

# THE STRUCTURAL RELATIONSHIP OF GLAUCONITE AND MICA

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## INTRODUCTION

The composition, properties and origin of glauconite have been investigated extensively in the past, but no attempt has been made to determine its structure. The writer in following up his work on other layer structures *x*-rayed eight glauconites under a number of different conditions and arrived at the conclusion that glauconite is a mica in structure. He is indebted to Dr. Clarence S. Ross and Dr. W. F. Foshag for gifts of analyzed and unanalyzed samples of glauconite. Mr. Gilman Berg was of great assistance in purifying some of the samples by the dielectric method. Generous grants from the Graduate School of the University of Minnesota have made this and previous structure studies possible.

Glauconites used in the investigation were:

1. St. Francis County, Missouri. From the St. Joseph Lead Company mine, near Bonnetterre. In the Bonnetterre dolomite (upper Cambrian). Analysis, Table 3, as given by C. S. Ross (1, p. 10). Optical properties by Ross: negative,  $\alpha=1.597$ ,  $\beta=1.618$ ,  $\gamma=1.619$ ;  $\gamma-\alpha=0.022$ ,  $2V=20^\circ$ ,  $2E=33^\circ$ . The acute bisectrix *X* is nearly but not quite normal to the basal cleavage, which is good. The absorption is  $Z=Y<X$ , pleochroism *Z* and *Y* lemon yellow, *X* dark bluish-green.

2. Huntington, Oregon. This is an unusual glauconite of which Ross (1, p. 4) says:

It forms large compact masses of an earthy texture. In thin section it resembles massive serpentine, with large, poorly defined, smearlike areas of birefracting material. No sharply defined crystals were observed and the cleavage is not well developed.

$\alpha=1.59$ ,  $\gamma=1.62 \pm .005$ ,  $2V=20^\circ-40^\circ$ , negative. Analysis, Table 3, quoted from paper by Ross.

3. Southeastern Minnesota. Franconia formation (upper Cambrian).

4. Black Hills, South Dakota. Deadwood formation (Cambrian).

5. Mobile County, Alabama (Eocene).

6. New Brunswick area, New Jersey (Eocene). United States National Museum No. 97761.

Two others of unknown origin.

## X-RAY DATA

From the beginning of this study it was considered highly probable, based on previous optical data, that glauconite is very similar

to the layer structures of the micas, kaolinites, vermiculites, or chlorites. This view had been held by a number of mineralogists for years. On account of the nature of the material the powder method of  $x$ -ray analysis provided the only means of attack. Throughout the work Fe K radiation from a modified Ksanda ion tube was used. Exposures varied from 20 to 50 hours at an average of 7 ma. at 30 kv. The radii of the cameras were 57.3 mm. All powders were mounted with collodion on silk thread, and the rods thus formed were about 0.8 mm. in diameter. The glauconites were so clean when separated dielectrically that no foreign lines of quartz or other minerals could be detected in the powder spectrum photographs.

As may be seen in Table 1, the interplanar distances  $d$  of the various specimens are surprisingly uniform, and the relative intensities of the lines (estimated by eye) do not vary appreciably. However, the lines lack the sharpness found in micas of coarser crystallization. The broadening of the lines may be partly due to the extremely small size of the crystal grains of glauconite, which for a large portion of the material must be below the optimum particles sizes for the powder method. They were so fine that no grinding of the samples was necessary beyond simple crushing. Broadening of lines could also be caused by slight distortions in the crystal lattice, modifying it very slightly from monoclinic to triclinic symmetry.

Table 1 gives the dimensions of the unit cell of each specimen and the densities of two of them as determined with the pycnometer.<sup>1</sup> The density of No. 1 is the average of two determinations on about 0.3 gms. No. 6 was determined on about 2.5 gms. of material, which contained a few grains of quartz and limonite. The material from Oregon, No. 2, was not suitable for density determination on account of its exceedingly great porosity and fineness. The other glauconites were not available in large enough pure samples.

If a powder diagram of glauconite were compared with one of muscovite, no similarity probably would be noticed except for the basal reflections 002 and 006, which almost coincide. Even if an iron-rich mica (biotite) pattern is used for comparison the similarity is not conspicuous until allowance is made for the probable difference in the dimensions of their unit cells, and remembering

<sup>1</sup> To fill all pore space the contents of the pycnometer were boiled under reduced pressure.

TABLE 1. POWDER DIAGRAMS OF GLAUCONITES, Fe RADIATION.

