

*On the atomic arrangement and variability of the members  
of the montmorillonite group.*

(With Plate V.)

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ACCORDING to their atomic arrangement the minerals found in clays can be divided into the two-layer and the three-layer structures (1). The members of the first group have alternating silica and alumina layers, e.g. kaolinite; the members of the second group have one alumina (or magnesium or iron) layer between two silica layers, e.g. pyrophyllite.<sup>1</sup> The clay minerals can also be classified into two groups according to their power to diffract X-rays. The first group gives good powder photographs with twenty to forty well-developed lines if copper or iron radiations are used, whereas the second group gives poor diagrams with only a few lines, usually under fifteen, some of which are wide and indistinct. Exposure times for the second group are about two to three times as large as those for the first group. The poor diffracting power for X-rays may be due either to a lack of regularity ('roughness') of the lattice, or to an extremely small size of the single crystallites. It is possible that both effects are active to some extent, but the lack of regularity of the lattice is probably the main reason. Neither the microscopic evidence nor sedimentation data based on Stokes's law show these minerals to have particles smaller than  $10^{-6}$  cm., though it is possible that the optical effects such as double refraction are due to aggregation, and it is clear that the equivalent radius is an unsatisfactory measure for plate-shaped particles. Both classifications are shown on p. 141.

The crystal-structures of the minerals giving poor X-ray diagrams are largely derived by analogies and are not as well proved as the structures of the minerals which give good X-ray diagrams. There are

<sup>1</sup> The micas, chlorites, vermiculites, &c. can be considered as subgroups of the three-layer type.

	Formula	Good powder diagrams.	Poor powder diagrams.
Two layers ...	$\text{Si}_2\text{O}_5 \cdot \text{Al}_2(\text{OH})_4$	{ Kaolinite Dickite Nacrite Anauxite Pyrophyllite	Metahalloysite
Three layers ...	$\left\{ \begin{array}{l} \text{Si}_2\text{O}_5 \cdot \text{Al}_2(\text{OH})_2 \cdot \text{Si}_2\text{O}_5 \\ \text{Si}_2\text{O}_5 \cdot \text{Mg}_2(\text{OH})_2 \cdot \text{Si}_2\text{O}_5 \\ \text{Si}_2\text{O}_5 \cdot \text{Fe}_2(\text{OH})_2 \cdot \text{Si}_2\text{O}_5 \end{array} \right.$		Talc — <sup>2</sup>

also other differences between the two types, apart from crystal size and definition, some of which will be discussed later on.

The minerals of the three-layer type having poor X-ray powder diagrams, which are shown in heavy print in the above classification, are the subject of the present contribution. They contain, in the air-dry state, 20–23 % of water and show reversible lattice shrinkage and expansion according to their water content. Pyrophyllite and talc, on the other hand, contain about 5 % of water in the air-dry state and have no lattice shrinkage.

Six samples, including montmorillonite, nontronite, and beidellite were investigated. Their chemical composition and refractive indices are given in table I.<sup>3</sup> The chemical data are taken from the literature (3–7). The refractive indices were determined on samples in equilibrium with an atmosphere of 50 % relative humidity and on samples dried at 110° C., using a mixture of olive oil, cinnamon oil, and, if necessary,  $\alpha$ -monobromonaphthalene as immersion liquid, as recommended by C. W. Correns and M. Mehmel (8). A sodium lamp was used as light source and the highest indices observed on many grains were taken as  $n_\gamma$ .<sup>4</sup> The difference in refractive indices between the two nontronites is specially remarkable in view of their chemical similarity. They also differed in colour, no. IV being yellower and no. V greener.

<sup>1</sup> The term 'magnesium-beidellite' is used in this paper to describe the 'bentonitic magnesian clay-mineral' from Hector, California, described by Foshag and Woodford (7) and used in this work as sample VI in table I.

<sup>2</sup> No mineral of the composition  $\text{Fe}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$  has apparently been observed giving a powder diagram similar to the talc diagram with a basal spacing of 9.4 Å., and a dehydration curve showing a sudden loss of about 4.3 per cent. of water between 450° and 550° C. Gruner (2) claims, however, that he obtained such a material, at least as far as the X-ray evidence goes, by heating nontronite in a bomb to 575° C.

<sup>3</sup> The numbers I to VI of this table will be used in the following to denominate the minerals. My thanks are due to Prof. F. Heide for the material of I, to Dr. W. F. Foshag for II and III, to Dr. J. Orceel for IV and V, and to Dr. R. E. Grim for VI.

<sup>4</sup> The double refraction of all samples was of the order of 0.02 to 0.03 and was, apparently, not affected by the water content of the sample.

TABLE I. Percentage composition and refractive indices of samples investigated.

