated for chlorite-type structures and observed data.

Structure (a), Fe atoms filling all sites in brucite layer.
 Structure (b), Fe atoms randomly distributed.
 Structure (c), Fe atoms filling all sites in talc layer.

<i>hkl</i>	<i>d</i> (kX).	Calculated data			<i>d</i> (kX).	Intensity.	Notes.
		(a).	(b).	(c).			
		$F^2 \times 10^{-2}$					
001	14.05	2	25	128	(14)	usually absent	1
002	7.03	330	330	330	7.04-7.06	10	—
003	4.684	333	156	47	4.65-4.67	2-3	2
004	3.513	487	487	487	3.513-3.514	10	—
005	2.810	32	109	230	—	—	—
006	2.342	27	27	27	2.330-2.346	0.5	—
007	2.007	108	41	5	2.006-2.007	3	—
008	1.756	5	5	5	—	—	—
009	1.561	2	4	30	—	—	3
0010	1.405	187	187	187	1.404	0.5	4
0011	1.277	0	10	40	—	—	—

Notes:

1. A very weak line is observed for specimen 4 only, which probably arises from an impurity.
2. The observed spacing is always less than (003). The reflection shows no enhancement due to orientation and its diffuseness and spacing both suggest (020) rather than (003).
3. An observed strong line at 1.550-1.558 is much more likely to be (060) than (009). Note that 4.65, the spacing of the probable (020), is exactly 3×1.55 .
4. This line was only recorded from an orientated specimen of no. 1.

The distribution of the 'octahedral atoms' between the brucite and talc layers cannot be decided immediately. Structures have been considered in which iron atoms occupy (a) all available positions in the

brucite layer, (c) all available positions in the talc layer, and (b) positions randomly distributed throughout both layers. The F_{001}^2 values calculated for these three distributions are tabulated in table III, where they are compared with the spacings and intensities of the nearest observed reflections.

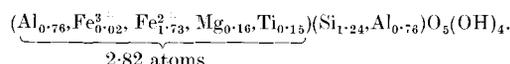
It is clear from table III that the observed data do not agree even qualitatively with any one of the three distributions. Moreover, since (a) and (c) are extreme cases in which the iron atoms are placed so far as possible wholly in the brucite or in the talc layer and (b) is an average case, one cannot hope to find any other distribution of the iron atoms in a chlorite-type structure which will fit the observed data more satisfactorily. Minor changes in composition would not materially alter this conclusion. *It is on these grounds that the conclusion is drawn that the chamosites examined in this investigation are not chlorite-type minerals.*

One result given in table III calls for special comment, namely the very weak intensity calculated for the 14 kX reflection when the iron atoms are concentrated in the brucite layer, i.e. arrangement (a). It is clearly possible for a chlorite-type structure to exist without any observable 14 kX line, but (and this is very important) there must also be strong or medium-strong (003) and (007) reflections. Engelhardt chose arrangement (b) for his structure and remarked that neither (a) nor (c) would fit the observed facts. But for the chamosites examined in the present work, (b) also is obviously wrong, since no trace of a line is found to correspond to (005) at 2.81 kX. It is unfortunate that Engelhardt's data are not conclusive on this point, since he suspected a chalybite line in this position. Moreover, the medium-strong (003) of arrangement (b) does not really fit the observations, since the observed line, although *near* to the (003) position, is certainly not correctly spaced for (003) and the character of the line, its band-like appearance, suggests (020) by comparison with other layer minerals. *The conclusion seems quite unavoidable that the structure is not that of a chlorite.*

Two other layer structures have been considered giving a 14 kX line and its higher orders, both of which were also considered by McMurchy (1934) in his work on the structure of chlorites. The first consists of kaolin-type layers with the kaolin units pointing alternately in opposite directions along the *c*-axis. The second arrangement consisted of the following sequence of layers: a kaolin layer, a talc layer, a kaolin layer of opposite orientation to the first, and a brucite layer. Both arrangements predict results quite incompatible with the observed data.