No.	1		2		3		4		5		6		Biotite*		
	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	
1	9.94	1	9.99	2	9.95	1	9.99	1	9.99	1	9.96	2	002	9.95	4
2	4.91	0.5	4.96	0.5	4.99	0.5	4.97	0.5	4.95	0.5	4.93	0.5	110 $\beta$ , 111 $\beta$	4.60	0.5
3	4.49	2	4.43	3 $\beta$	4.53	3	4.52	2	4.48	2	4.53	2	110, 111	3.68	1
4	3.67	2 $\beta$	3.63	1 $\beta$	3.64	1 $\beta$	3.64 $\beta$	2	3.63	1 $\beta$	3.65	2 $\beta$	023 $\beta$ , 113 $\beta$ , 006 $\beta$ , 024	3.333	5
5	3.313	3	3.313	3	3.323	3	3.323	2	3.323	2	3.313	3	006, 024	3.126	0.5
6	3.092	1 $\beta$	3.082	1 $\beta$	3.082	1 $\beta$	3.074	1 $\beta$	3.044	0.5 $\beta$	3.077	1	025, 115, 114	2.915	0.5
7	2.859	1	2.836	1	2.849	1	2.852	1	2.845	1	2.843	1	202 $\beta$ , 131 $\beta$ , 115, 116 $\beta$	2.701	<i>Ind.</i>
8	2.681	0.5	2.669	0.5	2.683	0.5	2.669	0.5	2.673	3	2.574	4	202 $\beta$ , 131, 116	2.630	2
9	2.582	4	2.573	4	2.582	3	2.566	3	2.573	3	2.574	4	204, 133	2.434 $\dagger$	1
10	2.402	2 $\beta$	2.392	3 $\beta$	2.399	3 $\beta$	2.392	2 $\beta$	2.384	2 $\beta$	2.394	2 $\beta$	040, 221, 041	2.260	0.5
11	2.256	0.5	2.248	0.5	2.269	1	2.256	0.5	2.256	0.5	2.267	0.5	206, 137, 0010	2.170	0.5
12	2.191				2.214	0.5	2.196	0.5	2.119	1 $\beta$	2.200	0.5	201 $\beta$ , 139, 0012	1.999	2-3
13	2.141	1 $\beta$	2.141	1 $\beta$	2.127	1 $\beta$	2.119	1 $\beta$	2.119	1 $\beta$	2.141	1 $\beta$	060, 331, 131 $\beta$ , 2010	1.846 $\dagger$	0.5
14	1.999	1 $\beta$	1.964	1 $\beta$	1.980	1 $\beta$	1.986	1 $\beta$	1.968	1 $\beta$	1.985	1 $\beta$	333, 331, 335, 333	1.701	0.5
15	1.823	0.5	1.703	0.5	1.823	0.5	1.827	0.5	1.711	0.5	1.709	0.5	0014, 335, 333	1.672	3
16	1.718	0.5	1.703	0.5	1.716	0.5	1.710	0.5	1.711	0.5	1.643	2 $\beta$	337, 335	1.539	4
17	1.656	2 $\beta$	1.645	2 $\beta$	1.650	3 $\beta$	1.649	2 $\beta$	1.649	2 $\beta$	1.590	0.5	2012, 131 $\beta$	1.433 $\dagger$	1
18					1.596	0.5 $\beta$	1.510	4	1.508	3	1.511	3	402, 260, 400, 262	1.399	0.5
19	1.516	4	1.512	4	1.514	6	1.496	0.5	1.508	3	1.491	0.5	0016, 264, 400 $\beta$	1.255	0.5
20	1.501	1	1.495	0.5	1.499	1	1.496	0.5	1.508	3	1.491	0.5	2014, 131 $\beta$ , 339	1.218	0.5
21					1.445	0.5					1.422	0.5			
22	1.379	0.5			1.375	0.5					1.375	0.5			
23	1.337	0.5 $\beta$			Broad	<i>Ind.</i>					1.343	0.5 $\beta$			
24	1.306	1	1.341	1 $\beta$	1.309	3	1.304	2	1.304	1	1.306	2			
25			1.284	1	1.284	1	1.304	2	1.304	1	1.279	0.5			
26	1.254	0.5	1.254	1	1.259	1	1.250	0.5	1.248	0.5	1.252	1			
27	1.204	0.5	1.203	0.5	1.205	1	1.201	0.5							
$\beta$	19.96		20.06		20.02		20.02		20.00		19.98				
$\beta$	9.10		9.07		9.06		9.06		9.05		9.10				
$\beta$	5.25		5.24		5.24		5.25		5.23		5.25				
$\beta$	95°		95°		95°		95°		95°		95°				
S.G.	2.855										2.81			3.151	

\* From Mora, Minnesota.  
 † Weak lines are also present at *d*=2.503, 1.910, 1.502, 1.474, 1.310.  
 $\beta$  = a line produced by K  $\beta$  radiation of iron.