		Montmorillonite	Beidellite		Nontronite		Magnesium-beidellite
			I.	II.	III.	IV.	
SiO <sub>2</sub>	...	49.21	45.32	47.28	44.0	44.30	53.68
TiO <sub>2</sub>	...	nil	—	—	—	0.18	—
Al <sub>2</sub> O <sub>3</sub>	...	22.61	27.84	20.27	3.6	5.37	0.60
Fe <sub>2</sub> O <sub>3</sub>	...	0.43	0.70	8.68	29.0	29.47	—
FeO	...	—	—	—	—	0.56	—
MnO	...	trace?	—	—	—	—	—
MgO	...	2.13	0.16	0.70	2.1	1.74	25.34
CaO	...	1.95	2.76	2.75	—	1.70	0.52
Na <sub>2</sub> O	...	0.45	0.10	0.97	—	—	3.00
K <sub>2</sub> O	...	trace	0.12	trace	—	—	0.07
Li <sub>2</sub> O	...	—	—	—	—	—	1.12
H <sub>2</sub> O+	...	9.34	14.48	6.65	18.7	8.52	8.24
H <sub>2</sub> O-	...	14.37	8.16	13.07		7.99	7.28
		100.49	99.64	100.37	97.4	99.83	99.85
<i>n<sub>y</sub></i> for sample at 50% rel. hum. ...	1.498	1.502	1.562	1.610	1.578	1.524	
<i>n<sub>y</sub></i> for sample dried at 100° C. ...	1.531	1.540	1.589	1.631	1.602	1.553	

I. Montmorillonite, Unter-Rupsroth, Rhön. F. Heide, 1927 (3).

II. Beidellite, Black Jack mine, Carson district, Owyhee Co., Idaho. E. V. Shannon, 1922 (4a).

III. Beidellite, Beidell, Saguache Co., Colorado. E. T. Wherry, 1917 (4b).

IV. Nontronite, Nontron, Dordogne; also clay 1-2. P. Berthier, 1927 (5).

V. Nontronite, Behenly, Madagascar. F. Raoult in A. Lacroix, 1922 (6).

VI. Magnesium-beidellite, Hector, San Bernardino Co., California; also Cl 0.31. W. F. Foshag, 1936 (7).

### *Chemical Composition and Isomorphous Replacement.*

A complete isomorphous series between beidellite and nontronite with the end-members  $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot m\text{H}_2\text{O}$  and  $\text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot m\text{H}_2\text{O}$  has been postulated by Larsen and Steiger (4) on chemical grounds. U. Hofmann, K. Endell, and D. Wilm (11), who first suggested a structure for montmorillonite, give the pyrophyllite formula plus water,  $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot m\text{H}_2\text{O}$ , with minor replacements, and J. W. Gruner (9) extends this for the whole group to the formula  $(\text{Fe}, \text{Al})_{2+\frac{2}{3}n}\text{Si}_{4-n}(\text{Al}, \text{Fe})_n\text{O}_{10}(\text{OH})_2 \cdot m\text{H}_2\text{O}$ , where  $n$  may vary between 0 and 1 and  $m$  between 2 and 5.5. The establishment of structural formulae of this kind has two difficulties. The first is the splitting of the analytical figures for water into hydroxyl groups and 'adsorbed' water, with the possible further complication of hydrogen ions. In micas, talc, pyrophyllite, and kaolinite, dehydration curves show well-defined breaks, and about the correct amount of water corresponding to the numbers of hydroxyl groups in the structure is

given off, usually above 450° C. All these minerals belong to the group which has well-developed powder photographs. The few dehydration curves for montmorillonite and nontronites which have been described and summarized by W. von Engelhardt (10) are, however, of a different character. Large amounts of water are given off gradually to about 200°, the curves then flatten and little water is released until about 350° to 450°, where a sudden release of about 2.3 % of water occurs, followed by a gradual further loss of one or two per cent. of water between 550° and 800°. One hydroxyl group per  $\text{Al}_2\text{Si}_4\text{O}_{10}$  unit corresponds to 2.5 % of water, and it would therefore appear from these curves that the structure contains only one hydroxyl group per  $\text{Al}_2\text{Si}_4\text{O}_{10}$  unit, or that the two hydroxyls, which are supposed to be present, and which would correspond to a dehydration loss of 5 %, are held with different energy and are therefore not structurally identical. Far too few observations have so far been made on these minerals, but unfortunately the small samples of material at my disposal were insufficient for detailed dehydration work. At present it appears from the available data that there is some reason to doubt the number of hydroxyl groups in the montmorillonite formula  $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot m\text{H}_2\text{O}$ . The method developed by Longchambon (12) for the study of dehydration curves of sepiolites and various minerals seems to provide a useful advance in technique.

The second difficulty in establishing structural formulae concerns isomorphous replacements. These replacements are known with certainty to occur in the muscovite structure, and it is only reasonable to suppose that they exist also in clay minerals of the three-layer type, but to what extent it is difficult to say. They are compatible with, but not strictly proved by, the X-ray evidence of powder photographs, a distinction which is often neglected in current literature.

