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*A magnesian chamosite from the Wenlock Limestone
of Wickwar, Gloucestershire.*

(With Plates VIII and IX.)

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General description (W.F.W.).

THE Little Avon river rises on the scarp slope of the Cotswolds near Hawkesbury, 14 miles north-east of Bristol, and flows in a westerly direction over Mesozoic strata, until half a mile south-east of Wickwar it cuts through the Triassic mantle and exposes to view three inliers of Wenlock Limestone (Whittard & Smith, 1944, p. 65 and map). The West Gloucestershire Water Company was interested in the valley as a possible site for an impounded reservoir, and as part of a preliminary survey a trial-shaft was sunk into the Wenlock Limestone of the southernmost inlier situated near Sturt Bridge. The shaft penetrated 28 feet of dolomitized siltstones and crinoidal limestones, and at a depth of 4 feet it entered a band of calcareous chamositic siltstone averaging 9 inches in thickness. The shaft had been completed and the sides boarded before we heard it had been sunk; the hand-specimens were therefore obtained from the tip-heaps, but there is no doubt that all the material originated from the same horizon.

The chamositic bed rests upon dolomitized crinoidal limestone; in some places the latter was partly dried and cracked, possibly through exposure in the littoral zone, before the chamositic silt formed and infilled the cracks. The contact between the two rocks is generally sharply defined and suggests a period of non-deposition which, however, was of too short duration to be described as a non-sequence. In other examples the contact is less definite because the lower two or three inches of the chamositic bed include many pieces of dolomitized fine-grained limestone, numerous crinoid ossicles, and derived colonies of *Favosites* and *Halysites*. The limestone fragments are not crinoidal; they are characteristically bent, internally contorted, and frequently exhibit re-entrant angles (pl. VIII).

Such structures indicate that somewhere near at hand a plastic calcareous mud was comminuted and incorporated in the chamositic silt; elsewhere entombed colonies of corals were uncovered, and crinoid ossicles were separated and concentrated by aqueous action from a calcareous mud rich in fossil remains. The rock is thus an example of an intraformational breccia; Hayes (1915, p. 67, pl. X) has described a similar rock from the Wabana iron ore. Agitated sea-water may have eroded the calcareous mud; alternatively, the incidence of a profoundly different chemical environment in which the chamosite was formed may have resulted in acidity variations in the sea-water, which induced convection currents and these caused the break-up of the plastic mud.

The calcareous chamositic siltstone is green in hand-specimen and carries innumerable, almost black, shiny ooliths which show a crude bedding. Microscopically,¹ the ooliths of chamosite are well formed, exhibit none of the spastolitic shapes described from the Dogger of Yorkshire (Rastall & Hemingway, 1940, p. 265), and there are no clastic ooliths indicating redeposition; they are usually flattened, sometimes globular or irregular in form, and range from 0.2 mm. to 0.5 mm. in length (pl. IX, figs. 1, 2). The fresh mineral presents a rich green colour; it is markedly pleochroic, being greenish-yellow for rays vibrating parallel to the oolitic layers, which possess positive elongation, and grass green for rays vibrating at right angles; the refractive index is 1.620 ± 0.002 (Na) and the specific gravity² 3.034; these figures compare with 1.63 and 3.14, and 1.665 and 3.34, determined for the more ferriferous chamosites described by Deans (1934, p. 57) from the Coal Measures of Cottingley Beck, west Yorkshire and by Hallimond (1939, p. 445) from the Frodingham ironstone of Lincolnshire. The chamosite loses its strong green colour when weathered, becomes brown, and eventually breaks down into limonite. The smooth concentric layers of the ooliths are emphasized by dark dust, mainly composed of rutile (?), which is concentrated into impersistent tenuous bands (pl. IX, fig. 3); a nucleus invariably occurs and may consist of subangular or angular calcite, a fragment of a crinoid ossicle or a microfossil, finely divided reddish-brown limonitic dust, or finely divided rutile (?) dust which is frequently associated with platy chamosite. The mineral is also present in microfossils and is developed as a muddy infilling to shells in which the shell substance has also been replaced by chamosite; the fossils, which are probably derived, include minute spirally coiled gastropods and also ostracods nearly related to *Beyrichia* and *Leperditia*.

The groundmass is composed of two distinct but intermingled rock-types, a chamositic siltstone and a calcareous mudstone (pl. IX, fig. 4). The siltstone contains most of the ooliths, for these are relatively scarce in the mudstone, and it consists of innumerable small flakes of chamosite, clastic quartz up to 25 μ across, occasional rhombohedra of dolomite, and minute flakes of colourless minerals; the last, in cross-section, show straight extinction and positive elongation and are probably a mica, but those examples with lower birefringence may perhaps be kaolinite. The calcareous mudstone contains some calcite, but it is

¹ The rock is friable and difficult to section; the best results were obtained by completing the grinding of the sections with 3F carborundum mixed in propylene glycol. The latter is used without dilution; it is a hygroscopic alcohol, miscible in water, and reduces the tearing action on the section during grinding.

² Determined with Clerici solution and refractometer, corrected to 21° C.

composed mainly of dolomite and ankerite (pl. IX, fig. 5); chalybite is much less commonly developed as demonstrated by the hydrogen peroxide test (Hallimond, 1925, p. 39).

The chamosite is remarkably fresh and clear-coloured when the age of the deposit is taken into account. The Silurian rocks have obviously only recently been cleared of part of their Triassic mantle and had remained covered since the Triassic sediments were laid over them. The freshness and the high magnesia content of the chamosite may be attributed to the action of saline solutions which during Triassic times heavily dolomitized the Wenlock Limestone (Whittard & Smith, 1944, p. 73). That solutions rich in magnesium salts had direct access to the chamositic siltstone is clearly indicated in thin-sections where dolomite is common in the matrix, and in hand-specimens where cracks up to $\frac{3}{4}$ inch wide are now infilled by heavily dolomitized sediment of Triassic age which encloses small fragments of red and green Keuper Marl.

