

# THE OPTICAL PROPERTIES AND CHEMICAL COMPOSITION OF GLAUCONITE

BY CLARENCE S. ROSS

*Geologist, United States Geological Survey*

## INTRODUCTION

Glauconite has long been a subject of study by mineralogists, by students of sediments, and by those interested in modern marine deposits. It is a mineral that has formed in every geologic age from the Cambrian to the present, and the related mineral greenalite is found in pre-Cambrian rocks.<sup>1</sup> Beds of nearly pure glauconite with wide lateral extent are not uncommon and it occurs in varying proportions in almost all types of sediments. Glauconite is one of the important materials now forming on the sea bottom, and the potassium content makes it a possible source of plant fertilizers. All this has inspired many studies of glauconite and much literature has accumulated on the subject, but nevertheless there has been little agreement as to the exact chemical composition of glauconite and its optical properties are but imperfectly known. The incomplete understanding of glauconite has led to the present study which includes a determination of the optical properties of material from several localities, and an investigation of the chemical relationships which appears to satisfactorily explain the variation in chemical composition.

## OCCURRENCE OF GLAUCONITE STUDIED

In 1915 L. A. Myllius brought to the attention of the writer a mineral from the lead mines of southeastern Missouri that had long been called "chlorite" or "chloritic material,"<sup>2</sup> and on investigation this proved to be glauconite.<sup>3</sup> Additional material was secured from some of the mining companies and Doctor Buehler, the State Geologist of Missouri. Diamond drill cores furnished by the St. Joseph Lead Co. contained some unusually good material, and this led to a thorough study of the Missouri glauconite. The

<sup>1</sup> Leith, C. K., U. S. Geol. Survey Mono., vol. 43, 1903, pp. 239-259.

<sup>2</sup> Buckley, E. R., Mo. Bur. Geol. Mines, vol. 9, pt. 1, p. 28, 1909.

<sup>3</sup> Ross, C. S., Econ. Geol., vol. 11, pp. 289-290, 1916.

glauconite of southeastern Missouri occurs in the Bonneterre dolomite of Upper Cambrian age, and is intimately associated with the lead ore, and locally forms 50 per cent or more of the rock. The grains vary in size and shape, and the relations to the inclosing rock have possibly been modified by recrystallization of the dolomite. The type of glauconite which is most abundant forms loose aggregates that commonly occur as more or less rounded grains. Another type forms wedge-shaped areas that are sharply bounded by euhedral dolomite crystals. Some of the glauconite in diamond drill cores from the St. Joseph Lead Co. mines forms small compact grains about 0.2 millimeter in diameter in dolomite and associated with a little detrital quartz. The individual grains of all these types are never truly amorphous and they leave no doubt of their crystalline character. They are composed predominantly of the fine grained aggregates of overlapping crystal plates that are characteristic of nearly all glauconites, but a large proportion of the grains in the compact type of glauconite from the St. Joseph Lead Co.'s drill cores are single crystal individuals, and an occasional grain of the other types shows this property.

A very careful study of the greensands of New Jersey has been made by Doctor Mansfield,<sup>4</sup> of the United States Geological Survey, who describes and figures glauconite grains, each of which is a single crystalline individual. Some of the New Jersey material was placed at the disposal of the writer by Doctor Mansfield and the optical properties of this glauconite have been determined.

Glauconite occurs in the bentonitic horizon of the Ordovician of Tennessee, Alabama, and Kentucky that has been described by Nelson.<sup>5</sup> At Singleton, Tenn., it is associated with quartz, feldspar, muscovite, and the claylike mineral, montmorillonite, that is characteristic of bentonite. A few of the glauconite grains have the structure of the usual cryptocrystalline aggregate, but a majority of them are single crystal individuals. Some crystals of glauconite lie between the lamellae of muscovite plates, and others are imbedded in montmorillonite crystals, and crystals of glauconite are often in parallel orientation with muscovite and montmorillonite.

Glauconite has also been studied from several other localities with determination of the optical properties. Individual crystals of glauconite were found after careful search in almost every sample studied, but sometimes hours of patient search were required before such a single individual was found.

---

<sup>4</sup> Mansfield, G. R., *Econ. Geol.*, vol. 15, pp. 547-566, 1920, U. S. Geol. Survey Bull. 527, 1922.

<sup>5</sup> Nelson, Wilbur A., *Geol. Soc. America, Bull.*, vol. 33, No. 3, pp. 605-615.