The importance of isomorphous replacements in the layer lattices of the clay minerals has been stressed by Marshall (13), Holzner (14), and others, and similar calculations were made for the six samples listed in table I. The analytical figures are recalculated, in table II, for the single atoms on the basis of a total of eleven oxygen atoms, after leaving out the water percentage in view of the uncertainty of the number of hydroxyl groups present. This corresponds to the composition of one half unit cell, if Hofmann's structure is taken as basis.

It can be seen from table II that the value of silicon varies between 3.4 and 3.9. In order to bring it to 4 a corresponding number of aluminium ions are taken, which are assumed to replace the silicon. For every aluminium ion which replaces one silicon ion one negative charge is

TABLE II. Number of atoms present for eleven oxygen atoms on recalculation of the chemical data of table I without water.

	I.	II.	III.	IV.	V.	VI.
Si ... ..	3.74	3.46	3.58	3.72	3.57	3.89
Al ... ..	2.03	2.50	1.81	0.36	0.51	0.05
Fe <sup>+++</sup> ... ..	0.03	0.04	0.50	1.84	1.79	—
Fe <sup>++</sup> ... ..	—	—	—	—	0.04	—
Mg ... ..	0.24	0.02	0.08	0.26	0.21	2.73
Ca ... ..	0.16	0.23	0.22	—	0.15	0.04
Ti ... ..	—	—	—	—	0.01	—
Li ... ..	—	—	—	—	—	0.33
K ... ..	—	0.01	—	—	—	0.01
Na ... ..	0.07	0.02	0.14	—	—	0.42

created on the lattice. In the case of the magnesium-beidellite, sample no. VI, there is not sufficient aluminium present to complete the silicon layers and a small amount of magnesium<sup>1</sup> ions is therefore taken to bring the number of silicon to 4. For every magnesium ion replacing silicon two negative charges are created. Table III shows the composition of the silica layers, and the sum of the negative charges created through the various replacements.

TABLE III. Atomic composition of the silica layers Si = 4 and negative charges produced.

	I.	II.	III.	IV.	V.	VI.
Si ... ..	3.74	3.46	3.58	3.72	3.57	3.89
Al ... ..	0.26	0.54	0.42	0.28	0.43	0.05
Mg ... ..	—	—	—	—	—	0.06
Negative charge ... ..	0.26	0.54	0.42	0.28	0.43	0.17

The next stage in the calculation is to build up the middle layer, which contains two aluminium, two iron, or three magnesium ions in the ideal case. If aluminium ions are replaced by magnesium ions, there are two possibilities. One magnesium can replace one aluminium and one new negative charge is created, or three magnesiums replace two aluminiums without change in the charge. This second case is possible because the aluminium ions fill only two-thirds of the available six-co-ordinated spaces in the structure, but, for reasons given below, we have used the first alternative in our calculation. In the case of the magnesium-beidellite, sample no. VI, lithium has been taken to complete the magnesium layer, again with a corresponding increase in the

<sup>1</sup> The replacement of silicon by magnesium is unlikely in view of the difference of the size of their ionic radii, but the amount of magnesium replacing silicon is very small, one ion out of 67, and there seems no better possibility to calculate the lattice.

negative charge. The composition of the middle layers and the charges created are shown in table IV.

TABLE IV. Atomic composition of the middle layer, Al = 2, Fe<sup>+++</sup> = 2, Mg = 3, and negative charges produced.

	I.	II.	III.	IV.	V.	VI.
Al ... ..	1.77	1.96	1.39	0.08	0.08	—
Fe <sup>+++</sup> ... ..	0.03	0.04	0.50	1.84	1.79	—
Fe <sup>++</sup> ... ..	—	—	—	—	0.04	—
Mg ... ..	0.20	—	0.08	0.08	0.08	2.67
Ca ... ..	—	—	0.03	—	(Ti 0.01)	—
Li ... ..	—	—	—	—	—	0.33
Negative charge ... ..	0.20	0.00	0.11	0.08	0.12	0.33

It is then found that after completing the structure a certain amount of cations, mainly calcium and sodium, is left over in every case. They may be called excess cations, and are shown in table V.

TABLE V. Atomic composition of excess cations.

	I.	II.	III.	IV.	V.	VI.
Ca ... ..	0.16	0.23	0.19	—	0.15	0.04
Na ... ..	0.07	0.02	0.14	—	—	0.42
Mg ... ..	0.04	0.02	—	0.18	0.13	—
K ... ..	—	0.01	—	—	—	0.01

On adding up the valencies of the excess cations it is found that they balance fairly well the total sum of the negative charges produced through the various isomorphous replacements<sup>1</sup> (table VI). This equivalence is believed not to be a chance result but to have a real significance.

TABLE VI. Sum of negative charges due to replacements, sum of positive charges due to excess cations, and base-exchange capacities of samples I to VI.