Occurring sporadically throughout all the slides, and particularly in the chamositic siltstone as distinct from the calcareous matrix, are spheruliths which can definitely be identified as phosphatic calculi or 'pearls' developed in polyzoa (pl. IX, figs. 6, 7). Oakley (1934, p. 296) determined their true nature and composition although other investigators, notably Sollas (1879, p. 501), had directed attention to their occurrence. The calculi are spherical to irregularly rounded in shape, of uniform size ranging from 0.3 mm. to 0.4 mm., white to yellowish-brown in colour, and exhibit a pearly lustre. In thin-sections they are usually colourless but may be yellow, possess a positive elongation in a direction parallel to the concentrically arranged layers, and under crossed nicols show a dark cross and a bluish-grey polarization colour; the refractive index is 1.605. The calculi effervesce in dilute hydrochloric acid, but not in 30 % acetic acid, as Mrs. Knight (1937, p. 5) ascertained when she investigated some of the limestones of Silurian age developed in the Malvern and west Midland outcrops; by using this strength of acetic acid she was able to isolate the calculi which occurred in the limestones detached from the parent polyzoa. The Wickwar calculi were hand-picked from a heavy mineral fraction separated from the crushed rock by the use of bromoform. According to Oakley the calculi are composed of dahllite, an apatite containing about 10 % of calcium carbonate. X-ray photographs of single pearls from Wickwar yielded weak powder patterns characteristic of apatite, but the weakness of the pattern may be due to the presence of some less well crystallized material.

Chemical and X-ray studies (F.A.B.).

In order to isolate oololiths for chemical and X-ray examination the siltstone was crushed and passed through sieves; the 60- and 40-mesh samples were placed in bromoform slightly diluted with benzene and the heavy fraction separated. This was hand-picked under a binocular microscope and a concentrate of chamositic oololiths selected for chemical analysis. In the first instance the chemical procedure followed was that of Ennos and Sutcliffe (1925, p. 115), although it was found necessary to boil the powdered oololiths in hydrochloric acid for five minutes. Appreciable quantities of copper and zinc were afterwards reported in a qualitative spectroscopic analysis, and a partial analysis was commissioned to determine the amounts of these constituents. Determinations of the total water content by the Penfield method and also of the water lost below 105° C.

were carried out on separate portions of the oololiths. The chemical analysis of the acid soluble portion of the mineral is given in table I.

TABLE I. Chemical analysis of magnesium chamosite, Wickwar, Gloucestershire.

		I.	II.	III.			I.	II.	III.
SiO ₂	...	20.35	26.40	24.9	P ₂ O ₅	...	0.85	—	—
Al ₂ O ₃	...	14.05	18.23	15.6	CO ₂	...	2.12	—	—
Fe ₂ O ₃	...	4.40	5.70	7.2	SO ₃	...	nil	—	—
FeO	...	19.94	25.87	35.0	Na ₂ O	...	0.13	0.17	—
MnO	...	0.03	0.04	0.4	K ₂ O	...	0.13	0.17	—
MgO	...	8.75	11.35	4.6	Insoluble	...	15.66	—	—
CaO	...	4.14	0.42	—	H ₂ O—	...	n.d.	1.05	—
TiO ₂	...	0.08	—	—	H ₂ O+	...	n.d.	10.60	[12.3]
							90.63	100.00	100.0

I. Chemical analysis by Geochemical Laboratories of 2.9 grams hand-picked oololiths, Wickwar, Gloucestershire. B.M. 1945,45. The sample was examined by methods similar to those adopted by Ennos and Sutcliffe (1925, p. 115). The acid extract was prepared by adding 150 ml. N/2 HCl to 0.7 gm. of rock powder, raising to boiling point in a period of 5 minutes, and then boiling for 5 minutes and allowing to cool for a further 20 minutes. The solution was filtered and the residue re-extracted in the same manner with 50 ml. N/2 HCl. The two acid extracts were combined and analysed. The insoluble residue was treated with 10% Na₂CO₃ solution and the silica so dissolved added to that in the acid extracts. In the case of the ferrous iron determination the extractions were made as described above, but omitting the Na₂CO₃ treatment, and the whole operation was carried out in an atmosphere of carbon dioxide. The ferric iron in this solution was rapidly titrated with titanous chloride in an atmosphere of carbon dioxide and the ferrous iron obtained by difference.

A further portion of 1 gm. was treated as above and the filtrate extracted with dithizone. This extract was shaken with dilute HCl to remove zinc and copper determined with sodium diethyl-dithio-carbonate; CuO 0.002%. Zinc could not be detected in the aqueous extract and is certainly less than 0.005%.

II. The total water content of a separate portion of hand-picked oololiths was obtained by heating $\frac{1}{2}$ gm. in a Penfield tube to a red heat and weighing the condensed water vapour. The figure obtained was 11.65%. Another portion of $\frac{1}{2}$ gm. lost 1.05% in weight when heated to 105° C. for 2 hours (F. A. Bannister). The partial analysis of column I was then recalculated omitting the insoluble residue, the phosphate and carbonate as dahllite and calcite, and the titania as rutile.

III. Chemical analysis by C. O. Harvey of chamosite from Frodingham, Lincolnshire, recalculated to 100%. (Hallimond, 1939, p. 445.)