*Ind.* = indistinct edge of line.  
 $\beta$  = broad line.  
 $\beta$  = very broad line.

that weak lines of mica would be absent in glauconite on account of their diffused character, even though the two structures were the same. Another factor to be considered is the preferred orientation of the mica lamellae parallel to the thread, which causes a much greater observed intensity for basal planes. This would not be the case with glauconite because each grain of powder constitutes an aggregate of still smaller particles.\*

#### EXPERIMENTAL DATA

There can be little doubt that next to talc the micas possess the most stable layer structures at high temperatures. Experiments on the stability of glauconites, biotites, and other layer structures were made at 750°C. The heating was carried out in air as well as in CO<sub>2</sub> over periods of twenty hours. Only the glauconites, biotites (other micas were not tested), and the almost iron-free sheridanite (12) did not collapse. Chlorites containing considerable iron, vermiculites, montmorillonite, nontronite, and stilpnomelane broke down under these conditions. Two of the diagrams of glauconite after heating are given in Table 2. They indicate a very slight expansion of the lattice in the direction normal to the cleavage and a corresponding contraction in the direction of the *b*-axis.

Other stability experiments were conducted in steel bombs entirely lined with gold. The glauconite was heated in solutions at temperatures as high as 300°C. over periods as long as seven days. Some of the experiments are given below, and the resultant *x*-ray diagrams are listed in Table 2.

1. No. 2 glauconite at 200°C. in water containing a very slight amount of NH<sub>4</sub>F. Five days. Table 2, column 3.
2. The same at 300°C. Table 2, column 4.

\* Except for one line (No. 4, Table I) the agreement would be quite excellent. This line is considerably stronger and broader than any corresponding line in biotite. It also has the appearance as if its outer edge is rather variable in position between 3.62Å and 3.67Å. Such anomalous behavior and intensity of a line, however, are not unique for glauconite. They may be found in other extremely fine-grained crystalline substances, as for example, nacrite, vermiculite, stilpnomelane, and montmorillonite. The finer the grain the more likely they will be. The writer has no explanation to offer for them at present. The biotite which is used for comparison in Tables 1 and 5 is from a granite at Mora, Minnesota (8). Its analysis is given in Table 3. This biotite is one of five analyzed biotites which were used for *x*-ray analysis. It is typical for all of them.

TABLE 2. POWDER DIAGRAMS OF GLAUCONITES SUBJECTED TO VARIOUS TREATMENTS

No.	Glauc. No. 1		2		2		2		2		6	
	750°C.		750°C.		H <sub>2</sub> O at 200°		H <sub>2</sub> O at 300°		Thallium		Thallium	
	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
1	10.14	2	10.17	3	10.13	2	9.99	2	9.99	1	9.99	2
2	4.48	1	4.49	2	4.95	0.5	4.99	0.5	4.48	1	4.53	2
3	3.66	0.5	3.62	1	4.50	1	4.51	2	3.59	1	3.65	0.5
4	3.333	4	3.368	3	3.62	3	3.64	1	3.59	1	3.65	0.5
5	3.126	0.5	3.368	3	3.295	3	3.304	2	3.285	2	3.304	3
6	2.863	0.5	2.852	0.5	3.066	1	3.066	1	3.052	1	3.074	1
7			2.702	0.5	2.836	1	2.838	1	2.829	0.5	2.852	1
8			2.852	0.5	2.647	0.5	2.669	0.5	2.669	0.5	2.683	0.5
9	2.571	3	2.577	3	2.562	4	2.573	3	2.551	3	2.568	4
10	2.389	2	2.387	2	2.383	3	2.392	2	2.370	2	2.389	3
11	2.247	0.5	2.248	0.5	2.248	1	2.244	1	2.247	1	2.263	1
12			2.187	1 <sub>b</sub>	2.187	1 <sub>b</sub>	2.191	1	2.187	1	2.207	1
13	2.142	0.5	2.141	0.5	2.121	1 <sub>b</sub>	2.130	1 <sub>b</sub>	2.127	1 <sub>b</sub>	2.135	1
14			1.968	0.5 <sub>b</sub>	1.968	0.5 <sub>b</sub>	1.983	0.5	1.962	1 <sub>b</sub>	1.985	1
15	1.820	0.5	1.831	0.5	1.812	0.5	1.810	0.5	1.805	0.5	1.817	0.5
16			1.653	1	1.708	0.5	1.697	0.5	1.699	1	1.705	0.5
17	1.655	1	1.653	1	1.637	2 <sub>ab</sub>	1.641	1 <sub>ab</sub>	1.636	2 <sub>ab</sub>	1.641	2 <sub>ab</sub>
18			1.509	3	1.586	0.5	1.589	0.5	1.580	0.5	1.589	0.5
19	1.506	2	1.492	0.5	1.504	4	1.508	3	1.503	3	1.510	4
20			1.439	0.5	1.489	0.5	1.508	3	1.485	1	1.489	1
21			1.366	0.5	1.435	0.5	1.448	0.5	1.428	0.5	1.428	0.5
22			1.355	0.5	Broad	<i>Ind.</i>					1.345	0.5 <sub>b</sub>
23	1.299	1	1.303	1	1.299	2	1.299	1	1.296	2	1.301	2
24	1.283	0.5				0.5	1.270	0.5	1.270	0.5		
25	1.247	0.5			1.249	0.5	1.249	0.5	1.250	0.5	1.252	1
26											1.200	0.5
27												

Sp. Gr. 3.02

*Ind.* = indistinct.  
*b* = broad.  
*ab* = very broad.