Most of the glauconite no doubt forms on the sea bottom in the manner commonly accepted,<sup>6</sup> but this method of origin can not apply to all occurrences. Glauconite is frequently observed that has formed in the cleavage cracks of other minerals, and also where it has partly or wholly replaced both silicates and carbonates. It is evident that glauconite has formed from solutions by direct precipitation and by replacement of preexisting minerals, and in many occurrences subsequent to the deposition of the inclosing sediments.

#### OPTICAL PROPERTIES

The glauconite from the Bonneterre dolomite, St. Joseph Lead Co. mines near Bonneterre, St. Francis County, Mo., is more completely crystalline and shows the optical properties more perfectly than any other material that has been observed. For this reason it will be described in detail and the other types of glauconite will be compared with it.

The grains of glauconite that occur as single crystals vary in habit. Some have perfect, parallel cleavage and are rectangular in the plane perpendicular to the cleavage and more or less rounded in a plane parallel to the cleavage. A few suggest a roughly hexagonal outline parallel to the cleavage but no completely euhedral crystals of glauconite have been observed. Part of the grains have a curved helminth-like habit and the cleavage is radial, and others have a core that represents a single crystal surrounded by a fine grained aggregate of crystal grains. The better crystals have a very perfect cleavage, a strong pleochroism from bright green to yellow, and a moderately high birefringence. Glauconite is therefore similar to the micas in habit.

The indices of refraction of glauconite from the Bonneterre dolomite of Bonneterre, Mo., are  $\alpha=1.597$ ,  $\beta=1.618$ ,  $\gamma=1.619$ ,  $\gamma-\alpha=.022$ ,  $\pm.003$ . Optical character negative (-). The acute bisectrix X is nearly, but not quite normal to the cleavage. X inclined to C about  $3^\circ$ . The absorption is  $Z=Y<X$ , Pleochroism Z and Y lemon yellow, X dark bluish green (dark Russian green of Ridgeway). The optical angle is nearly constant with  $2V=20^\circ$ ,  $2E=33^\circ$ . The dispersion is distinct  $\rho>v$ , but the absorption of the red by the blue-green mineral makes it very difficult to observe.

The other types of glauconite that have been studied show the same properties in somewhat less perfection of detail. The glauconite from Singleton, Tenn., contains a very large proportion of grains that are individual crystals. These have the same general habit as those just described, but the color is very pale yellow to pale green. The largest optical angle observed ( $2V=30^\circ$ ) is that of the glaucon-

<sup>6</sup> Challenger Rept., Deep-sea deposits, 1891, p. 383.

ite from Woodstown, N. J. The optical properties of the glauconites studied are given in the following table:

TABLE I.—*Optical properties of glauconite*

	Optical character	Cleavage 001	Indices of refraction			$\gamma - \alpha$	2 V	2 E
			$\alpha$	$\beta$	$\gamma$			
1. St. Francis Co., Mo. ....	(-)	Good....	1.597	1.618	1.619	0.022	20°	33°
2. Woodstown, N. J. ....	(-)	Good....	1.612	1.629	1.630	.018	30°	50°
3. Singleton, Tenn. ....	(-)	Good....	1.590	1.609	1.610	.020	20°-23°	33°-37°
4. Piscataway, Md. ....	(-)	Good....	1.590	1.614	1.615	.025	24°	38°
5. Cambrian of Mian. ....	(-)	Good....	1.612	1.643	1.644	.032	19°	31°
6. Tampico, Mexico. ....	(-)	Good....	1.610	1.629	1.630	.020	22°	35°
7. Black Hills, S. Dak. <sup>a</sup> ..	(-)	Good....	1.610	1.629	1.630	.020	20°	33°
8. Patuxent Quad., Md., near Croom.	(-)	Good....	1.591	1.615	1.616	.025	16°	24°
9. Huntington, Oreg. ....	(-)	Poor....	1.59	-----	1.62	.03	20°-40°	30°-60°

<sup>a</sup> Crystal individuals are very rare and the determinations are only approximate.

(1) Glauconite from St. Joseph Lead Co. mine, near Bonnetterre, St. Francis County, Mo. Upper Cambrian age.

(2) Glauconite from Woodstown, N. J. Cretaceous age.

(3) Glauconite from Singleton, Tenn. Ordovician age.

(4) Glauconite from Piscataway, 2 miles southeast of Fort Washington, Md. Cretaceous age.

(5) Glauconite from Cambrian, of Minnesota, locality unknown.

(6) Glauconite from Cretaceous of the Tampico oil district, Mexico.

(7) Glauconite from Cambrian of Deadwood, S. Dak.

(8) Glauconite from near Croom, Patuxent Quad., Md.

(9) Glauconite from Huntington, Oreg.