7. *Has chamosite a kaolin-type structure?*

The ideal formula of kaolinite is $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$, and of antigorite, $\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$. The composition of the chamosite specimen, no. 874, can be similarly written, namely:



There are therefore 2.82 atoms to occupy three octahedral positions, so that the composition is more nearly related to antigorite than to kaolinite.¹

Preliminary calculations of the basal intensities from a kaolin-type structure employing the atomic separations found in kaolinite itself showed very promising results; a more careful consideration was therefore given to the effect on the interatomic distances of replacing about 3 out of every 8 silicon atoms by aluminium and of filling octahedral positions with the larger Fe^{2+} ions.

The size of the tetrahedral $\text{Si}(\text{Al})\text{-O}$ group may be estimated from the basal plane dimensions. In kaolinite (Brindley and Robinson, 1946) b is 8.93 kX and in chamosite (see later) b is 9.31 kX. If the tetrahedral group is correspondingly expanded, the Si-O separation of 1.60 kX in kaolinite becomes 1.67 kX in chamosite, and the height of the tetrahedron, 2.19 kX in kaolinite, becomes 2.28 kX in chamosite. The value finally adopted for the height of the tetrahedron in chamosite is 2.34 kX, which gives a mean $(\text{Si}, \text{Al})\text{-O}$ distance of 1.71 kX.

The dimensions of the octahedral layer can be estimated from the known radius of the Fe^{2+} ion, which is about 0.83 Å, as compared with 0.57 Å, for Al. Assuming a regular octahedral grouping and taking the radius of oxygen to be 1.32 Å, we find for the thickness of an octahedral layer containing Al, 2.18 kX, and containing Fe^{2+} , 2.48 kX. Since the thickness found in kaolinite, 2.12 kX, is rather less than the calculated value, the same may be true for chamosite. The value finally adopted (arrangement (iii) of table IV) is 2.36 kX.

The observed and calculated reflected intensities are set out in table IV. The observed values include three reflections at 1.404, 1.165, and 1.004 kX obtained only with an orientated specimen of chamosite no. 874, which are not included in table II. Under the heading 'calculated data' are

¹ I shall, however, continue to refer to the structure as being of 'kaolin-type', meaning thereby that it is built of a tetrahedral Si-O sheet combined with an octahedral $\text{X-O}(\text{OH})$ sheet, which is characteristic of all the kaolin minerals. In this sense, the *structure* (though not the *composition*) of antigorite is also of kaolin-type.

given values of $F^2 A \phi(\theta)$ where F is the structure factor of the cell, A the absorption factor, and $\phi(\theta)$ includes the polarization and other angular factors which occur in the full expression for the reflected intensity, and θ is the Bragg angle of reflection. These are to be compared with the observed intensities in the final column. The table shows values for four sets of atomic parameters; altogether nine have been considered. While these four sets of parameters reproduce the main features of the experimental results, namely very strong (001) and (002) reflections and the remainder weak or absent, there is a progressive improvement in going from (i) to (iii) or (iv). The observed (001) and (002) reflections have comparable intensities with (002) just greater than (001) which agrees with arrangement (iv). The fact that (003) and (004) are absent is explained best by arrangement (iii). The last three reflections are scarcely visible and the fact that the calculated values exceed very little, if at all, the values for (003) and (004) is probably about right. On the whole, arrangement (iii) gives the best general agreement with the observed data. It is interesting to note that with these parameters, the layers of oxygen atoms are equally spaced throughout the structure, their heights above the basal plane being 0, 2.34, 4.70, and 7.03 kX.

TABLE IV. Comparison of observed and calculated basal reflections from chamosite assuming various kaolin-type structures.