Unfortunately the insoluble residue, amounting to 15.66%, has not been retained for study, and it was decided to prepare a fresh sample of the residue for thorough examination. Accordingly, $\frac{1}{2}$ gm. finely powdered oololiths was treated with hydrochloric acid and the silica set free removed with sodium carbonate solution following the procedure of Ennos and Sutcliffe. This treatment, however, is not always successful in completely decomposing the chlorite. Dixon found (1930, p. 99), in his analyses of chamositic mudstone from Ayrshire, that the times specified for acid treatment were insufficient; and Pulfrey (1933, p. 421) obtained a residue of 12% from a chlorite from Llandegai, North Wales, which completely dissolved when the times were doubled and the reaction carried out just below boiling point. In the experiment now being described, the weighed residue after filtering, washing, and drying was 50%, and the change from a green to a buff tint of the powdered chamosite was not complete. Accordingly, the modified treatment adopted in the chemical analysis by the Geochemical Laboratories was repeated on the residue. Instead of carrying out the acid reactions and silica solution in sodium carbonate on a steam-bath, the acid and

alkali solutions were boiled. Further attack on the chamosite residue took place and the green colour of the powdered ooliths disappeared. The weighed residue after both treatments was only 5.94 %, and yielded an X-ray powder photograph showing quartz as the dominant constituent. Having evaporated the supernatant suspension, obtained by shaking the residue with water, a second powder photograph showed that all the quartz had been removed and that the dispersed particles were chiefly rutile. This determination was confirmed by Dr. M. H. Hey, who reported much titanium present in a portion of the residue used for X-ray examination. Little difficulty was experienced in determining the quartz in the residue with the polarizing microscope, but rutile particles could not be recognized, probably because of their smaller size. No constituent in addition to rutile and quartz was determined with certainty, although one or two weak diffraction lines on the powder photographs remain unexplained. Hence the maximum content of quartz and rutile in the magnesian chamosite is 5.94 %.

We are now left with nearly 10 % of residue in the chemical analysis (table I) unaccounted for. So far as our experiments are concerned, and those of other workers who obtained a variable amount of residue when they varied the procedure of acid solution, this residue in addition to quartz and rutile was made up of residual chamosite. It has become apparent during the present work that the acid solution method is a valuable adjunct to a more direct method of chemical analysis, since it concentrates accessory minerals insoluble in acid in a form suitable for X-ray, spectrographic, and chemical examination. Direct analysis, including a proper determination of the water is, however, essential, particularly when, as in the present instance, the ooliths have been picked free from matrix and the principal accessory minerals successfully determined.

Hallimond decided from his study of the chemical composition of minerals of the chlorite family that chamosite cannot be distinguished solely by chemical analysis from iron-rich chlorites like daphnite, but that 'additional tests especially by X-ray and solubility' are 'essential for complete identification' (1939, p. 451). I have shown in an appendix to Hallimond's paper (p. 459) that X-ray photographs of chamosite are indeed diagnostic and serve to distinguish them from other members of the chlorite group. With this work in mind the present study was suggested. A few of the dark-green ooliths, hand-picked from the Wickwar siltstone for chemical analysis, were reserved for optical examination and X-ray study. These had been broken and wherever possible the nucleus was removed. X-ray rotation photographs of single oolith fragments from this sample were first taken, and the only visible differences in pattern revealed were due to the presence of a trace of relatively coarse-grained quartz in some of the ooliths. This mineral when present yielded only one very weak flecked diffraction line at 3.35 Å. Recent unpublished work by Dr. M. H. Hey and one of the authors on a bauxite, found to contain 2 % free silica as quartz, suggests that none of the single ooliths from Wickwar contains more than 5 % quartz and that the majority contain less. A powder photograph of a few ooliths and another obtained at a later date from a larger sample both yielded the same pattern as the individual oolith fragments, with a certain loss of definition of the weaker lines due to powdering. The single ooliths also yield, when suitably mounted on the X-ray goniometer, powder photographs with enhancement of the intensities of the lines due to the basal diffractions. A single oolith is therefore an aggregate

of tiny flakes mostly lying tangential to the surface. This effect of orientation of the individual flakes parallel to the surface of the ooliths is diminished in photographs of powdered ooliths. With due allowance for this orientation effect and the variability of the trace of quartz present, all the photographs of the Wickwar ooliths yield the same powder pattern of chlorite type with a strong basal reflection at 14 Å.

The pattern can be distinguished from that of iron-rich chamosite from Frodingham (pl. VIII, figs. 2 and 3), and it is also different from all chlorites I have so far examined, although it resembles that of diabantite (pl. VIII, fig. 5), a chlorite containing a high percentage of magnesium as well as ferrous iron. The powder data, given in table II, reveal those differences in pattern which are

TABLE II. Powder data for magnesian chamosite.

	1.	2.	3.	4.		1.	2.	3.	4.
002	14 s	—	—	15 Å. vs		—	1.74 vw	—	1.74 Å.mw
004	7.1 vs	7.1 vs	6.93 vs	7.15 s		1.72 w	1.72 w	—	1.70 mw
006	4.73 w	—	—	4.80 w		1.67 w	1.68 w	—	—
	4.69 ms	4.63 m	4.63 m	4.62 m		1.63 vw	—	—	—
008	3.53 vs	3.53 s	3.50 s	3.58 ms		1.573 mw	—	—	—
	—	—	—	3.04 mw	060	1.552 ms	1.557 s	1.556 m	1.545 ms
	2.83 m	—	2.779 mw	2.87 vw		1.517 m	1.524 ms	1.524 w	1.518 w
	2.69 w	2.69 ms	2.689 vw	2.66 m		1.479 vw	—	1.473 vw	—
	2.61 w	—	—	—		1.424 m	1.427 m	1.425 vw	1.427 mw
	2.60 vw	—	—	2.60 m		1.395 m	—	—	—
	2.52 vw	2.53 ms	2.507 ms	2.53 m		1.361 vw	1.350 w	—	—
	2.46 mw	2.47 mw	—	2.47 m		1.333 vw	1.328 w	—	1.331 w
	2.39 mw	2.40 mw	—	2.40 w		1.301 vw	1.303 w	—	1.303 vw
	2.28 w	—	2.330 vvw	2.29 vw		1.228 vw	—	—	—
	2.14 vw	2.16 w	2.134 mw	2.145 vw		1.183 w	—	—	—
	2.08 vw	—	—	—		1.136 vw	—	—	—
	2.01 m	2.02 vw	—	2.02 vw		1.104 vw	—	—	—
	1.89 w	—	—	1.90 vw		1.047 m	1.052 m	—	1.053 vw
	1.83 vw	1.78 vw	1.767 w	—		1.014 w	1.020 w	—	—