3. No. 2 glauconite at 300°C. in  $\text{NaHCO}_3$  (concentrated solution at room temperature). Nine days. Gave a new mineral not yet identified.

4. No. 2 glauconite at 300°C. in  $\text{MgCl}_2$  solution (5 gms.  $\text{MgCl}_2$  in 20 cc. water) Seven days. The result was a forcing apart of the mica layers and an approach to vermiculite.

In all experiments the air above the solutions was replaced by  $\text{CO}_2$ .

Ammonium fluoride was added in experiments No. 1 and 2 in the hope of increasing the mobility of the ions. It may have had this effect for the lines in the diagrams of the bomb experiments seem to be slightly sharper. On the other hand, the anomalous line, No. 4, which was mentioned above, becomes rather weak or disappears entirely. This is also true for the specimens heated to 750°C.

Further experiments dealt with the possible replacement of the K ions. If such replacement occurred, shifts of lines might be of value in interpreting the structure. Experiment No. 3 proved a failure in this respect since it formed a new compound. Thallium has been mentioned by Holzner as replacing K in stilpnomelane (15), and also  $\text{H}_2\text{O}$  in stilpnochloran (16). The writer repeated his experiments with essentially similar results. In the case of glauconite considerable amounts of thallium seem to be taken into the structure judging by the increase of the specific gravity of glauconite No. 6 from 2.81 to 3.02 after boiling in thallium nitrate solution for four hours.<sup>2</sup> No appreciable intensity differences were noticed in the powder diagrams of such treated material (see columns 5 and 6, Table 2). Thallium has an atomic number of 81 as compared with 19 for potassium. Its diffractive power, therefore, should be more than four times that of K and when substituted in the structure it should change the intensities markedly. That such a change is not noticeable to the eye is chiefly because at the most only 25 per cent of the K ions were replaced by Tl. The density of the mineral would reach values between 3.9 and 4.0 if the replacement were complete. This makes it probable that only K ions which were at or near the surface of the mineral particles were replaced. It would explain why in biotite (Mora, Minnesota) the density increased from 3.151 to only 3.161 after treatment with thallium nitrate solution. The particle size in the biotite is very much larger and so its surface is only a small fraction of that exposed in glauconite.

<sup>2</sup> After treatment the material was washed very carefully in boiling water several times for long periods.

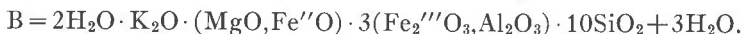
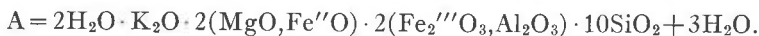
CHEMICAL CONSIDERATIONS

Many glauconite analyses have been published, some of them excellent, others of doubtful material. For the present discussion only three publications need be mentioned since they contain the latest reliable information. Hallimond (2 and 3) on the basis of twelve selected analyses came to the conclusion that:

In the groups  $R_2O_3$  and RO the molecular proportions are not constant and do not stand in any simple ratio to the silica and alkalis; the ordinary substitutions of alumina for ferric iron and magnesia for ferrous iron are therefore insufficient to explain the analyses. If, however, the  $(Fe, Mg)O$  and  $(Fe, Al)_2O_3$  are treated as mutually replaceable, considerable improvement can be brought about.

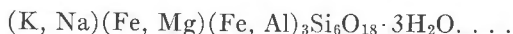
He gave the formula:  $R_2O \cdot 4(R_2O_3, RO) \cdot 10SiO_2 \cdot nH_2O$ .

C. S. Ross (1) four years later in a similar study in which seventeen analyses were used, considered glauconite an isomorphous mixture of two end members with the formulas:



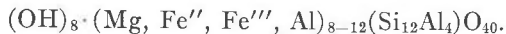
Schneider (4) a year later wrote:

The composition and variability of glauconite are more accurately expressed by the formula:



The present writer averaged the analyses of each of the three investigators and compared the results. They are remarkably similar. It would be difficult to say which is closest to the truth. They bear out the contention that glauconite is a definite species.