I. Heights of atoms above basal plane of unit cell, in kX.

	(i).	(ii).	(iii).	(iv).	Kaolinite.
6 oxygens	0	0	0	0	0
2.48 silicons, 1.52 aluminiums ...	0.66	0.66	0.66	0.66	0.60
4 oxygens, 2 hydroxyls. ...	2.34	2.34	2.34	2.34	2.19
5.64 ¹ octahedral atoms ¹ , Fe ²⁺ , Al	3.33	3.42	3.52	3.58	3.25
6 hydroxyls	4.34	4.50	4.70	4.82	4.31

II. Comparison of observed and calculated basal reflections.

<i>hkl</i>	<i>d</i> (kX).	Calculated data				Observed data	
		$F^2 A \phi(\theta) \times 10^{-3}$				<i>d</i> (kX).	Estimated intensity.
i.	ii.	iii.	iv.				
001	7.026	448	367	276	219	7.04-7.06	10
002	3.513	329	315	268	236	3.513-3.514	10
003	2.341	19	14	11	11	2.333-2.346	0.5
004	1.756	3	6	13	21	—	—
005	1.405	13	16	23	27	1.404	0.5
006	1.170	17	18	16½	14	1.165 ¹	0.5
007	1.004	9	11	12	18	1.004 ¹	0.5

¹ These reflections were only recorded from an orientated specimen of no. 874 and are not included in table II.

The agreement between the observed and calculated values is obviously much better for the kaolin-type than for the chlorite-type structure. The final decision, however, must be based on a full consideration of the whole diffraction pattern. The agreement shown in table IV is, however, amply good enough to justify carrying the analysis further.

8. *A kaolin-type unit cell for chamosite.*

The unit-cell dimensions may be determined in a manner similar to that used for other layer silicate minerals. These generally give a strong (060) reflection in the neighbourhood of 1.5 kX, and the strong line consistently obtained at about 1.55 kX for chamosite may be tentatively indexed as (060). This is justified later (cf. table V). A comparison with the kaolin family of minerals suggests that the line at about 4.6 kX may be the (020). Considering the numerical data for specimen no. 874 of table II, we then have $d_{(020)}$ 4.66 kX, b 9.32 kX; $d_{(060)}$ 1.552 kX, b 9.312 kX.

For layer silicate minerals a is approximately $b/\sqrt{3}$. We therefore have provisionally a 5.38, b 9.31 kX, and the thickness of the layer can be taken as $2 \times d_{(002)} = 7.026$ kX. It remains to consider the direction of the c -axis. If the cell is monoclinic, it remains only to find the β -angle and this can be done by comparing $(1/d)^2$ for the observed reflections with a calculated plot of $(1/d)^2$ against β for all possible reflections.

This procedure leads to two values of β , each of which accounts for the majority of the reflections, namely, β 90° and β 103°–104°. The first value gives an ortho-hexagonal cell which recalls Engelhardt's solution, while the second gives a monoclinic cell closely similar to that of kaolinite, though the latter is strictly triclinic, as shown by Brindley and Robinson (1946). Although many lines are common to both these unit cells, at least so far as their *spacings* are concerned, certain lines, including some of quite considerable intensity, can be explained only by the one or the other cell. This raises the question whether the true unit-cell is larger than either and contains both of them as sub-units, or whether actual chamosites are mixtures of two forms.

The first of these possibilities was extensively investigated. The β -angle of about 104° corresponds to a displacement of successive layers by $a/3$, a displacement which occurs in many layer silicate minerals. As previously described (Brindley, 1949), an orthorhombic cell of height about 3×7 kX containing three kaolin-type layers is a possible solution so far as purely geometrical questions are involved (text-fig. 1); all the observed reflections can be indexed with this type of cell, and, if correct,

this would be a very interesting solution, because Hendricks (1939) has already arrived at a similar conclusion for cronstedtite. The immediate objections to it are: (a) that it predicts a much larger total number of reflections than are observed, and (b) that a 3-layer cell suggests a well-organized crystalline structure which, on general grounds, seems unlikely for a material so poorly crystalline as chamosite. Nevertheless, many arrangements of kaolin-type layers in a 3-layer cell have been systematically examined, but in every case they predicted strong reflections in positions where none are observed.