1. Magnesian chamosite, Wickwar, Gloucestershire; B.M. 1944.45. a 5.37, b 9.31, c^* 28.24 Å. (pl. VIII, fig. 3).

2. Chamosite, Frodingham, Lincolnshire. a 5.39, b 9.34, c^* 28.24 Å. (pl. VIII, fig. 2).

3. Chamosite, Schmiedefeld, Thuringia; 002 observed but not measured. (Engelhardt, 1942, p. 148.) a 5.39, b 9.34, c^* 28.00 Å.

4. Diabantite, Connecticut valley, U.S.A.; B.M. 53917. a 5.35, b 9.27, c^* 28.64 Å. (pl. VIII, fig. 5).

1, 2, and 4 are lists of the spacings in Ångström units and estimated intensities of X-ray powder photographs taken with unfiltered iron radiation, λ 1.934 Å., in a cylindrical camera, diameter 6 cm. Under 3 are listed von Engelhardt's measurements using iron radiation filtered with manganese, camera diameter 5.75 cm. c^* = $c \sin \beta$ is the basal spacing.

not so readily apparent on the reproduced photographs. The mode of occurrence and physical properties relate the Wickwar mineral more closely to chamosite than any other chlorite, whilst the partial chemical analysis shows that it differs from chamosites previously studied in possessing a much higher percentage of magnesium. The higher magnesium content is related to the lower specific gravity and refractive index and probably accounts for the difference in X-ray patterns. Although the chemical technique employed is not beyond criticism, we consider that the partial chemical analysis is sufficiently accurate to show that the Wickwar mineral is the first magnesium-rich chamosite to be described, and suggest that it should be referred to as a magnesian chamosite.

The only lines on the powder photographs of chamosite which can be indexed with certainty are the basal diffractions 00 l and the diffraction 060 (see table II). McMurchy (1934, p. 427), using a powder camera with larger diameter (11.46 cm.),

was able to index all the diffractions from sheridanite and then obtained good agreement between the observed intensities and those calculated on the assumption of Pauling's crystal-structure (1934, p. 580). Engelhardt (1942, p. 148) has given powder data for chamosite from Schmiedefeld using material previously studied by Jung (1931, p. 281), and his results obtained with filtered iron radiation in a camera 5.75 cm. diameter are also given for comparison in table II. It is apparent that his values are close to those for Frodingham material. He has attempted to index the observed diffractions, utilizing McMurchy's for sheridanite, but found that it was necessary to make β 90° , i.e. to use a unit cell of orthorhombic dimensions. He has then deduced a structure related to that of chlorite. An attempt to index the observed diffractions of magnesian chamosite by utilizing McMurchy's data and Engelhardt's assumption that β is 90° has not been successful, the number of possible indices for all lines other than those readily assigned to basal diffractions and 060 being high even for lines close to the centre of the film. It is difficult to see how any reliance can be placed upon indexing of the diffractions of general type hkl of a substance of orthorhombic or lower symmetry merely from a powder photograph taken in a small camera. Unless this can be done unequivocally, little progress can be made towards a more detailed study of the crystal-structure of magnesian chamosite. The relative intensities of the 00*l* lines, however, do show a correspondence with McMurchy's data, i.e. with increase in iron content 004 and 008 increase in intensity relative to 002, 006, and 0.0.10 (see table II). This at least suggests that the sequence of layers is similar in chamosite to those in Pauling's structure of chlorite, and that the replacement of magnesium by iron alters the relative intensities of the basal diffractions in a similar manner.

It is important in X-ray work on fine-grained sedimentary minerals to be sure that minor constituents are not overlooked. Owing to an intimate mixing of such minerals during deposition, physical separation is not always possible and even microscopic examination sometimes fails. The evidence must then be sought by X-ray methods. The orientation of chamosite flakes in the individual ooliths would also be probably accompanied by similar parallel alinement of flakes of any other mineral with a layer structure that may be present. The sensitivity of the X-ray method can be greatly increased for the determination of layer-structure minerals if an orientated aggregate of a fine-grained mineral sample is prepared. Accordingly, a few magnesian chamosite ooliths were crushed and deposited from a benzene suspension upon a thin film of cellulose acetate lying on a surface of water. The film was then mounted with its plane vertical and oscillation and rotation photographs taken. These showed enhanced basal diffractions, due to chamosite, of greater intensity than those previously obtained from individual ooliths, but no additional lines could be detected. No member of the mica group, therefore, is present in sufficient quantity to be recorded. A layer-structure mineral like kaolinite would be very difficult to detect in the presence of chamosite, owing to the coincidence of their strong basal diffractions. This mineral, however, is almost insoluble in N/2 HCl and would have been detected in the residue if present. So far the only accessory minerals that can be observed with certainty in the ooliths are quartz and rutile. Of these two, rutile would be difficult to detect on the powder photographs of the untreated ooliths, owing to the closeness of its strong powder-line spacings to those of quartz.