	I.	II.	III.	IV.	V.	VI.
Negative charges on lattice	0.46	0.54	0.53	0.36	0.55	0.50
Positive charges of excess cations ... ..	0.47	0.53	0.52	0.36	0.56	0.51
Exchange capacities ... ..	0.47	0.54	0.46	—	—	0.06

The base-exchange capacities of the montmorillonite and beidellite samples nos. I, II, III, VI were determined by Dr. R. K. Schofield<sup>2</sup> and the results recalculated on the basis of half the dehydrated unit cells

<sup>1</sup> In Marshall's calculations ((13) pp. 438-440) it seems that the sum of the negative charges is listed as cations per unit cell, otherwise, as far as a recalculation of his data shows, the fit is too good.

<sup>2</sup> My best thanks are due to Dr. Schofield for these data which were obtained by a new and unpublished method, based on the reduction in the titrateable acidities to pH 6.75, which is brought about by treating the acid-washed materials with *N*-potassium chloride solution.

of the composition given in tables III and IV, i.e.  $\text{Si}_{3.74}\text{Al}_{2.03}\text{Fe}_{0.03}\text{Mg}_{0.20}\text{O}_{11}$  for montmorillonite, sample no. I. In table VI the sum of the negative charges produced, the sum of the valencies of the excess cations, and the base-exchange capacities are listed together. The agreement is good, except in the case of the magnesium-beidellite, sample no. VI, where the exchange capacity is much too low. It is possible that this low result is connected with the fact that sodium is the main exchange ion in this case, but work on this question will be continued. In all other cases it seems that the excess cations balance the negative charges on the lattice which are due to isomorphous replacements and that they are all exchangeable. This result should be compared with Marshall's (13, p. 446) statement:

'The mono and bivalent bases present in clays thus fall into four categories. (1) Those needed to complete the framework, chiefly Mg replacing Al. (2) Those which partly balance the charge on the framework and are incorporated within it. Mg, K, Na, and Ca may all be present in this non-exchangeable form. (3) Exchangeable cations which also contribute to balancing the charge on the framework, but which are situated between the layers and are there associated with water molecules. (4) Cations of the electrical double layer surrounding the particles.

The new result represents a considerable simplification of Marshall's statement, his categories 1 and 3 are retained, but category 2 is rejected, and 4 arises from and is included in 3.

It has been mentioned above that for the calculation of the middle aluminium layer two possibilities of replacing aluminium by magnesium exist, the ratio Mg to Al can be either 1:1 with an increase in the negative charge, or 3:2 without increase in charge. If for a given material the excess cations balance the negative charges for one method of calculating the middle layer, the balance remains if the other method is used, but the total sum of excess cations or charges will be different. The ratio 1:1 has been used, because in this case the base-exchange capacities give the same value as the excess cations for montmorillonite and beidellite, samples I to III. It seems also that in micas there is a strong tendency for the number of cations in the middle layer to be either two or three, or very nearly two or three, but not any intermediate value (Holzner (25), Niggli (26)). It must be repeated, however, that these calculations are at present hypothetical and only justified by the fact that the results seem reasonable.<sup>1</sup> They are compatible with, but

<sup>1</sup> When better dehydration curves are available it will be necessary to consider the possibility that the negative charge on the lattice is reduced by a  $\text{O}'' \rightarrow \text{OH}$  transformation. This seems to account for the analyses of certain micas. Brammall (23).

not proved by, the X-ray evidence, and would give the following picture.

The three-layer lattice has a certain amount of aluminium ions replacing silicon ions in four-co-ordination. In the muscovite structure every fourth silicon is replaced by aluminium. In the montmorillonite group one out of six is the upper limit for published analyses and one out of forty the lower one. The middle layer has the ideal compositions of either  $2\text{Al}^{+++}$  (montmorillonite),  $2\text{Fe}^{+++}$  (nontronite), or  $3\text{Mg}^{++}$  (magnesium-beidellite), and  $\text{Li}^+$  or  $\text{Ca}^{++}$  ions can replace those three ions to a small extent. How far mixtures of the three end-members occur is not yet known. The negative charges due to the various replacements are balanced by cations, which are held on the outside of the three-layer units and which are exchangeable. This result would confirm and extend a rule proposed by van der Meulen (24), that the amount of aluminium replacing silicon in four-co-ordination is a measure of the exchange capacity, but it is believed that a further condition is that the balancing ions are accessible.

#### *X-ray data.*

Hofmann (11, 22) and collaborators have suggested an atomic arrangement for montmorillonite, which is identical with the pyrophyllite structure, as far as the three-layer units are concerned. These units are separated by gaps which are filled with water and vary in size according to the moisture content of the sample. Apparently the layers are all parallel and equidistant without further orientation. The powder diagram consists of a series of reflections from the basal spacing plus cross-grating spectra due to the hexagonal arrangement of the three-layer unit. Nontronite and beidellite are said to have the same structure, and these results are confirmed with minor modifications (monoclinic as against rhombic unit cell) by Gruner (9). Gruner's X-ray data for nontronites show, however, considerable differences for different samples, and, on the whole, too many lines. Accurate data for beidellite do not seem to have been published anywhere. Kerr (15) states that the magnesium-beidellite from Hector, California, gives the same powder diagram as nontronite, but he records no spacings larger than  $4.5^\circ \text{ \AA}$ .