The mineral from Huntington, Oreg., was a mineral specimen submitted to the Geological Survey for identification and the exact nature of its occurrence is not known. 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. The chemical composition, which is represented by analysis 13 (Table II) differs from typical glauconite only in being low in RO bases. The indices of refraction are  $\alpha=1.59$ ,  $\beta=1.62\pm.005$ , the axial angle is variable, 20°-40°, optical character (-). Thus the chemical composition and optical properties are those of glauconite, but the habit and structure are different from those of any previously described glauconite.

#### CHEMICAL COMPOSITION

The number of good analyses of glauconite is not large and many of those published are worthless, because in most of the older analyses iron has been determined in only one form of oxidation, because very impure material has frequently been used for analysis, and because methods of purification have frequently been faulty. Glinka <sup>7</sup> gives a number of analyses of Russian glauconites, but the results indicate that some of the material was very impure and some of the analyses show an unusually high content of potash. Sonstadt's

<sup>7</sup> Glinka, K., Zeitschr. Kryst. Min., vol. 39, 1899, p. 390 (abstract from Russian original).

heavy solution (potassium iodide and mercury iodide) was used in the separation of the glauconite, and since this mineral exchanges bases so readily that it can be used as a water softener, it is probable that the original potassium content was considerably augmented. On account of the possible error in potash content all of Glinka's analyses have been rejected, though some of them may undoubtedly be good.

Glauconite of undoubted purity contains very little calcium, and in fact there is commonly only enough calcium to combine with phosphorus when carbonates are completely absent. Silica is always low where calcium is high, and it is evident that calcium is present as an impurity, probably as calcite and possibly as gypsum in some specimens. For this reason all analyses that contained 1 per cent or more of calcium oxide ( $\text{CaO}$ ) have been rejected and the calcium in the analyses used has not been included among the essential bases in the derivation of the chemical formula.

The analyses of glauconite that have been made on the best material usually contain only small proportions of sodium, but it has been suggested<sup>8</sup> that there may be a sodium form of glauconite. This the writer is unable to confirm or disprove, but 3 analyses containing over 1 per cent of sodium oxide ( $\text{Na}_2\text{O}$ ) have been included in the tables.

The modern glauconites dredged from the sea bottom are fine-grained and earthy and so their purification for analysis has been very difficult. The analyses of three such specimens have been deemed good enough to be used in the chemical interpretation of glauconite, but most of those given in the literature were obviously made on very impure material. In Table II are listed 17 analyses that appear to be good enough to be used in an interpretation of the chemical composition of glauconite.

As a first step in interpreting these analyses  $\text{Al}_2\text{O}_3$  was combined with  $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}$  with  $\text{MgO}$ ,  $\text{Na}_2\text{O}$  with  $\text{K}_2\text{O}$ ,  $\text{H}_2\text{O}$  was left out of consideration for the time being, and small amounts of  $\text{P}_2\text{O}_5$ ,  $\text{CaO}$ , etc., were disregarded as they no doubt form impurities. The composition was then recalculated to 100 per cent and  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ , and  $\text{K}_2\text{O}$  plotted on a three component diagram (not reproduced here). The ratio between  $\text{K}_2\text{O}$  and  $\text{SiO}_2$  is constant and so the relations were not obscured by neglecting  $\text{SiO}_2$  for the time being and thus the failure to plot four interdependent variables. The dots representing composition fell along a fairly straight line and it was evident that glauconite contains only two components or end members. The analyses that were inferior were also plotted and proved to be fairly close to the line of ideal composition and even those that were very poor indicated no systematic variation from the ideal.

<sup>8</sup> Hallimond, A. F., *Mineralogical Magazine*, vol. 19, No. 98, pp. 332-333, 1922.

One of these end members is evidently composed of  $R_2O:RO:R_2O_3:SiO_2$  in the ratios 1:2:2:10 and the variation in composition was toward a second end member where  $R_2O:RO:R_2O_3:SiO_2=1:1:3:10$ . All the analyses of glauconite given in Table II and also the analyses that were rejected for various reasons lie between these two end members, but there is a possibility of a wider range of composition as the chemical relationships permit variation between 1:3:1:10 and 1:0:4:10.

The ratio of  $K_2O$  to  $SiO_2$  is approximately 1 to 10 as the average for all analyses used is 1 to 9.7.

The chemical composition of the ideal end members as just obtained and the analyses of glauconite have been graphically plotted on two coordinates in Figure 1. The elements that isomorphously replace one another have been combined as previously described and recalculated to 100 per cent so that only  $K_2O$ ,  $MgO$ ,  $Fe_2O_3$ ,  $SiO_2$ , and  $H_2O$  are considered. Water was included in the calculations but was not plotted as its line is very close to that of  $MgO$  and thus involved an overlapping of points.