It is probable that most of the quartz found in the residue and all the phosphate and carbonate found by analysis are enclosed in the nuclei of the chamosite oolites. Some of these nuclei are probably similar to the matrix in composition. In the absence of any special study of the mineral composition of the matrix, we shall assume that the phosphate and carbonate are present as dahllite and calcite. These minerals account for 3.82 % of the lime found by analysis and only 0.32 % CaO is assumed to be combined in the magnesian chamosite. The small percentage of titania has been neglected on the assumption that it represents rutile dissolved in hydrochloric acid. In table I, therefore, the recalculated analysis omits carbonate, phosphate, and titania. The oxygen percentage thus obtained, combined with the specific gravity and probable unit-cell dimensions of magnesian chamosite derived from powder data, yields an (O,OH) content of 72.95, in fair agreement with the figure of 72 demanded by Pauling's chlorite structure.

TABLE III. Dimensions and atomic contents of unit cells of magnesian chamosite, &c.

		1.	2.	3.	4.	5.	6.
16	{ Si	11.32	11.50	11.43	11.69	11.96	12.20
	{ Al	4.68	4.50	4.57	4.31	4.04	3.80
12	{ Al	4.53	4.85	3.88	4.33	4.49	4.91
	{ Fe ^m	1.84	—	2.50	—	2.26	—
	{ Fe ^r	5.63	7.15	5.62	7.67	5.25	7.09
R	{ Fe ^r	3.65	4.14	7.80	8.56	7.66	8.39
	{ Mg	7.25	7.36	3.13	3.20	2.99	3.05
	{ Ca	0.19	0.20	—	—	—	—
	{ Mn	0.01	0.01	0.17	0.18	—	—
	{ Na	0.14	0.14	—	—	—	—
	{ K	0.09	0.09	—	—	—	—
	{ H	30.32	30.78	—	—	—	—
	{ R	11.33	11.94	11.10	11.94	10.65	11.44
	a (Å.)	5.37	—	5.39	—	5.39	—
	b	9.31	—	9.34	—	9.34	—
	c*	28.24	—	28.24	—	28.00	—
	Sp. gr.	3.034	—	3.34	—	3.19	—
	n	1.620	—	1.665	—	1.658	—

1. Magnesian chamosite, Wickwar, Gloucestershire; B.M. 1944,45. Atomic contents of unit cell calculated from chemical analysis, column 2, table I, excluding H₂O and assuming 72 (O,OH) per unit cell. The actual number of oxygens and hydroxyls calculated from chemical analysis, unit-cell dimensions, and specific gravity is 72.95.

3. Chamosite, Frodingham, Lincolnshire, calculated from C. O. Harvoy's analysis, column 3, table I (Hallimond, 1939, p. 445), assuming 56 oxygen atoms per unit cell.

5. Chamosite, Schmiedefeld, Thuringia, calculated from Jung's analysis (1931, p. 281), assuming 56 oxygen atoms per unit cell.

2, 4, and 6 recalculated from 1, 3, and 5 respectively, assuming that all the iron content was originally ferrous.

Table III shows that the atomic contents of the unit cell of magnesian chamosite yield a low summation of metal ions. This is true of all available analyses of chamosite and also of some other chlorites when they are calculated on a basis of 56 oxygen atoms. Holzner (1938, p. 389), following a suggestion of Winchell (1936, p. 642), recalculated various chlorite analyses on the assumption that the ferric content arose from oxidation of the ferrous ions in the crystal-structure subsequent to formation of the mineral. He adduces as evidence the low water content of such specimens and the summation of the metal ions to 40 per 56

oxygens when all the iron content is reckoned as ferrous. He also recalculated other analyses of ferriferous chlorites which possess normal water content and yield the ideal summation of 40 metal ions when the ferric content is counted as such. These chlorites he considers to be unchanged and to have possessed ferric ions at the time of their formation. There is little doubt that Holzner's assumptions are correct for certain chlorites; the ion summations are too close to 40 to be fortuitous. Moreover, it seems likely that fine-grained chamosites might very well have undergone partial oxidation since their formation. Certainly the recalculation of both the chamosite analyses on Holzner's assumption leads to excellent agreement with the structural formula for chlorites (see table III). That chamosites originally contained no ferric, only ferrous, ions is probably true, but low ion summations of the recalculated analyses may be explained by errors in chemical analysis or admixture of the chamosite with small amounts of undetected minerals soluble in acid. Table IV gives the unit cell dimensions

TABLE IV. Unit-cell dimensions and atomic contents of chlorites related in composition to chamosite.

		I.	II.	III.			I.	II.	III.
16	{ Si ...	10.82	9.67	13.69	<i>a</i> ...	5.40	5.37	5.35 Å.	
	{ Al ...	5.18	6.33	2.31	<i>b</i> ...	9.36	9.30	9.27	
	{ Al ...	5.40	3.33	3.06	<i>c</i> * ...	28.20	28.00	28.64	
12	{ Fe ^{'''} ...	0.71	3.04	0.70	Sp. gr. ...	3.08	3.187	2.79	
	{ Fe ^{''} ...	5.89	5.63	8.24	ω ...	1.655	1.662	1.612	
	{ Mg ^{''} ...	—	—	—	ϵ ...	1.646	—	—	
R	{ Fe ^{''} ...	7.59	9.11	0.41					
	{ Mg ^{''} ...	3.70	2.87	10.13					
	{ Ca ...	0.05	—	0.49					
	{ Mn ...	0.18	—	0.14					
	{ Na ...	—	—	0.20					
	{ K ...	—	—	—					
	R ...	11.52	11.98	11.37					

I. Daphnite, Tolgus mine, Cornwall; analysis by C. O. Harvey (Hallimond, 1939, p. 443).

II. Thuringite, Schmiedefeld, Thuringia; analysis by H. Jung (1930, p. 186).

III. Diabantite, Farmington Hills, Connecticut; analysis by G. W. Hawes (1875, p. 455).

and atomic contents for chlorites related in composition to chamosite. Chamosite and magnesian chamosite have approximately the same content of silicon; daphnite and thuringite have less; and diabantite markedly more. Diabantite also contains more magnesium than does magnesian chamosite, so that this pair of minerals can be distinguished from each other by chemical analysis more satisfactorily than iron-rich chamosite from daphnite and thuringite.