Further consideration was therefore given to the second possibility, namely, that two forms of chamosite exist, a monoclinic and an orthorhombic or ortho-hexagonal form. It was considered that such a mixture might explain the marked variations observed in chamosite powder diagrams and, as will now be shown, this seems to be confirmed by the detailed results.

The unit-cell dimensions giving the best overall agreement with the measured spacings are:

Ortho-hexagonal cell: a 5.38, b 9.314, c 7.026 kX.

Monoclinic cell: a 5.40, b 9.314, c $\sin \beta$ 7.026 kX, β 104.5°.

The a parameter of the ortho-hexagonal cell was taken to be exactly $b/\sqrt{3} = 5.38$ kX which differs scarcely appreciably from the figure 5.40 kX chosen for the monoclinic cell; no real difference is implied between these two parameters. The symmetry of the atomic arrangement is $C3m$, provided the octahedral positions are occupied randomly by Fe^{2+} , Mg, Al . . . atoms. For the monoclinic cell, a 5.40 was found to give the best agreement with the measured spacings and in so far as all the octahedral positions are equally filled, the space-group is Cm .

9. Comparison of observed and calculated data.

The calculated spacings and intensities for the hexagonal and monoclinic structures are set out in table V together with the observed data for specimen 1 of table II. The spacings have been calculated down to

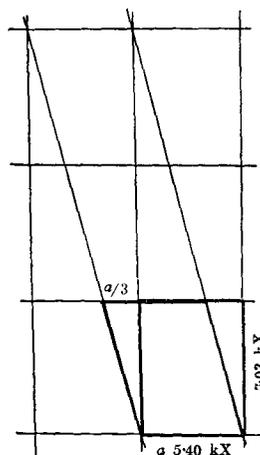


FIG. 1. Comparison of ortho-hexagonal and monoclinic unit-cells. The two cells are shown by heavy lines in projection on the ac -plane.

TABLE V. Comparison of observed data with calculated data for monoclinic and hexagonal structures.

$$I \text{ (calc.)} = pF^2\phi(\theta) \times 10^{-4}.$$

$$I \text{ (obs.)} = \text{Visually estimated intensities on scale } 10, 9, 8 \dots 1, \frac{1}{2}.$$

Monoclinic structure			Specimen no. 874 (See table II)		Hexagonal structure		
$d(\text{kX})$.	hkl .	I (calc.)	$d(\text{kX})$.	I (obs.)	$d(\text{kX})$.	hkl .	I (calc.)
7.026	001	70	7.04	10	7.026	001	70
4.657	020	7	4.66	2	4.657	020	21
4.559	110	14	4.57	2			
4.274	11 $\bar{1}$	11	4.27	$\frac{1}{2}$			
3.880	021	8	3.891	1	3.880	021	25
3.513	002	38	3.513	10	3.513	002	38
3.492	111	6					
3.132	11 $\bar{2}$	4					
2.804	022	3	2.796	?	2.804	022	7
2.679	20 $\bar{1}$	13	2.673	4	2.688	200	8
2.669	130	19					
			2.514	9	2.511	201	88
2.405	20 $\bar{2}$	27	2.399	4			
2.396	131	55					
			2.332	$\frac{1}{2}$			
2.271	201	4					
2.270	13 $\bar{2}$	9	2.269	$\frac{1}{2}$			
			2.137	6	2.210	041	2
					2.135	202	48
2.012	20 $\bar{3}$	8					
2.005	132	15	2.007	1			
					1.941	042	3
1.898	13 $\bar{3}$	5	1.890	1			
1.884	202	3					
			1.765	4	1.766	203	30
					1.760	240	2
			1.69	?	1.707	241	3
			1.662	$\frac{1}{2}$			
1.664	20 $\bar{1}$	6			1.651	043	2
1.658	133	12					
1.562	134	13					
1.561	203	5					
1.558	33 $\bar{1}$	14	1.552	7			
1.552	060	7			1.552	060	21
1.521	33 $\bar{2}$	3					
1.520	330	5	1.518	3			
1.516	061	4			1.516	061	11
			1.470	1	1.471	204	23
1.425	33 $\bar{3}$	2					
1.422	331	2	1.422	1			
1.420	062	2			1.420	062	6
1.405	005	3	1.404	$\frac{1}{2}$ ¹	1.405	005	3
					1.403	044	2
			1.358	$\frac{1}{2}$			
1.347	40 $\bar{1}$	1					
1.343	26 $\bar{1}$	5	1.344	$\frac{1}{2}$	1.344	400	2
			1.323	$\frac{1}{2}$	1.320	401	14
1.314	13 $\bar{5}$	5					
1.314	204	3					
1.307	400	3					
1.303	26 $\bar{2}$	4					