X-ray powder diagrams of the air-dry minerals listed in table I were taken with copper and iron radiations. Technical details have been given in previous communications (18). The results are given in table VII, and some of the diagrams in plate V. All materials give the same type



TABLE VII. X-ray powder diagrams of minerals I to VI, taken with copper and iron K $\alpha$  radiations.

	I.	II.	III.	IV.	V.	VI.	Indices accord- ing to (22) or marked?
1.	15.3 vs	15.1 vs	15.2 m	15.4 vs	15.6 vs	15.8 s	(001)
2.	5.15 s	5.03 s	5.05 w	—	—	—	(003)
3.	4.50 vs	4.45 vs	4.51 vs	4.56 vs	4.55 vs	4.57 vs	(110) (020)
4.	—	—	3.36 w <sup>1</sup>	—	—	—	—
5.	3.07 vs	3.02 vs	3.03 w	3.11 <sup>2</sup> vs 3.03 w	3.11 vs 2.98 w	3.23 w 3.08 w	(005)
6.	2.61 <sup>2</sup> vs	2.60 vs	2.60 w	2.64 s	2.62 s	2.65 s	(130) (200)
7.	2.41 w	2.49 w	2.54 w	2.56 w	2.56 w	2.48 m	(006)?
8.	2.240 w	2.38 w	2.38 w	2.43 w	—	—	(220) (040)
		2.240 w	2.240 w	—	—	—	
		2.164 w	2.164 w	—	—	—	
9.	2.155 w	2.090 w	2.140 w	—	—	—	(007)?
10.	1.905 vw	1.890 vw	—	—	—	—	(008)?
11.	1.708 m	1.694 s	1.700 s	1.715 w	1.716 w	1.748 <sup>3</sup> m	(240) (310)
		1.654 w	1.640 w	1.668 w	1.668 w	1.689 w	(150)
12.	1.497 vs	1.488 vs	1.500 vs	1.518 vs	1.519 vs	1.527 vs	(330) (060)
13.	1.292 m	1.284 m	1.302 w	1.318 w	1.316 w	1.320 s	(260) (400)
			1.285 w	1.300 w	1.300 w	1.301 s	(0.0.12)?
14.	1.247 m	1.241 m	1.245 w	1.258 w	1.266 w	1.267 vw	(350) (170) (420)
15.	0.970 vw	0.970 vw	—	—	1.246 w	—	(190) (460) (530)
16.	0.863 vw	0.862 vw	—	—	—	0.990 w	(390) (600)
a...	5.17Å.	5.14	5.17	5.23	5.23	5.24Å.	
b...	8.98Å.	8.93	9.00	9.11	9.11	9.16Å.	

<sup>1</sup> Probably quartz line.<sup>2</sup> Edges of broad line.<sup>3</sup> Separated into two lines, when iron radiation is used.

of powder diagram, but there are slight differences with regard to positions and intensities of lines.

The differences in position of the lines can be summarized by using Hofmann's indices (060) and (400) for the lines nos. 12 and 13 to calculate the length of the axes  $a$  and  $b$  of the unit cells. The figures are given in table VII and are compared with the corresponding figures for the hydroxides of aluminium and magnesium and for talc and pyrophyllite in table VIII.

TABLE VIII. Length of  $a$  and  $b$  axes of various minerals in Å. units.

	Montmorillonite.	Nontronite. <sup>1</sup>	Mg-Beidellite.
$a$ ... ..	5.15	5.23	5.24
$b$ ... ..	8.95	9.11	9.16
	Hydrargillite.	—	Brucite.
$a'$ ... ..	5.06	—	5.38
$b'$ ... ..	8.62	—	9.36
	Pyrophyllite.	—	Talc.
$a$ ... ..	5.14	—	5.26
$b$ ... ..	8.90	—	9.10

The differences in the intensities of lines affect the higher orders of the basal spacing, mainly the lines nos. 2 and 5, which are very weak or absent, if iron or magnesium replace aluminium in the structure. The replacement of silicon by aluminium does not seem to affect the powder diagram in any way; the diagrams of samples nos. I and II are almost identical.

The magnesium-beidellite diagram shows also another peculiarity. Whereas the lines nos. 13 and 14 have about equal intensity in all other samples, no. 13 is strong and no. 14 very weak for the magnesium-beidellite.

#### *Lattice Shrinkage.*

All six materials investigated show reversible lattice shrinkage upon dehydration. From the position of the first order reflection of the basal spacing the following values are obtained:

at 50 % relative humidity ... ..	15-15.5 Å.
at 110° C. ... ..	12-12.5 Å.
at 300° C. ... ..	about 10 Å.