Whilst discussing the chemistry of chamosite it should be mentioned that the empirical formula $2\text{SiO}_2 \cdot \text{R}_2\text{O}_3 \cdot 3\text{RO} \cdot \text{aq}$, employed by Hallimond (1939, p. 446) is only a rough approximation to those proportions to be expected on the basis of Pauling's structural formula for the chlorites. The crystal-structure is based upon mica-like layers bonded, not by alkali atoms, but by sheets of brucite. The general formula for such a structure is $[\text{Si}_{16-n}\text{Al}_n][\text{R}_n'''\text{R}_{24-n}'']\text{O}_{40}(\text{OH})_{32}$. Values of total RO and R_2O_3 ($\text{SiO}_2 = 200$) and $\text{Si}/\text{Al}_{\text{IV}}^1$ for the tetrahedral layer can

¹ Al_{IV} represents aluminium atoms with fourfold co-ordination (i.e. forming tetrahedral groups AlO_4) which link up with SiO_4 groups to form the tetrahedral layer ($\text{Si} + \text{Al} = 16$) of the chlorite structure.

be calculated for various values of n and the smooth curves drawn as in text-fig. 1. When chemical analyses of various chlorites are calculated to yield the values shown in table V, then these can also be plotted and fall very near to the theoretical curves. For a theoretical value of $\text{Si}/\text{Al}_{\text{IV}} = 2$ the corresponding values of R_2O_3 and RO are 100 and 350, yielding $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 3\frac{1}{2}\text{RO}$, which approaches the empirical formula fairly closely. The actual values of $\text{Si}/\text{Al}_{\text{IV}}$

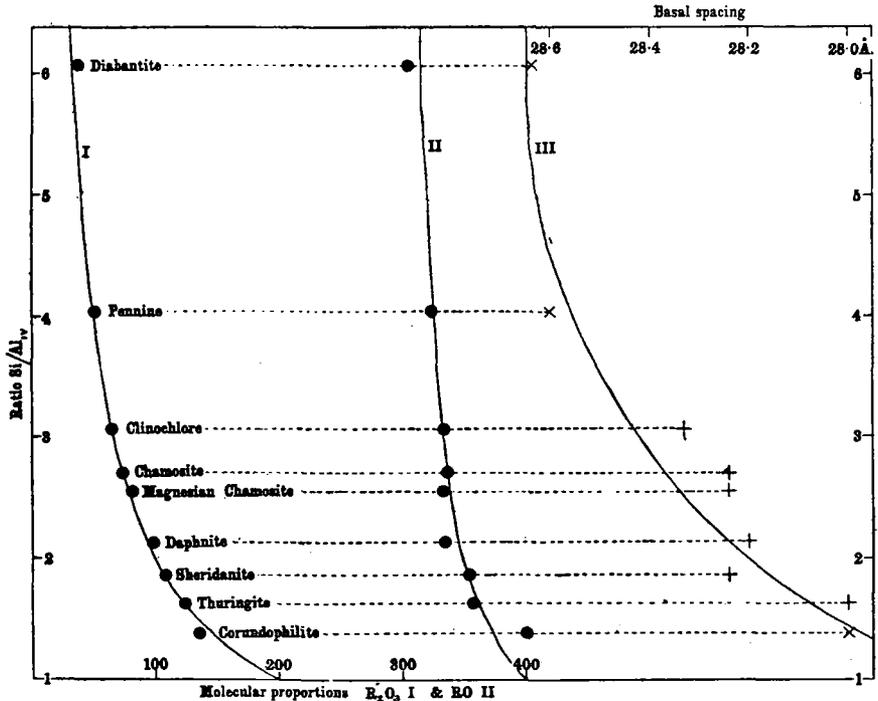


FIG. 1. Values of the molecular proportions of total R_2O_3 ($\text{SiO}_2 = 200$) (curve I), values of total RO ($\text{SiO}_2 = 200$) (curve II), plotted with various values of the atomic ratio $\text{Si}/\text{Al}_{\text{IV}}$ from the structural formula of the chlorites, $(\text{Si}, \text{Al}_{\text{IV}})_{16}(\text{R}''', \text{R}'')_{24}\text{O}_{40}(\text{OH})_{32}$. Values of these quantities calculated direct from chemical analyses of various chlorites, are shown as black spots.

Curve III.—Values of the basal spacing $c^* = c \sin \beta$ in \AA , plotted with $\text{Si}/\text{Al}_{\text{IV}}$. Crosses + represent X-ray and chemical data obtained on the same specimen; \times represent X-ray and chemical data obtained on different specimens from the same locality.

for chamosite and magnesian chamosite are, however, greater than 2 and the values of R_2O_3 are 335.5 and 328 respectively. Table V also gives the basal spacings $c^* = c \sin \beta$ for those chlorites whose chemical analyses have been plotted on the first two curves of text-fig. 1. Curve III in the same figure shows that as $\text{Si}/\text{Al}_{\text{IV}}$ increases so the basal spacing increases. This is to be expected, since the charge on the mica-like layers will become smaller with decrease in Al and the layers will not be as tightly bonded together. Text-fig. 1 is a satisfactory method of showing graphically how far chemical analyses of chlorites approach the ideal structural formula quoted above.

TABLE V. Variation of the molecular proportions R_2O_3 and RO ($SiO_2 = 200$) and of the basal spacing with the ratio Si/Al_v for various chlorites (text-fig. 1).