Real difficulty is encountered when one tries to reconcile this glauconite formula with the structure of mica. The structural formula of mica per unit cell is:



Therefore a biotite hardly ever contains more than 40 per cent  $SiO_2$  while glauconite varies between 46 and 51 per cent  $SiO_2$ . The distribution of ions in a typical mica structure is shown diagrammatically in Fig. 1.

Further discussion is best restricted to a glauconite of which we have almost complete data. Glauconite No. 1, whose chemical composition is given in Table 3 is chosen. Its molecular proportions are found in column 1, Table 4. On the assumption that all  $SiO_2$

is contained in the  $(\text{Si}_3\text{Al})\text{O}_{10}$  tetrahedral layers typical of mica the number of  $\text{SiO}_2$  "molecules" in a unit cell is twelve. The number

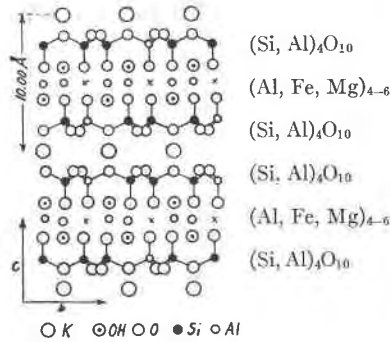


FIG. 1. Diagram showing the sequence of ionic planes in muscovite.

of the other oxides is of corresponding size as shown in column 2. Column 3 gives the number of ions. Adjusting the ions now on the

TABLE 3. ANALYSES OF GLAUCONITES AND BIOTITE X-RAYED.

	Glaucouite No. 1	Glaucouite No. 2	Biotite* Mora, Minn.
$\text{SiO}_2$	48.66	49.05	35.67
$\text{Al}_2\text{O}_3$	8.46	7.96	14.56
$\text{Fe}_2\text{O}_3$	18.80	19.66	3.03
FeO	3.98	0.75	23.23
MgO	3.56	1.17	9.24
CaO	0.62	2.34	1.13
$\text{Na}_2\text{O}$	None	0.78	0.49
$\text{K}_2\text{O}$	8.31	6.18	8.06
$\text{H}_2\text{O}-$	1.94	11.79	0.23
$\text{H}_2\text{O}+$	4.62		1.02
$\text{TiO}_2$			3.32
$\text{Cr}_2\text{O}_3$			0.03
F			0.16
Total	98.95	99.68	100.22
With $\text{CO}_2$	99.08		

No. 1. Glenn V. Brown, analyst.

No. 2. E. P. Henderson, analyst.

\* F. F. Grout, analyst.

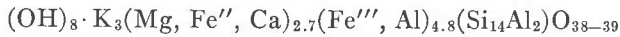


basis of the number of K ions present, a typical mica would have in its structure the proportional amounts shown in column 4. This would leave an excess of SiO<sub>2</sub> and H<sub>2</sub>O. Is this excess of SiO<sub>2</sub> and H<sub>2</sub>O present as submicroscopic opal or adsorbed hydrated SiO<sub>2</sub> around the mica particles? Such SiO<sub>2</sub> would not be easily detectable by x-rays. There is a serious objection to such an hypothesis. It could not explain the relative constancy of SiO<sub>2</sub> in glauconites. The optical properties should also be much more variable.

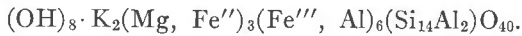
TABLE 4. MOLECULAR AND IONIC RATIOS IN GLAUCONITE NO. 1

	1	2	3	4	5
	Molecular Ratios	No. of "Oxide Molecules"	No. of Ions	Ratio of Ions in Mica	No. of Ions in Glauconite
SiO <sub>2</sub>	.8102	12.0	12.0 Si	7.8	14.0 Si
Al <sub>2</sub> O <sub>3</sub>	.0830	1.22	2.4		2.8 Al
Fe <sub>2</sub> O <sub>3</sub>	.1177	1.74	3.5 Fe'''		4.0 Fe'''
FeO	.0554	0.82	0.8 Fe''		1.0 Fe''
MgO	.0883	1.31	1.3 Mg	7.8	1.5 Mg
CaO	.0110	0.16	0.2 Ca		0.2 Ca
K <sub>2</sub> O	.0882	1.31	2.6 K	2.6	3.0 K
H <sub>2</sub> O-	.1076	1.59	1.6 H <sub>2</sub> O		
H <sub>2</sub> O+	.2564	3.80	7.6 OH	5.2	6.1 OH