These values are not very accurate, but they are correct within 5 %. The loss upon ignition on material in equilibrium with an atmosphere of 50 % relative humidity was determined on small samples of all

<sup>1</sup> Similar values for nontronite are reported by J. W. Gruner (9).

minerals except the nontronites, where the few milligrams of material at my disposal were insufficient for this determination. The values are:

	I.	II.	III.	VI.
Ignition loss as per cent. of air-dry sample ...	23.1	19.6	17.7	24.1

The water in montmorillonite is believed to enter between the three-layer units in the form of sheets of spheres in close-packing. It regulates, therefore, the basal spacing, and changes in the water content cause the reversible lattice shrinkage and expansion. The intensities of the higher orders of the basal spacing are strongly affected by the water content. Our data, given in table VII, show that the intensities of the higher orders of the basal reflection for a *given* water content vary also according to the composition of the middle layer.

Calculations showing the effect of change in water content have recently been made by Bradley, Grim, and Clark (19) and by Maegdefrau and Hofmann (22). These authors assume two layers of water to be present between the three-layer units for material with a basal spacing of about 15 Å. No values for structure factors or other details of calculation are given in either paper, but the X-ray methods are different, and presumably different formulae are used for the decrease of the intensity with increasing angle  $\theta$ . The values of these authors for (001), (003), and (005) are given in table IX.

TABLE IX. Calculated and observed intensities for (001), (003), and (005) for montmorillonite, given by Maegdefrau and Hofmann (for powder line) and by W. F. Bradley, R. E. Grim, and C. L. Clark (crystal plane reflection).

		Maegdefrau and Hofmann		Bradley, Grim, and Clark.	
		Calc.	Obs.	Calc.	Obs.
(001)	...	160	>5	22.3	<i>vs</i>
(003)	...	3	1	2	<i>m</i>
(005)	...	8	2	15.8	<i>vs</i>

In order to see how these intensities are affected if all the aluminium in montmorillonite (2Al) is replaced by magnesium (3Mg) as in magnesium-beidellite, or by iron (2Fe<sup>+++</sup>) as in nontronite, rough intensity calculations were made assuming equal scattering power for O<sup>''</sup>, OH', and H<sub>2</sub>O and using Bragg and West's empirical *F* values (21). These calculations were made for the case of a powder line on a cylindrical film (*a*) and for the case of a crystal plane reflection (*b*). The results are shown in table X where the intensity of (001) for montmorillonite (2Al) is made equal to the values given by Maegdefrau and Hofmann (22) (*a*), and by Bradley, Grim, and Clark (19) (*b*).

TABLE X. Calculated and observed intensities for (001), (003), and (005) for montmorillonite (2Al), nontronite (2Fe<sup>+++</sup>), and magnesium-beidellite (3Mg), (a) for powder line, (b) for crystal plane reflection.

	2Al		2Fe		3Mg	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
(a) { (001)	160	<i>vs</i>	376	<i>vs</i>	234	<i>vs</i>
(a) { (003)	2.8	<i>s</i>	0.19	—	0.75	—
(a) { (005)	22.3	<i>vs</i>	34.3	<i>vw</i>	26.4	<i>w</i>
(b) { (001)	22.3	<i>vs</i>	51.8	<i>vs</i>	32.1	<i>s</i>
(b) { (003)	1.2	<i>s</i>	0.08	—	0.32	—
(b) { (005)	15	<i>vs</i>	23.2	<i>vw</i>	17.9	<i>w</i>

The effect of the substitution works in the right direction and is reasonably strong for (003), where it could explain the observed intensities, but the agreement is not too good for (005), where the observed intensities decrease very much, whereas the calculated ones increase or decrease very little, if equal (001) intensities are taken as a basis of comparison. More data are needed before definite conclusions can be drawn from these observations.

The results of the X-ray data confirm the hypotheses put forward under the heading of isomorphous replacements in so far as they show the samples I to VI to belong to the same general structural type. The whole group is, accordingly, best represented in a ternary diagram with the end-members montmorillonite,  $\text{Al}_2\text{Si}_4\text{O}_{11}$  (A), nontronite,  $\text{Fe}_2\text{Si}_4\text{O}_{11}$  (B), and magnesium-beidellite  $\text{Mg}_3\text{Si}_4\text{O}_{11}$  (C) if the completely dehydrated formulae are used. Iron-free beidellite would coincide with A although the ratio of silica to alumina is different. In fig. 1 the six samples investigated are plotted in this way together with a few beidellites, faratsihite, and attapulgitite. Attapulgitite belongs to this group according to Kerr (15), but this is contradicted by Lapparent (16), who finds that this material has a basal spacing of 10.2 Å. The field for beidellites is also indicated, based on Larsen's data. It would perhaps be better to have a new name for C instead of magnesium-beidellite and to call all members of the group beidellites. It is possible that other beidellites in this sense along the BC line occur among saponites and bowlingites (17). How far minerals corresponding to points in the interior of the triangle exist cannot be said at present.