¹ Obtained from ordered aggregate specimen only.

a value of 1.3 kX and since both cells are centred on the *c*-face, reflections occur only when $(h+k)$ is an even number. The calculated intensities have been taken to be given by the expression $pF^2\phi(\theta)$, where F is the structure factor of the cell, p the multiplicity factor, and

$$\phi(\theta) = (1 + \cos^2 2\theta) / (\sin^2 \theta \cos \theta),$$

where θ is the Bragg reflection angle. No allowance has been made for absorption, which if included would reduce the calculated values for the lower orders relative to those for the higher orders. The total number of possible reflections from spacings greater than 1.3 kX is very great, being 88 for the monoclinic structure and 30 for the hexagonal. Many of these are extremely weak, and to avoid giving an unnecessarily extensive table, the weakest reflections have been omitted from table V. The strongest reflections have values of $pF^2\phi(\theta)$ of the order of 100×10^4 and all reflections weaker than 2×10^4 are omitted. In general, only reflections with $k = 3n$, where n is integral, are sufficiently strong to be incorporated in the table.

To facilitate the comparison of the observed and calculated results, the observed values for specimen 1 alone are incorporated in table V. It is evident that certain observed reflections are wholly monoclinic in origin, others are wholly hexagonal, while others are of mixed origin. It is seen that all the strong and medium-strong lines calculated for the two structures are present in the observed data with about the right intensities if the two types of structure are present in roughly equal proportions. Furthermore, all the observed spacings can be correlated very closely with the calculated values. The calculated results are compared with the powder diagram of material no. 874 in pl. XII.

It seems worth while, therefore, to inquire a little more carefully into the question of the relative proportions of the two components. If the important trio of lines already mentioned, at 2.67, 2.51, 2.40 kX, is considered, it is seen that a mixture of the two components of varying proportions will explain at least qualitatively the marked variation which is observed in their relative intensities. It will be sufficient to examine quantitatively the group of reflections from 2.67 down to 1.52 kX; higher-order lines are too weak to be usefully considered and likewise the lower orders, apart from the basal reflections which are of no help in this connexion.

Table VI sets out a comparison between the observed and calculated relative intensities for different proportions of the two components (monoclinic and hexagonal) for the chamosite specimens 1-6 considered in table II. The observed intensities are visual estimates and therefore

should not be taken too precisely; the calculated intensities are the sums of the $pF^2\phi(\theta)$ values scaled in each case to the value given for the 2.51 kX line. The assumed percentages of the two components are given at the head of each column. It is seen that the scheme accounts reasonably well for the observed variations of intensity from specimen to specimen and especially for the marked changes of the 2.67, 2.51, 2.40 kX trio.