The black dots in Figure 1 represent end members and the circles represent analyses. The vertical coordinate on the diagram shows the chemical composition in per cent, and the horizontal coordinate the proportion of the two end members. Thus the chemical composition of a glauconite is represented graphically by four circles lying on a single vertical line, the upper one being  $SiO_2$ , the next  $R_2O_3$  recalculated as  $Fe_2O_3$ , the next  $R_2O$  recalculated as  $K_2O$ , and the lowest  $RO$  recalculated as  $MgO$ . The departure from the theoretical composition is shown by the distance of the circles from the curve, and where the analyses exactly conform to theory the circles fall directly upon the curve. With few exceptions the circles fall very close to this ideal line and the analyses thus plotted represent so consistent a series that it seems evident that the end members have been correctly deduced. It will be seen that  $MgO$  decreases as  $Fe_2O_3$  increases; that  $SiO_2$  decreases in per cent, but not in ratio as  $Fe_2O_3$  increases; and that the ratio of  $K_2O$  to  $SiO_2$  is constant.

The same relationships are shown numerically in Table II. The three component diagram was used to determine the proportion of the two end members represented in each glauconite analysis. An ideal composition based on this deduced proportion was then calculated for each analysis given in the table, and the column immediately following the analysis gives the ratio of this ideal composition to the actual composition. Thus 100 represents exact agreement of an element in the analysis with the assumed proportion, and a departure from 100 shows a failure of the element to conform to the ideal composition. If an analysis conformed exactly to theory, 100 would

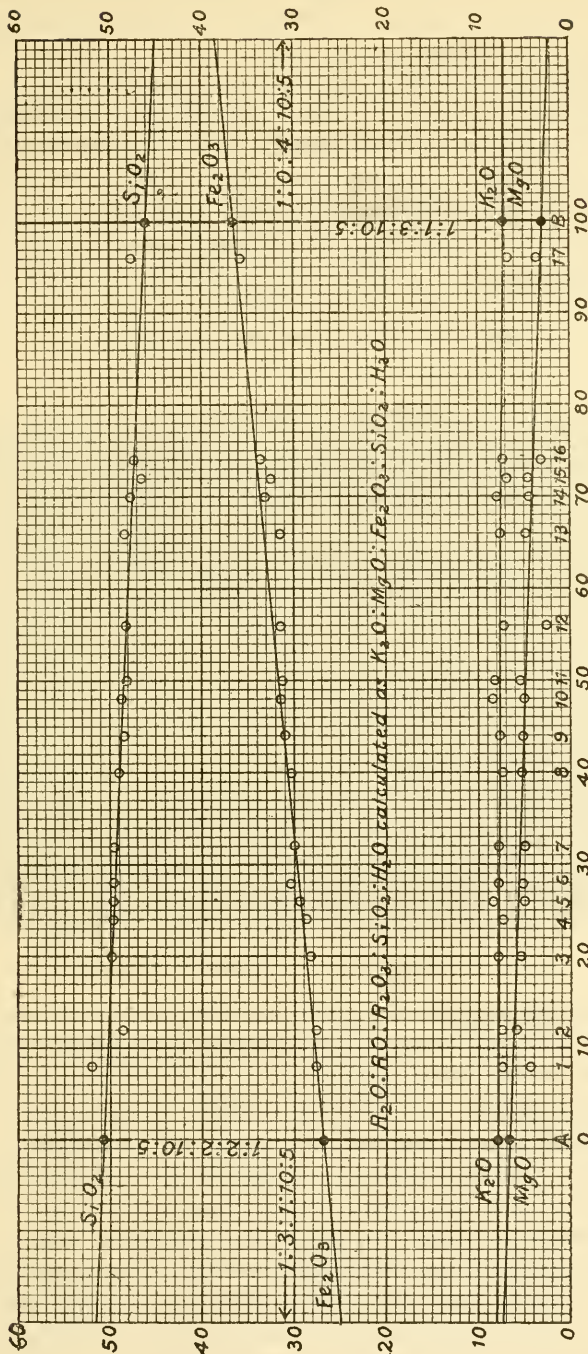


FIG. 1.—GRAPHIC PRESENTATION OF GLAUCONITE ANALYSES SHOWING VARIATION IN COMPOSITION BETWEEN END MEMBERS

follow  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ , and  $\text{MgO}$ . The number at the head of the column of ratios shows the proportion of the end members in the make-up of that analysis.