Species.	Si/Al_v .	R_2O_3 .	RO.	c^* .	Reference.
Diabantite	6.08	36.83	304.5	28.64 Å.	Hawes, 1875, p. 455.
Pennine	4.05	50.12	322.7	28.60	Tschermak, 1891, p. 45.
Clinochlore	3.07	64.89	333.3	28.33	Smith, 1924, p. 242.
Chamosite	2.71	73.89	335.5	28.24	Table III, p. 106.
Magnesian chamosite	2.56	81.30	332.0	28.24	Table III, p. 106.
Daphnite	2.14	97.81	334.5	28.20	Hallimond, 1939, p. 443.
Sheridanite	1.87	106.9	353.0	28.24	Shannon, 1922, p. 241.
Thuringite	1.64	122.9	356.8	28.00	Pulfrey, 1933, p. 421.
Corundophilite ...	1.39	135.3	398.5	28.00	Shannon, 1920, p. 375.

Spacing data by F. A. Bannister excepting for sheridanite (McMurchy, 1934, p. 423).

During the selection of chamosite ooliths from Wickwar for chemical analysis and X-ray work, dark-green casts of fossils not exceeding $\frac{1}{2}$ mm. across were occasionally encountered. In appearance the microfossil casts resemble so closely the ooliths of magnesian chamosite that no difference in powder pattern was expected. The pattern of two different microfossil casts gave, in addition to the magnesian chamosite pattern, a relatively strong line at 2.51 Å (pl. VIII, fig. 4). At first sight this might be thought to indicate admixture with iron-rich chamosite, since, as can be seen from table II, both chamosite from Frodingham and Schmiedefeld show a fairly strong line with nearly the same spacing. The specific gravity 2.90 and refractive index 1.61 are, however, both lower than the values for magnesian chamosite 3.034 and 1.620. The most reasonable assumption to fit these facts is that the microfossil casts are mixtures in fairly constant proportions from one to another of magnesian chamosite and serpentine. Too little material is available for a determination of the magnesia and silica contents of the mixture, but if it is assumed that the serpentine has specific gravity 2.65 and refractive index 1.56, then the microfossil casts should contain 20 to 30 % serpentine. The relative intensities of the powder lines due to magnesian chamosite and to serpentine alone are of the right order to confirm this approximate estimate of the proportions of the two constituents in the microfossil casts. It should be noted that the admixture of 25 % serpentine with magnesian chamosite would raise the percentages of silica and magnesia to 30 and 18.5 % respectively. It has not been overlooked that possible admixture of normal iron-rich chamosite with sufficient serpentine would yield a chemical analysis with the correct content of magnesia for magnesian chamosite and only a slightly higher figure for silica. For instance, addition of 20 % serpentine to an iron-rich chamosite with a composition like that of the Frodingham mineral would yield a mixture close in composition to magnesian chamosite. The powder pattern of this mixture would, however, show marked differences from that of the magnesian chamosite ooliths from Wickwar.

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The specimens here described and figured have been kindly presented to the Mineral Department, British Museum (Natural History), by Professor Whittard.

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EXPLANATION OF PLATES VIII AND IX.

PLATE VIII, FIG. 1. Intraformational breccia, Wenlock Limestone, lower shaft, Little Avon river, Wickwar, Gloucestershire. Note the dolomitized, heavily crinoidal limestone (L) succeeded above by calcareous, chamositic siltstone (C); the latter contains irregularly-shaped pieces of non-crinoidal, calcareous mudstone, a section of the compound coral *Halysites*, and numerous detrital crinoid ossicles. At the lower right-hand corner the polished surface has obliquely cut across a joint now infilled with Triassic material (T). The specimen was photographed under water. B.M. 1945,46. $\times \frac{1}{2}$.

X-ray powder patterns taken in a cylindrical camera, diameter 6 cm. with unfiltered Fe radiation:

FIG. 2. Chamosite, Frodingham, Lincolnshire.

FIG. 3. Magnesian chamosite, Wickwar, Gloucestershire. B.M. 1945,46.

FIG. 4. Magnesian chamosite and serpentine microfossil, Wickwar, Gloucestershire.

FIG. 5. Diabantite, Connecticut valley, U.S.A. B.M. 53917.

PLATE IX. Photomicrographs of magnesian chamosite and 'pearls' from the Wenlock Limestone, lower shaft, Wickwar, Gloucestershire.

FIG. 1. Fresh chamositic ooliths, some with a nucleus of calcite, contained in a calcareous, chamositic siltstone matrix. B.M. 1945,47. $\times 21$.

FIG. 2. Fresh ooliths of chamosite scattered in a calcareous matrix rich in dolomite, ankerite, and limonite. B.M. 1945,48. $\times 21$.

FIG. 3. Weathered, calcareous, chamositic siltstone in which much of the chamosite in the matrix has been converted into limonite. The chamosite ooliths are yellowish-green in colour and show a pronounced banding due to a finely divided mineral believed to be rutile. B.M. 1945,49. $\times 21$.

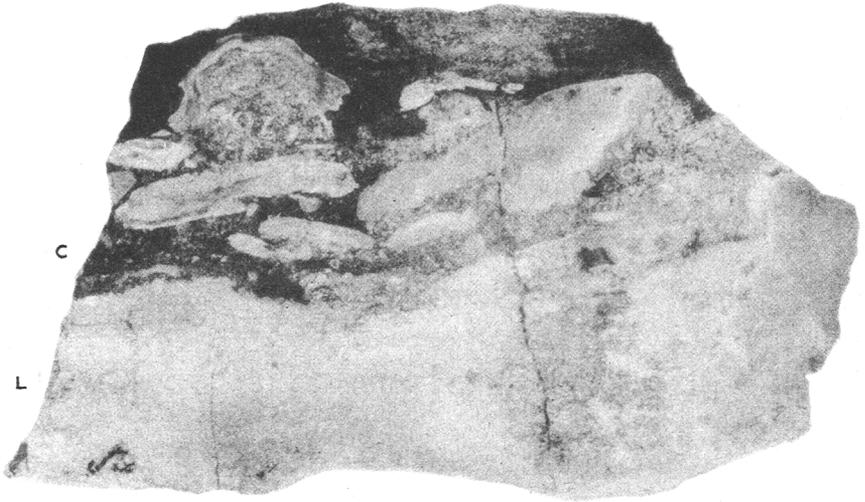
FIG. 4. Chamositic siltstone (dark patches) intermingled with calcareous mudstone which has been dolomitized. B.M. 1945,50. $\times 21$.