TABLE VI. To illustrate the extent to which the powder data of chamosite specimens 1-6 can be interpreted in terms of a mixture of monoclinic (M) and hexagonal (H) forms.

d (kX)	55 % M, 45 % H			33 % M, 67 % H		10 % M, 90 % H			
	I (Obs.)			I (Obs.)		I (Obs.)			
	Observed, Specimen (1)	I (Calc.)	Specimens (2) (3)	I (Calc.)	Specimen (1)	I (Calc.)	Specimens (4) (5) (6)		
2.673	5	8	9	$2\frac{1}{2}$	4	1	3	2	4
2.514	10	10	10	10	9	7	7	5	6
2.399	11	9	10	$4\frac{1}{2}$	4	$\frac{1}{2}$	0	0	0
2.269	2	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	0	0
2.137	$5\frac{1}{2}$	5	4	$5\frac{1}{2}$	6	4	4	$\frac{1}{2}$	1
2.007	3	5	3	1	1	0	0	0	$\frac{1}{2}$
1.890	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1	0	0	0	?
1.765	$3\frac{1}{2}$	3	2	$3\frac{1}{2}$	4	$2\frac{1}{2}$	2	$\frac{1}{2}$	0
1.552	$7\frac{1}{2}$	7	8	$4\frac{1}{2}$	7	2	6	2	5
1.518	3	3	2	2	3	1	3	$\frac{1}{2}$	2

10. Disorder in the chamosite structures.

Fine-grained hydro-silicate minerals having structures of a layer type, such as the clay minerals, commonly show diffraction effects due to irregular stacking of the layers. A very frequent type of irregularity arises from displacements of layers parallel to the b -axis by integral multiples of $b/3$ and if these displacements are strictly random, then (hkl) reflections occur only when $k = 3n$. Now in the case of chamosite almost all reflections with $k \neq 3n$ are in any case too weak to be observed; note that in table V all reflections are recorded for which $pF^2\phi(\theta) > 2 \times 10^4$ and practically the only reflections with $k \neq 3n$ which can be observed separately are the (020), (110), and (11 $\bar{1}$). Of these, the (11 $\bar{1}$) is extremely weak and the (020) and (110) occur as a very close doublet. These reflections, however, show the characteristic banded appearance found with other minerals in which the layers are randomly displaced. Such displacements therefore probably exist in chamosite as in many other layer silicates.

An important question is whether the two forms (hexagonal and

monoclinic) occur separately or are closely intergrown. Since they differ only in the way the layers are stacked, there is no geometrical reason why they should not be intergrown. The question arises whether the two forms may occur in the form of a single structure with 'mistakes' in the sense used by Wilson (1949) in describing the structure of cobalt: this metal normally consists of a mixture of cubic and hexagonal forms as a result of 'mistakes' in the stacking sequence. The monoclinic and hexagonal forms of chamosite differ only in the arrangement of the layers relative to the a -axis, the monoclinic structure having an $a/3$ displacement and the hexagonal structure zero displacement in the a -direction between layers. A structure which contained a statistical distribution of $a/3$ and zero displacements between layers would give (hkl) reflections only for $h = 0, 3, 6, \dots$. Actually many strong reflections occur with $h = 1$ and 2. The two forms of chamosite cannot therefore be attributed to random a -axis displacements of layers within a single structure.

If the two forms are intergrown, the individual units must therefore be sufficiently well developed to diffract as individual crystals. Alternatively, the two forms may exist separately. Attempts to modify the ratio of the two forms by a differential acid attack has not yielded positive results.