The alkali content of many micas is considerably lower than the formulas require. This is also true for glauconites. The deficiency is not serious. It means that not all the K positions between the layers (Fig. 1) need to be occupied. The number of "holes" depends probably upon the number of (Al, Fe''') ions replacing Si, for theoretically for every (Al, Fe''') ion in the (Si, Al)<sub>4</sub>O<sub>10</sub> tetrahedral layer there should be a K ion in the structure. Under the condition under which glauconites form, a deficiency of Al<sub>2</sub>O<sub>3</sub> (soluble in some form) is probably the rule, while the supply of SiO<sub>2</sub> in colloidal or other solution is abundant. This would favor a mica structure with a minimum of Al and maximum of Si ions in the (Si, Al)<sub>4</sub>O<sub>10</sub> portions of the layers. On the assumption that of the sixteen (Si, Al) positions in the unit cell only two were occupied by Al instead of four, the Si could be distributed over fourteen positions, and other adjustments made accordingly, as shown in column 5, Table 4. The actual formula for this particular case would be, disregarding excess H<sub>2</sub>O:



while the structural formula would be:



On taking the "molecules" of this actual formula and placing them into the unit cell, a theoretical density of 2.83 is obtained which is slightly less than the one found (2.855). Three  $\text{H}_2\text{O}$  molecules of the analysis are disregarded in this calculation, which is justified by the dehydration curve found by C. S. Ross for this glauconite (1, p. 8).

The Si ions theoretically are confined to the  $(\text{Si}, \text{Al})_4\text{O}_{10}$  tetrahedral layers. But there are reasons to believe that they can and do enter other portions of the structure. While they may not become ions with a covalency of six like  $\text{Fe}'''$  and Al they probably do replace a few of these occasionally. The best known example of this kind seems to be anauxite (9, p. 87). In kaolinite the ratio  $\text{SiO}_2:\text{Al}_2\text{O}_3$  is usually close to 2:1, while in anauxite, which has the same structure, it may be as high as 3:1. It is probable that anauxite, just as glauconite, forms under conditions where the mass action of  $\text{SiO}_2$  produced a kaolinite high in  $\text{SiO}_2$ . There is, however, no avoiding the fact that the unit cell can accommodate at the most fourteen to fifteen Si ions in order to remain below a density of 3.0 (which is probably never exceeded by any glauconite). With fourteen Si ions in the cell, the ratio of  $\text{Si}:(\text{Al}, \text{Fe}, \text{Mg})$  is 12:9.5 in column 5, Table 4. This is a trifle too low for the structure proposed which calls for at least 14:10. It is possible that a vacancy or "hole" exists in each unit cell (statistically speaking) which in a mica that formed under conditions of high mobility of ions does not usually exist. That such vacancies may exist in silicates is well known. Due to such deficiency in cations in glauconite OH might easily take the place of O to balance the electrostatic charges. A structural formula covering *all* these proposed changes would be:  $(\text{OH})_{6-10} \cdot \text{K}_{2-3}(\text{Mg}, \text{Fe}''', \text{Ca})_{1-3}(\text{Fe}''', \text{Al}, \text{Si})_{3-6}(\text{Si}_{13-14}\text{Al}_{2-3})\text{O}_{38-40}$

#### CALCULATIONS OF STRUCTURES

While the powder spectrum photographs of glauconite and mica seem to agree within reasonable limits it was thought best to calculate interplanar distances and intensities for both and compare them with the observed. The muscovite structure  $\text{C}_{2h}^6$  as found

by Pauling (5) and Jackson and West (6) was used for the calculations. Its corrected coordinates are given by Jackson and West (7). The formula as given by Wyckoff (14, p. 165):

$$I \propto j(A^2 + B^2) \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

was used for intensity calculations. The value of the frequency factor  $j$  is explained by Wyckoff (14, p. 177).  $I$  was divided by 5000 to obtain values of suitable size. The ionic numbers of the atoms were used for their scattering power  $F$ . O and OH = 10, Si and Al = 10. The Fe<sup>II</sup>, Fe<sup>III</sup>, Al and Mg combinations which occupy the Al positions were assumed in such proportions to give each a scattering power of 20. It was assumed that all K positions are occupied. K = 18. Any reduction in their number would materially influence the theoretical intensities as indicated in column A, Table 5 by the + and - signs for the first twenty planes. Column B gives the calculated intensities as they would be if Fe<sup>III</sup> occupied the Al positions in the (Si<sub>3</sub>Al) tetrahedral layers and all of the Al ions were in the positions between the tetrahedral layers. For this case the assumption was also made that only two-thirds of the K positions are occupied. This does not mean that all Al is actually replaced by Fe<sup>III</sup> in the positions of the (Si<sub>3</sub>Al)O<sub>10</sub> tetrahedral layers. It is simply a possibility. Values somewhere between  $A$  and  $B$  are most likely the best.

The intensities for biotite, Table 5, were calculated as those of column  $A$ , Table 5, except that the additional four Al positions of the structure which are vacant in muscovite were also filled with ions of scattering power,  $F = 20$ .

Considering the nature of the formula used, the agreement between observed and calculated intensities is fair for most planes. The  $hhl$  and  $Okh$  reflections do not agree any better than for other layer structures in which this behavior was pointed out previously (11, p. 417).