FIG. 5. Calcareous mudstone matrix containing numerous rhombohedra of dolomite and ankerite; note the dark centres to the crystals. B.M. 1945,51. $\times 35$.

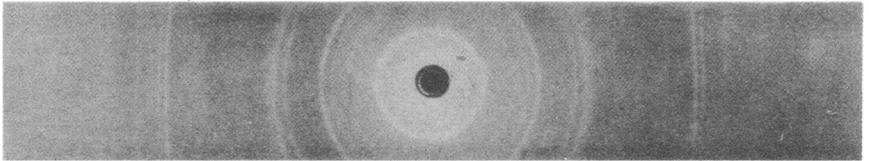
FIG. 6. Detrital 'pearl' with a nucleus of chloritic matter which may be chamosite. B.M. 1945,52. $\times 35$.

FIG. 7. Irregularly-shaped detrital 'pearl'. B.M. 1945,53. $\times 56$.

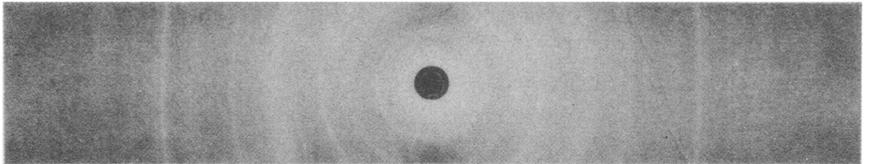
Photographs for pl. VIII, fig. 1, and pl. IX, figs. 1-7, by E. W. Seavill.



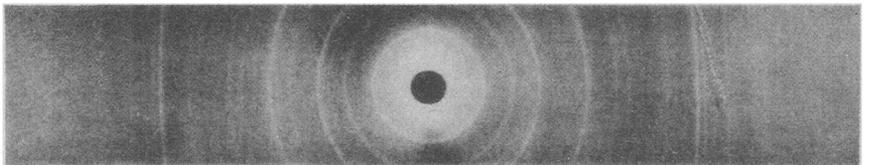
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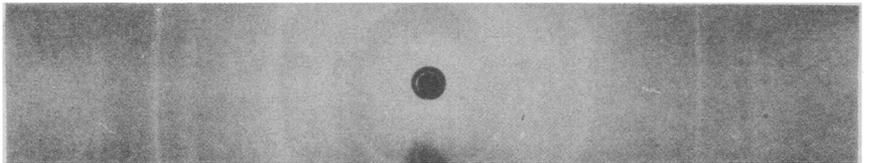
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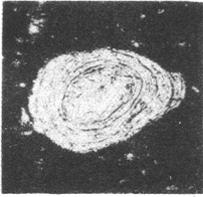


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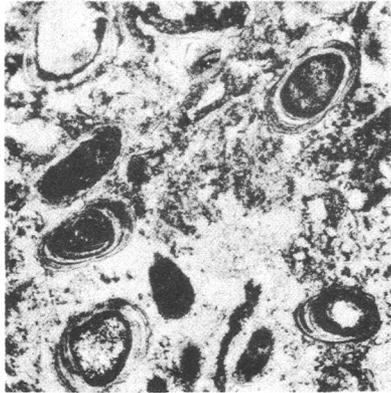


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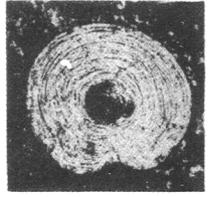
F. A. BANNISTER AND W. F. WHITTARD: MAGNESIAN CHAMOSITE.



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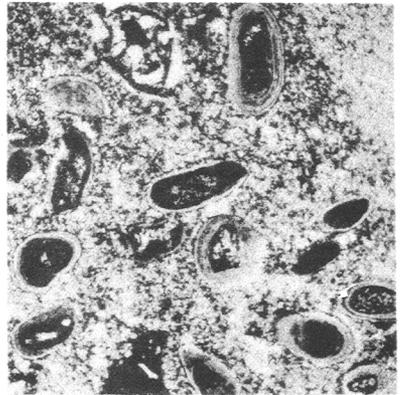
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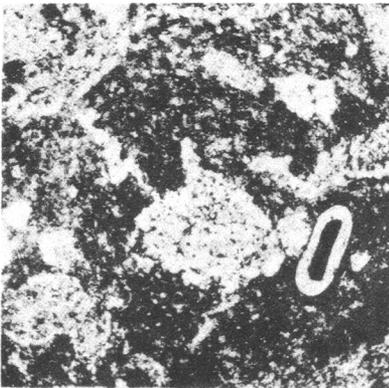
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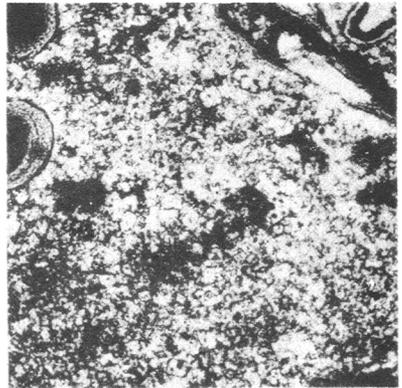
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