The analyses of glauconite given in the table have been compiled from various sources and the water has not been determined under similarly controlled conditions, and in most of them it has not even been determined separately below and above  $100^\circ$ . For these reasons they give no reliable evidence of the part water plays in the composition of glauconite. However, the water content of the unusually pure glauconite from the Bonnetterre dolomite of Bonnetterre, Mo., has been carefully determined for different temperatures in the chemical laboratory of the United States Geological Survey, and the dehydration curve is given in Figure 2.

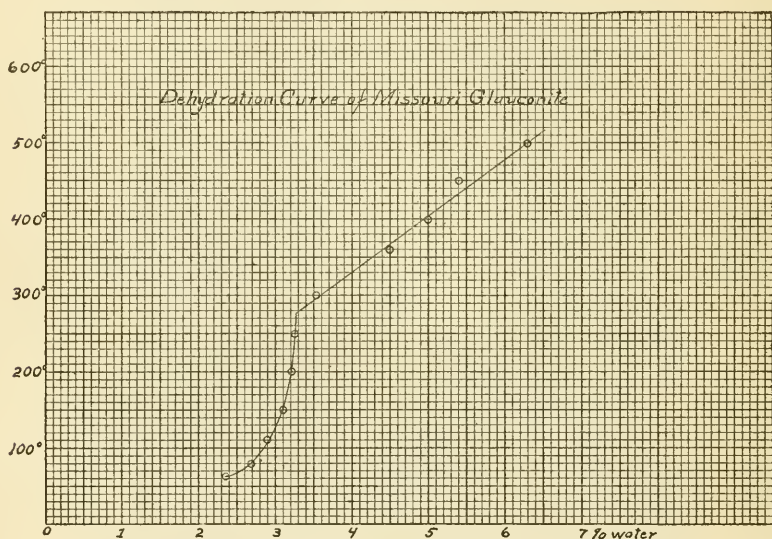
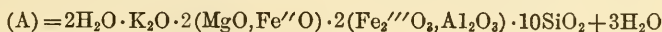


FIG. 2.—DEHYDRATION CURVE OF MISSOURI GLAUCONITE.

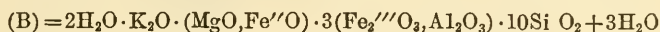
There is a sharp break in the curve at  $280^\circ$  and below that temperature about 3.30, and above about 3.26 per cent of the water is given off, the total water in the sample being 6.56 per cent of the whole. There is good reason for believing that the water above this sharp break is constitutional and below is water of crystallization or adsorbed water. ( $2\text{H}_2\text{O}$ ) seems to represent the constitutional water in the formula for glauconite, since that amount would demand 3.06 per cent, and since the ratio of theoretical water to water given off about  $280^\circ$  is 3.06 to 3.26 or 1.06. Glauconite is a finely micaceous mineral and minerals of this type adsorb water freely. For this reason it is probable that the water given off below  $280^\circ$  is adsorbed water and not water of crystallization. The total water in glauconite is somewhat variable, but the average is about  $5\text{H}_2\text{O}$ .



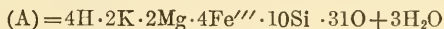
The foregoing considerations indicate that the chemical composition of glauconite can be completely explained if it is considered to be an isomorphous mixture of two end members with the formulas



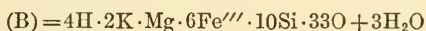
and



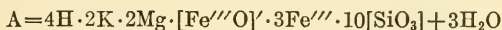
The two formulas are nearly identical, the only difference being that in (A) there is 2MgO instead of 1MgO as in (B), and this is compensated for by there being 1 Fe<sub>2</sub>O<sub>3</sub> less in (A) than in (B). These formulas may be written in several different forms as follows:



and



There is an excess of but one oxygen over the 1 to 3 ratio of the silicic acid, and in order to make this compound a metasilicate this oxygen can theoretically be combined only with the ferric iron so that the formulas may be written:



and

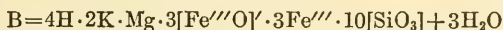


TABLE II.—Analyses of glauconite

A	1	2	3	4	5	6	7	8	9
100 : 0	92 : 8	88 : 12	80 : 20	70 : 24	74 : 26	72 : 28	68 : 32	60 : 40	54 : 44
SiO <sub>2</sub> .....	50.62	49.76	49.47	50.70	50.58	51.15	50.36	51.24	49.42
Al <sub>2</sub> O <sub>3</sub> .....	3.80	8.18	5.59	19.80	6.72	7.61	7.04	12.22	10.23
FeO.....	27.06	16.00	19.46	1.00	19.50	18.83	19.13	13.44	16.01
Fe.....	6.02	3.77	3.36	8.60	2.96	2.78	3.95	3.06	3.00
MgO.....	10.57	3.97	3.96	3.70	4.10	4.54	4.08	3.93	3.78
CaO.....	10.54	0.41	0.60	0.32	0.34	1.01	0.91	0.10	0.31
Na <sub>2</sub> O.....		0.52	0.16	0.50	0.04		1.58	0.31	0.26
K <sub>2</sub> O.....	7.94	7.57	8.04	8.20	8.26	7.80	6.62	7.50	7.91
H <sub>2</sub> O.....	9.14	9.82	8.54	8.50	7.76	7.56	6.32	8.20	8.08
Total.....	98.86	100.00	100.80	100.00	100.83	100.27	100.34	100.00	99.80