The indices of two or three weak reflections were not calculated on account of the very large amount of labor involved in comparison to the benefits that could be derived. On the other hand, several dozen calculated reflections of low intensity were omitted from Table 5 on account of lack of space. The rate of decrease in observed intensities in the layer structures whose particles are

TABLE 5. THEORETICAL AND OBSERVED INTENSITIES FOR UNIT CELLS OF GLAUCONITE AND BIOTITE

		Glaucosite			Biotite from Mora, Minn.		
Observed Int.	Theoretical Intensity		$\bar{d}$	Indices	$\bar{d}$	Theoretical Intensity	Observed Int.
	A	B					
1-2	190+	160	9.970	002	10.015	390	4
	0	27	4.985	004	5.007	5	
2	3-	2	4.537	020	4.616	3	$\frac{1}{2}$
	21+	39	4.522	110	4.601	21	
	52+	56	4.484	11 $\bar{1}$	4.562	4	
	8+	24	4.422	021	4.497	8	
	14-	4	4.341	111	4.408	1	
	0	2	4.241	112	4.308	0	
1-2b	14+	14	4.128	022	4.192	1	5
	3	0	4.007	112	4.065	3	
	48-	31	3.878	11 $\bar{3}$	3.932	6	
	32-	27	3.746	023	3.797	32	
2-3	0+	0	3.615	113	3.661	16	5
	52-	48	3.484	11 $\bar{4}$	3.526	52	
1b	70-	42	3.349	024	3.394	22	$\frac{1}{2}$
	72+	77	3.323	006	3.338	111	
Ind.	64-	62	3.231	114	3.266	64	5
	2-	4	3.111	11 $\bar{5}$	3.143	4	
	59-	55	2.996	025	3.026	59	
	51-	40	2.886	115	2.913	16	
	42-	36	2.781	116	2.807	42	
	0	0	2.682	026	2.705	10	
	14	23	2.608	200	2.654	5	
	24	26	2.608	13 $\bar{1}$	2.654	8	
	25	19	2.587	116	2.609	25	
	3-4	34	26	2.579	20 $\bar{2}$	2.624	
	78	62	2.579	131	2.624	118	
2	2	1	2.492	008	2.503	8	1
	2	9	2.471	202	2.512	0	
	5	20	2.471	13 $\bar{3}$	2.512	0	
	60	62	2.399	20 $\bar{4}$	2.436	83	
	101	119	2.399	133	2.436	142	
$\frac{1}{2}$	17	11	2.268	040	2.307	6	$\frac{1}{2}b$
	34	23	2.266	22 $\bar{1}$	2.306	34	
	1	1	2.261	220	2.301	2	
	31	21	2.253	041	2.292	31	
	27	18	2.242	22 $\bar{2}$	2.281	8	
	0	0	2.233	204	2.264	0	
	0	0	2.233	13 $\bar{5}$	2.264	2	
	26	18	2.228	221	2.266	26	

TABLE 5. CONTINUED.

Glaucosite			Biotite from Mora, Minn.				
Observed Int.	Theoretical Intensity		<i>d</i>	Indices	<i>d</i>	Theoretical Intensity	Observed Int.
	<i>A</i>	<i>B</i>					
1 <i>b</i>	0	0	2.211	042	2.249	4	1-2
	19	13	2.170	222	2.206	5	
	6	4	2.146	043	2.181	6	
	70	45	2.145	206	2.173	90	
	133	85	2.145	135	2.173	173	
1 <i>b</i>	5	7	2.064	044	2.096	0	2-3
	46	53	1.994	0010	2.003	33	
	20	12	1.971	206	1.994	30	
	40	27	1.971	137	1.994	61	
	7	4	1.886	208	1.908	12	
2 <i>b</i>	13	9	1.886	137	1.908	25	$\frac{1}{2}$
	0	0	1.729	208	1.746	1	
	0	0	1.729	139	1.746	2	
	11	4	1.662	0012	1.669	17	
	40	37	1.656	2010	1.672	52	
4	78	71	1.656	139	1.672	101	3
	18	15	1.621	313	1.647	7	
	13	10	1.621	315	1.647	4	
	13	12	1.575	314	1.599	13	
	29	23	1.522	2010	1.535	38	
$\frac{1}{2}$ -1	51	42	1.522	1311	1.535	68	4
	50	47	1.512	060	1.538	60	
	104	94	1.512	331	1.538	121	
	28	27	1.495	335	1.520	41	
	24	21	1.495	331	1.520	35	
$\frac{1}{2}$	4	5	1.461	2012	1.473	8	0.5
	6	6	1.461	1311	1.473	12	
	10	2	1.447	335	1.471	18	
	7	2	1.447	333	1.471	13	
	5	6	1.424	0014	1.430	7	
<i>b Ind.</i>	1	1	1.376	337	1.397	0	1
	1	1	1.376	335	1.397	0	
	41	46	1.350	2012	1.360	50	
	83	93	1.350	1313	1.360	105	
	23	27	1.308	402	1.331	17	
2	58	70	1.308	260	1.331	44	$\frac{1}{2}$ -1
	41	37	1.304	400	1.327	50	
	59	56	1.304	262	1.327	75	
	3	8	1.299	2014	1.309	1	
	8	10	1.299	1313	1.309	4	

TABLE 5. CONTINUED.