11. *Thermal study of chamosite.*

Through the courtesy of Prof. A. L. Roberts of the Fuel Department of this University, Dr. R. W. Grimshaw recorded differential thermal analysis curves of specimens no. 874 and B/O. Since about half a gram of material is required for this purpose it is more difficult to obtain this quantity free from impurities than the small quantity required for X-ray analysis. The sample of B/O contained some impurities, mainly goethite and gibbsite, which also contributed to the thermal record. The goethite was also found in the X-ray examination, while the gibbsite was also recognized by X-rays, but was avoided in the material chosen for X-ray examination. The main fact which emerges from the thermal analysis is that the chamosite in both specimens shows a marked endothermic peak commencing at about 450° C. and having a maximum at about 550° C. This is very similar to the thermal behaviour of kaolinite, halloysite, and kaolin-type fireclays (Grimshaw, Heaton, and Roberts, 1945).

Following the X-ray and thermal study of magnesian chlorites by Brindley and Ali (1950), Youell and the writer have applied a similar

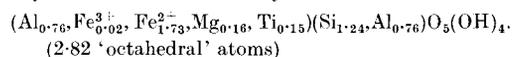
analysis to daphnite (an iron chlorite of very similar chemical composition to chamosite) and to the following chamosite specimens: no. 874 from Ayrshire, B/O from Co. Antrim, and the Wabana material. The enhancement of the 14 kX line from daphnite due to dehydration of the 'brucite' layer of the structure was entirely in accordance with the behaviour of other chlorites. The chamosites, however, gave no such effect, but showed a decomposition resulting in an amorphous state presumably similar to that of the kaolin minerals when heated to about 550° C. The very weak 14 kX line shown by the Wabana material was considered with particular care; when the bulk of the material had decomposed, this weak 14 kX line remained slightly enhanced. These results clearly suggested that the bulk of this material was similar to the other chamosites and of kaolin-type, with a small amount of chlorite impurity.

12. *Summary and conclusions.*

Previous X-ray examinations of chamosites by Bannister and by Engelhardt are discussed and also the recent X-ray and thermal studies of Orcel, Hénin, and Caillère on phylitic minerals in iron ores. Engelhardt suggested a chlorite-type structure for a Schmiedefeld chamosite, while Orcel et al. find evidence for both chlorite-type and kaolin- (or antigorite-) type structures.

X-ray powder data are presented for six chamosites from different localities. Detailed consideration of the recorded reflections and their intensities shows that a chlorite-type structure is unlikely for these materials. A kaolin-type structure is shown to fit the observed data, but two structural forms are thought to co-exist, a monoclinic form and an ortho-hexagonal form. The ratio of monoclinic to ortho-hexagonal form ranges from about 55/45 to 10/90.

For one analysed chamosite from Ayrshire, the formula can be written



Thermal examination of three of the six materials is briefly described. Differential thermal analyses by Grimshaw and combined thermal and X-ray study by Brindley and Youell support the view that these minerals have kaolin-type structures.

Finally, there is a question of nomenclature to be considered. The name chamosite is now so widely used and understood that probably only confusion would result if an attempt were made to restrict its use to either a chlorite-type or a kaolin-type of mineral. On the other hand,

if (as now seems certain) both structural types exist, then the question arises whether one name can continue to be used for two structural types. The writer prefers to leave this question of nomenclature open for the present.

Acknowledgements.—Finally, I wish to record my thanks to Dr. K. W. Andrews (United Steels Ltd., Stocksbridge), Dr. F. A. Bannister (British Museum), Mr. V. A. Eyles (Geological Survey), and Prof. J. H. Taylor (King's College, University of London) for materials used in this investigation, and for discussions on the chamosite problem. I wish also to thank Prof. K. C. Dunham (Durham University), Mr. Eyles, and Prof. Taylor for contributing the geological and petrographical notes given in the Appendix; it should be stated that this does not imply their acceptance of the views expressed in the paper.

I wish to acknowledge also that the data recorded in table II were obtained partly by Dr. J. Goodyear when working with me on the mineralogical composition of certain lateritic deposits. In connexion with the thermal study of chamosites, I wish to thank Dr. R. W. Grimshaw for differential thermal curves and Mr. R. F. Youell for assistance with the combined X-ray and thermal examination.