	10	11	12	13	14	15	16	17	B
	52 : 48	50 : 50	44 : 56	66 : 34	30 : 70	28 : 72	26 : 74	4 : 96	0 : 100
SiO <sub>2</sub> .....	49.23	1.00	48.66	0.98	48.12	1.01	49.09	0.97	46.90
Al <sub>2</sub> O <sub>3</sub> .....	7.11	8.46	8.46	9.16	19.66	4.06	13.21	4.06	7.09
Fe <sub>2</sub> O <sub>3</sub> .....	20.89	1.00	18.80	.99	19.10	.98	10.56	.96	23.95
FeO.....	3.06	3.98	3.47	7.96	3.10	3.06	27.09	1.00	1.00
MgO.....	3.44	.99	3.56	1.10	2.36	1.06	3.60	.64	.98
CaO.....	Tr.	0.62	0.76	0.62	2.41	.95	0.70	.20	3.10
Na <sub>2</sub> O.....	0.11	None.	0.22	0.78	0.34	0.55	0.20	1.28	3.07
K <sub>2</sub> O.....	8.51	1.10	8.31	7.08	7.76	1.21	6.16	7.02	7.21
H <sub>2</sub> O.....	1.83	1.94	1.07	11.79	7.00	11.64	9.25	7.12	6.90
H <sub>2</sub> O+.....	4.88	4.62	10.06	99.68	100.09	100.02	99.24	100.29	
Total.....	99.06	99.08	100.33	99.68	100.09	100.02	99.24	100.29	

## 1 Carbonates.

- 1 Including  $\text{P}_2\text{O}_5=1.06$ ;  $\text{CO}_2=0.56$ .  
 2 Including  $\text{P}_2\text{O}_5=0.27$ ;  $\text{CO}_2=0.30$ .  
 3 Including  $\text{TiO}_2=0.02$ ;  $\text{P}_2\text{O}_5=.26$ ;  $\text{MnO}=0.06$ ;  $\text{Li}_2\text{O}=0.01$ .  
 4 Including Insol.=80.  
 5 Including  $\text{CO}_2$ ;  $\text{H}_2\text{O}$  above  $280^\circ=3.26$ ; below  $280^\circ=3.30$ ;  $\text{P}_2\text{O}_5=0.12$ ;  $\text{MnO}=0.01$ ,  $\text{CO}_2$ .  
 A. Ideal End Member.  
 1. Havre, France, Haushofer, K., Journ. prakt. Chemie, vol. 102, p. 38, 1886.  
 2. Grodno, Poland, A. Kupffer, Archiv Naturk. Liv., Ebst- und Kurlands, ser. I, Min. Wiss. Dorpat, 1870, vol. 5, p. 123.  
 3. G-13C. Elmwood Road, N. J., Mansfield, G. R., Econ. Geology, vol. 15, No. 7, p. 557, 1920.  
 4. Island Orleans, Quebec, Hunt, Geol. of Canada, 1863, p. 487.  
 5. G-7C. Sewell, N. J., Econ. Geology, vol. 15, No. 7, p. 557, 1920.  
 6. Agulhas Bank, South Africa, at 110 Fathoms. W. A. Caspari, Proc. Roy. Soc. Edinburgh, 1910, vol. 30, pp. 364-373.  
 7. Monte Brione, Lake Garda, Italy, Sitzungsber. Akad. München, vol. 26, 1896, p. 545.  
 8. Karva-Oro, Ontika, Esthonia. A. Kupffer, Archiv Naturk. Liv., Ebst- und Kurlands, ser. I, Min. Wiss. Dorpat, 1870, vol. 5, p. 123.  
 9. Svir River, Olonets, Russia. (Also quartz 0.80.) A. Kupffer, Archiv Naturk. Liv., Ebst- und Kurlands, ser. I, Min. Wiss. Dorpat, 1870, vol. 5, p. 123.  
 10. Big Goose Canyon, 15 miles S. W. of Sheridan, Bighorn Mtns., Wyo. George Steiger, analyst, U. S. Geological Survey, Bull. 591, 1915, p. 340.  
 11. St. Joseph Lead Co. mines, St. Joseph, Mo. U. S., Geol. Surv. Chem. Lab., Glenn V. Brown, analyst.  
 12. Lewes, Sussex. E. G. Radley, Mineralogical Mag., vol. 19, 1920-1922, p. 331.  
 13. Huntington, Oregon. E. P. Henderson, analyst.  
 14. Challenger office, described by L. N. Collet ("Les Depots Marine") Encyclopedie Scientifique, p. 167, Paris, 1908.  
 15. Ashgrove, Elgin, Scotland. M. F. Heddle, Trans. R. Soc. Edinburgh, 1879, vol. 29, p. 79.  
 16. Agulhas Bank, South Africa, C. W. von Gumbel Sitzungsber. math.-physik. Cl. Akad. Wiss. München, 1886, vol. 16, pp. 417-449.  
 17. Pacific Ocean, off Panama, at depth of 556 fathoms. W. A. Caspari, Proc. Roy. Soc. Edinburgh, 1910, vol. 30, pp. 364-373.  
 B. Ideal End Member.