Glaucouite			Biotite from Mora, Minn.				
Observed Int.	Theoretical Intensity		$d$	Indices	$d$	Theo- retical Inten- sity	Observed Int.
	A	B					
$\frac{1}{2}$ } 1 } $\frac{1}{2}$ }	9	10	1.293	339	1.311	16	} $\frac{1}{2}$
	9	7	1.293	337	1.311	16	
	21	14	1.290	404	1.312	27	
	0	1	1.290	262	1.312	1	} $\frac{1}{2}$
	18	20	1.279	402	1.301	24	
	28	55	1.279	264	1.301	63	
	8	10	1.252	406	1.272	12	} $\frac{1}{2}$
	14	19	1.252	264	1.272	23	
	31	26	1.246	0016	1.251	43	
	20	18	1.236	404	1.256	27	} 1
	4	0	1.236	266	1.256	9	
	13	7	1.207	2014	1.216	18	
	31	20	1.207	1315	1.216	43	} $\frac{1}{2}$
	11	15	1.205	339	1.220	5	
	0	2	1.205	3311	1.220	1	
0	0	1.199	408	1.218	1		
1	2	1.199	266	1.218	3		
	$c_0$		20.03		20.11		
	$b_0$		9.07		9.23		
	$a_0$		5.24		5.33		
	$\beta$		95° 00'		95° 04'		

$b$  = unusually broad line.

*Ind.* = indistinct.

below their optimum size as in glaucouite shows a noteworthy behavior. As the third index of planes increases—in other words, as the angles of the planes which they make with the basal plane become relatively small—the decrease in intensity is considerably greater than expected from the formula given. Therefore, “steep” planes reflect relatively more intensely. The calculated sizes of the unit cells and  $\beta$  angles, Table 5, of biotite and glaucouite agree quite well with those observed. The mean value of  $\beta$  for all glaucouites is close to 95°.

CONCLUSIONS

It is shown by powder spectrum photographs that the structures of glauconite and mica are almost identical. The constants of the minerals, choosing a biotite for comparison, are:

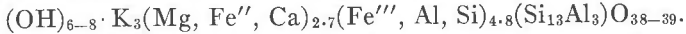
	Glauconite) (Avge. of 6 specimens)	Biotite (Mora, Minnesota)
$c_0$ .....	20.03 Å	20.11 Å
$b_0$ .....	9.07	9.23
$a_0$ .....	5.24	5.33
$\beta$ angle.....	95°00'	95°04'
Axial ratio=	.5773:1.000:2.208	.5773:1.000:2.179

The theoretical plane 100 for a  $\beta$  angle of 90° as usually quoted for biotite becomes the plane 30 $\bar{2}$  in this new orientation, which corresponds to that of muscovite.

Glauconite is as stable as biotite at temperatures as high as 750°C., which is additional proof of its structure. Glauconite absorbs considerable amounts of thallium ions which probably replace K ions to an extent not exceeding 25 per cent.

*The high SiO<sub>2</sub> and H<sub>2</sub>O content of glauconite seems to be due to the environment in which it is formed.* Excess of soluble SiO<sub>2</sub> over available soluble Al<sub>2</sub>O<sub>3</sub> gives rise to a higher Si:Al ratio in the (Si, Al)<sub>4</sub>O<sub>10</sub> tetrahedral layers than in mica. It may even cause substitution of a few Si ions for Fe<sup>'''</sup> or Al in approximately the positions having a covalency of 6. These Si ions would not necessarily be hexavalent, however.

It is also thought that in comparison with a muscovite glauconite may have occasional vacant positions or "holes" in its structure. A formula which would take into account such probabilities is: (OH)<sub>6-10</sub> · K<sub>2-3</sub>(Mg, Fe<sup>''</sup>, Ca)<sub>1-3</sub>(Fe<sup>'''</sup>, Al, Si)<sub>3-6</sub>(Si<sub>13-14</sub>Al<sub>2-3</sub>)O<sub>38-40</sub>. The formula for a specific case (glauconite No. 1) is:



Calcium probably would be permissible to only a fraction of a per cent in glauconite. Of the H<sub>2</sub>O given in analyses, probably about half may be adsorbed.

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