It seems that all members of the group are subject to fairly large isomorphous substitutions leading to a negative charge on the lattice of 0.5 units per  $\text{R}_2\text{Si}_4\text{O}_{11}$ , if  $\text{R}_2$  stands for 2Al, 2Fe<sup>+++</sup>, 3Mg, as elaborated above. This would correspond to exchange capacities of the order of 100 milli-equivalents for 100 grams of air-dry material. The excess

cations are able to hold loosely large amounts of water which govern the basal spacing. The ideal end-members mentioned above have no substitutions, no negative charge, no excess cations, and therefore no loosely held water. They belong to a different structural type, the pyrophyllite-talc type (compare p. 141). This seems to be the reason why

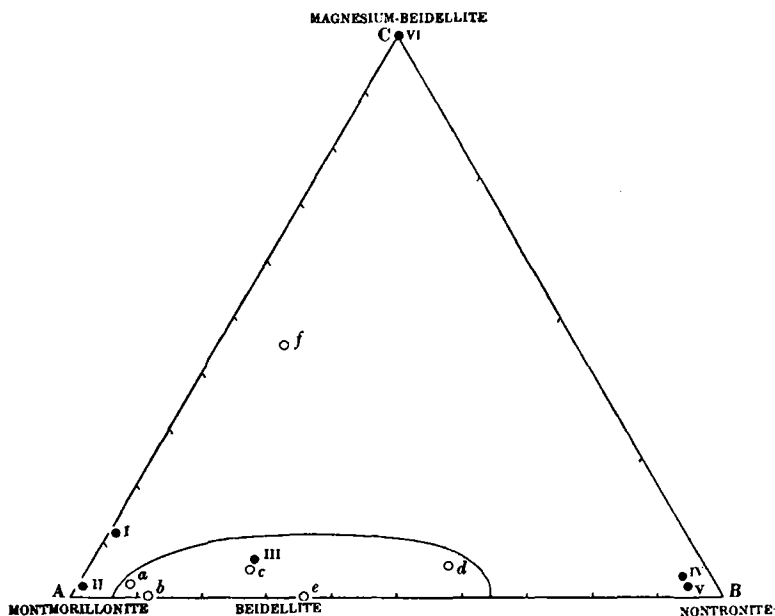


FIG. 1. Ternary diagram of the montmorillonite group. Points I-VI correspond to the six samples investigated; *a* to *d* to other beidellites; *e* to faratsihite; and *f* to attapulgit.

all montmorillonites, beidellites, and nontronites contain appreciable amounts of magnesium and calcium, a fact which has led to conflicting opinions in the literature. Lapparent (16) believes that the montmorillonite structure contains  $\text{SiMg}(\text{OH})_6$  layers alternating with the usual three-layer units, in analogy with the structure of the chlorites. But this seems not to take into account the reversible lattice shrinkage. With a basal spacing of  $10.2 \text{ \AA}$ . corresponding to montmorillonite heated to  $300^\circ \text{C}$ . there would be no room for this group. In a recent classification of clay minerals Lapparent (20) puts the beidellites tentatively into the kaolin group. This also does not agree with the data given in this paper.

Montmorillonite heated to 300° C. and pyrophyllite give powder diagrams which show very large differences.<sup>1</sup> Their structures are supposed to be identical except perhaps for lack of orientation of the successive three-layer units. This lack of orientation may be due to the comparatively large amount of isomorphous replacement in the lattice which would prevent a regular three-dimensional lattice arrangement, but the possibility cannot be excluded that the structure of montmorillonite is altogether different from the one proposed by Hofmann.<sup>2</sup> His admittedly rough intensity calculations for the (*hk*0) lines (22, p. 316) show large variations upon replacement of aluminium by iron or magnesium, contrary to the observed facts. He has, therefore, to introduce several additional hypotheses in order to make these calculations fit the experimental data. It still seems that the experimental evidence is insufficient to prove or disprove his structure which certainly is a very useful first approximation, and has been used as a basis for discussion in this paper.

In conclusion, the author wishes to thank Sir William Bragg and the managers of the Royal Institution for laboratory facilities at the Davy Faraday Laboratory, where part of the X-ray work was carried out, and Dr. E. M. Crowther for his help in the preparation of the manuscript.

#### *Summary.*

A classification of some clay minerals is made according to their lattice structure, and to the quality of their powder diagrams. The importance of the latter criterion is emphasized.

The montmorillonite group is shown to have three end-members, montmorillonite,  $\text{Al}_2\text{Si}_4\text{O}_{11}$ , nontronite,  $\text{Fe}_2\text{Si}_4\text{O}_{11}$ , magnesium-beidellite,  $\text{Mg}_3\text{Si}_4\text{O}_{11}$ . The formulae given correspond to the completely dehydrated end-members, free from isomorphous replacements.