## PREVIOUS STUDIES OF GLAUCONITE.

The complete crystallinity of glauconite has been widely recognized. Lacroix<sup>9</sup> described crystal grains and gives the optical properties as follows:

*Form and mode of occurrence.*—Glauconite occurs in the form of rounded grains similar to grains of powder; they are rarely greater than 0.1 mm. in diameter. The masses of glauconite which form true beds in certain sedimentary horizons are formed by small granules of the nature of agglomerates with or without calcite or marly material. The crystallinity of glauconite is visible only under the microscope and often only with the strongest magnification; when the mineral shows the form of overlapping plates. More rarely one may observe true crystals of glauconite which may reach a fraction of a millimeter in size and be formed entirely of plates or a piling up of lamellae which are probably hexagonal; the latter are often warped after the manner of a variety of ripidolite, helminth, or of kaolinite. These are the crystals that lend themselves to a study of the optical properties.

*Cleavage.*—Cleavage *p.* (001) analogous to that of the micas and chlorites.

*Color and luster.*—Olive green, dark green. By alteration becomes more or less a deep yellow.

*Appearance.*—Earthy. Transparent in thin section and more or less of a deep green.

*Optical properties.*—The negative acute bisectrix is more or less normal to the perfect cleavage.

$$2E = 30^{\circ} \text{ to } 40^{\circ}$$

Sometimes glauconite is nearly uniaxial (Saint-Laurent var.).

The birefringence is probably not determinable with great precision. However, in sufficiently thin plates I have been able to ascertain that it is approximately  $n_g - n_p = 0.020$ .

By analogy with the micas and chlorites one may suppose that glauconite is monoclinic. I have obtained in a few sections which were almost perpendicular to the cleavage, extinction angles of  $1^{\circ}$  or  $2^{\circ}$  with the trace of the perfect cleavage, but it is hardly possible to draw exact conclusions because the orientation of the sections examined is in doubt.

The most thorough microscopic study of glauconite ever made is that by Cayeux.<sup>10</sup> He finds that the great majority of the grains of glauconite are characterized by a cryptocrystalline structure, but he describes and pictures glauconite grains with strong pleochroism and cleavage similar to that in micas or chlorites.

Cayeux agrees with Lacroix as to the probable crystal habit of glauconite.

Caspari<sup>11</sup> has made a study of glauconite now forming and has the following to say of the state of aggregation of glauconite:

Owing to the birefringence and pleochroism exhibited by submarine glauconite when examined under the microscope, it has hitherto been usual to

<sup>9</sup> Lacroix, A., *Mineralogie de la France et de ses Colonies*, vol. 1, Premier, pp. 406, 407, 408, 1893–1895.

<sup>10</sup> Cayeux, Lucien, *Etude Micrographique des Terrains Sedimentaries*, ch. 4, pp. 163–184, 1897.

<sup>11</sup> Caspari, W. A., *Proc. Roy. Soc. Edinburgh*, 1910, vol. 30, pp. 364–373.

regard glauconite as a crystalline mineral; indeed, Collet and Lee definitely relegate it to the monoclinic system. Against this we have to set the fact that in the submarine mineral, whether granular or pulverulent, nothing in the least like a crystal-contour has ever been noted. It is true that fossil "glauconites," embedded in continental formations, have been from time to time described, which are morphologically as well as optically crystalline. These, however, cannot be accepted as identical with recent submarine glauconite, though they may perhaps be metamorphic derivatives of it; in the absence of analyses it is not unlawful to suspect that some of them may be a quite distinct mineral, possibly chlorite.