To the Department of Scientific and Industrial Research and to the Government Grant Committee of the Royal Society I tender thanks for grants providing, respectively, a research assistant and equipment.

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APPENDIX

Geological and petrographical notes on the chamosite materials employed in this investigation.

By Prof. K. C. DUNHAM, Mr. V. A. EYLES, and Prof. J. H. TAYLOR.

Geological data for specimens 87A, C/1, and B/0. By V. A. EYLES.

Material from Ayrshire (Geological Survey Lab. nos. 754 and 874).—Hard greenish-grey clay of Millstone Grit age, occurring in association with other clays of varying composition, some of which are lateritic in origin and derived from the alteration of olivine-basalts.

Material from Knowehead, Co. Antrim. (C/1).—Green-stained basaltic lithomarge (a kaolinized basalt) occurring in association with the Tertiary basalts of Antrim. The production of chamosite in the rock is believed to result from the action of reducing solutions acting on ferric oxide (or hydrated oxide) and halloysite present in the lithomarge.

Material from Carnlough, Co. Antrim. (B/0).—Green and buff lateritic lithomarge occurring in association with the Tertiary basalts of Antrim; a heterogeneous rock, the green portions of which contain chamosite probably similar in origin to the Knowehead chamosite (C/1), other parts of the rock, containing gibbsite, being truly lateritic in origin.

It is probable that the Ayrshire chamosite was formed under similar conditions to that from Knowehead and Carnlough, though the field evidence is not so clear on this point. I should think, in the case of the two specimens from Ireland, the chamosite was formed from halloysite;

and the Ayrshire chamosite could well have been formed in the same way, though possibly from kaolinite rather than halloysite. In each locality the mineral was formed, not by sub-aerial weathering, but as the result of climatic conditions at the surface which caused the formation and downward percolation of *reducing* solutions (laterite and lithomarge were originally formed under *oxidizing* conditions).

So far as I have investigated the matter, I do not think, either in Ireland or Ayrshire, that the chamosite, once formed, has suffered any alteration from sub-aerial weathering processes.

In the case of the Irish occurrences, it can be said that the rocks containing chamosite probably suffered a very mild degree of baking as a result of the heat action of later flows of basalt that covered up the interbasaltic horizon, and though the temperature attained is likely to have been somewhat lower than 150° C. it may have been maintained for a considerable time. As to pressure, the rocks were, subsequently to the formation of the chamosite, buried under a cover of some hundreds of feet of basalt.

In the case of the Ayrshire (Millstone Grit) chamosite, the rocks in which it is contained must have been buried subsequently to a depth of the order of 4000 feet by later formations, mainly sediments—in fact, I have suggested elsewhere that the formation of boehmite and some diaspore in associated rocks results from the pressure of the superincumbent rocks. Some rise in temperature as a result of burial is also implied—of the order of 30° to 40° C. above surface temperature, possibly rather more than this, as later the rocks were pierced by dikes, sills, and volcanic vents.

Petrographical data for specimens 874, C/1 and B/0. By K. C. DUNHAM.

Material from Ayrshire. (Geol. Survey Lab. no. 874; slice no. S. 22084.) 300 yards W. 20° N. of Gateside farm, 2 miles E. of Ayr; 1-inch S. 14, 6-inch Ayr 33 NE.—A pale greenish-grey rock, containing what appear to be angular fragments up to 0.15 mm. long of clear, pale-green, feebly-birefringent material. These are set in a matrix of very pale-green material, cloudy with tiny inclusions of the order of a few microns in diameter. Scattered through the rock there are opaque granules, mostly white by reflected light (opal or anatase?). The pale-green material has refractive indices within the range 1.640–1.650. A few small areas of chalybite, marginally oxidized, are present. (Anatase confirmed by X-rays, G.W.B.)

Material from Knowehead. (V. A. Eyles, C/1, Geol. Survey slice