One montmorillonite, two beidellites, two nontronites, and one magnesium-beidellite are studied in detail. Their isomorphous replacements are calculated on the basis of eleven oxygen atoms and the excess cations are found to balance the negative charges resulting from the replacements. Similar calculations with the same result have previously been made by Marshall. Base-exchange determinations on three of

<sup>1</sup> For this reason we do not think that Bradley, Grim, and Clark's terminology of first, second, and third hydrate of pyrophyllite for montmorillonite at various stages of hydration is satisfactory.

<sup>2</sup> It is, for example, possible to keep the silicon-oxygen framework unchanged and to distribute the aluminium ions over the four-co-ordinated spaces of the middle layer.

these materials show that all excess cations are exchangeable, but that in the case of magnesium-beidellite there are discrepancies, which require further investigation.

The hypothesis is made, that a certain amount of isomorphous replacement of silicon by aluminium and perhaps of aluminium by magnesium is essential for this structural type and may explain both the high water content, which is due to the excess cations, and the poor diffracting power for X-rays, which is due to the lack of regularity of the lattice.

Dehydration data given in the literature are discussed and the lack of agreement for the amount of hydroxyls given in the usual formula  $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$  is pointed out.

X-ray powder data for the six samples and values for the lattice shrinkage upon dehydration are given. They show all samples to belong to the same structural type. The replacement of aluminium by iron and magnesium within the lattice causes an increase in the lattice dimensions and for air-dry material a decrease of the intensities of (003) and (005). Rough intensity calculations on the basis of Hofmann's montmorillonite structure (22) show corresponding values for (003) but too high values for (005), and the need for further experiments is pointed out.

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Since going to press, X-ray diagrams of two samples of attapulgite (p. 151), kindly sent by Professor J. de Lapparent, show this material to be distinctly different from montmorillonite and not to show the characteristic lattice shrinkage.

#### EXPLANATION OF PLATE V.

X-ray powder photographs of clay minerals of the montmorillonite group and of pyrophyllite.

- FIG. 1. Pyrophyllite.
- FIG. 2. Montmorillonite.
- FIG. 3. Magnesium-beidellite.
- FIG. 4. Magnesium-beidellite.
- FIG. 5. Nontronite.

Figs. 1 to 3 were taken with Cu-K $\alpha$  and figs. 4 and 5 with Fe-K $\alpha$  radiation. The intensities in the centre have been reduced through partial shading in making the prints.

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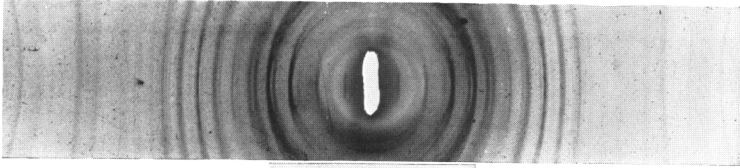


Fig. 1. PYROPHYLLITE

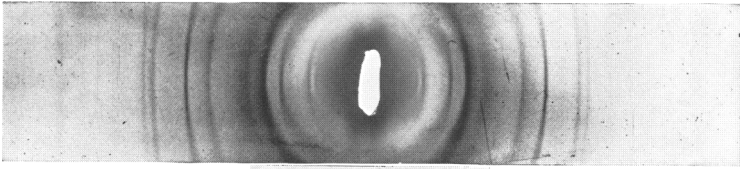


Fig. 2. MONTMORILLONITE

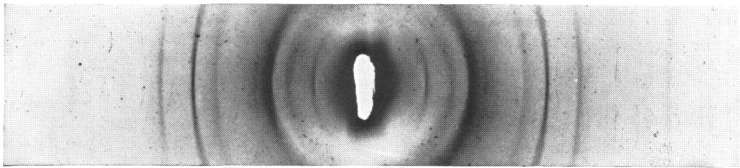


Fig. 3. MAGNESIUM-BEIDELLITE

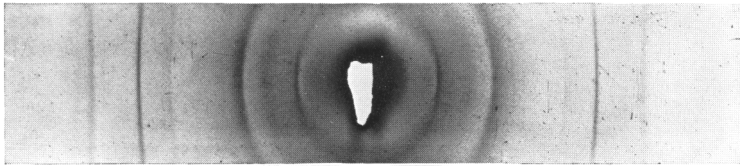


Fig. 4. MAGNESIUM-BEIDELLITE

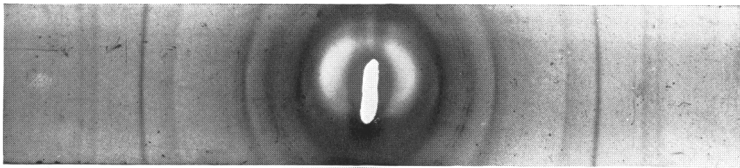


Fig. 5. NONTRONITE