On the other hand, certain properties of glauconite indicating a state of aggregation differing from that of ordinary crystalline minerals have been referred to above. Some additional light is shed on this point by the behavior of glauconite as regards hydration. It is a peculiarity of colloid minerals (e. g. clays) and of zeolites that they absorb somewhat large proportions of water, according to the moistness of the air with which they are in contact, without forming definite hydrates. In order to ascertain whether glauconite falls into this class, a series of experiments was made.

After describing a series of experiments the writer (Caspari) comes to the following conclusions:

Firstly, glauconite becomes a highly hydrated mineral in presence of moist air (whilst still remaining an apparently dry powder). No doubt this is the condition in which it exists in its native element, a third or more of its weight consisting of water. Secondly, it is evident, without drawing up a curve, that the hydration decreases continuously with the tension of aqueous vapour in equilibrium, whence it follows that there are no definite hydrates representing a series of distinct molecular species. Thirdly, there is a marked parallelism as regards hydration between glauconite and red clay.

It is well known that this kind of water absorption, which is especially characteristic of colloids, is also shared by the unquestionably crystalline zeolites. The inference, then, which we may now draw as to the nature of glauconite is that it is certainly not an ordinary crystalline silicate like feldspar or mica, but that it must be either a zeolite or a colloid. As between these two alternatives, it is less easy to decide. The property possessed by glauconite of absorbing dyes is again common to both colloids and zeolites. In favor of the view that glauconite is a colloid, we have the absence of crystal-contours and the ease with which it forms colloidal suspensions and solutions. Evidence of crystalline habit, on the other hand, is afforded by the optical anisotropy of glauconite. To this, however, it may be rejoined that isotropic matter in a state of strain is equally capable of showing birefringence. That glauconite may exist under some such strain seems not unlikely when we consider the structure of glauconite grains, in which the glauconite proper would appear to be inclosed by a network of foreign substance; and the vehemence with which the grains fly into powder under the action of acid and alkaline solutions points in the same direction. On the whole, then, though it would be premature to regard the matter as settled, the probability is that glauconite is essentially a colloidal silicate.

In describing the material he has concentrated Caspari says:<sup>12</sup>

A small proportion of the particles, especially the larger ones, retain the characteristic birefringence of granular glauconite.

<sup>12</sup> Proc. Roy. Soc. Edinburgh, vol. 30, 1910, p. 367.

All the postulates upon which Caspari bases his conclusions as to the colloidal nature of glauconite are partly or wholly wrong. Clays contain varying proportions of minerals of colloidal size, and in many the amount of colloidal material that can be identified is small.<sup>13</sup> It is quite incorrect to assume that clays are wholly colloidal or even predominantly colloidal as he seems to do when he refers to "colloidal minerals (i. e. clay)." Again colloids are not necessarily noncrystalline, for most colloids are finely dispersed crystalline material. The crystallinity of most colloids has been emphasized by Svedberg who says,<sup>14</sup> "almost all particles in colloids are small crystals," and this is undoubtedly the condition of the alkali and acid treated material investigated by Caspari. Adsorption (the absorption of Caspari) of water is a function of great surface area and does not necessarily denote colloidal form, and a finely divided micaceous material like glauconite has tremendous surface area and thus possesses the structure most conducive to great adsorptive powers, for adsorption is not a property that suddenly springs into existence as soon as the degree of subdivision reaches  $100\mu\mu$  which has been set arbitrarily as the upper limit for colloidal size.

Thus Caspari's conclusion that glauconite is a noncrystalline colloid has little to stand upon especially as he chose to disregard properties like pleochroism and birefringence which he observed and recorded, and to base his conclusions entirely upon erroneous postulates and a faulty reasoning. There is nothing in the data cited to indicate that glauconite is not an ordinary crystalline silicate that contains much adsorbed water.

The most thorough chemical study of glauconite that has been published is that by Hallimond,<sup>15</sup> of which the essential parts are given below:

In Table III is given the molecular proportions of 12 analyses of glauconite and a comparison of these ratios leads to the following conclusion:

TABLE III.—*Molecular proportions*

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub>	FeO+MgO	K <sub>2</sub> O+Na <sub>2</sub> O	R <sub>2</sub> O <sub>3</sub> +RO
1-----	1, 000	218	182	107	400
2-----	1, 000	243	164	107	407
3-----	1, 000	238	163	99	401
4-----	1, 000	201	166	105	367
5-----	1, 000	263	132	102	395
6-----	1, 000	267	87	110	354
7-----	1, 000	272	188	117	460
8-----	1, 000	263	130	103	393
9-----	1, 000	261	144	106	405
10-----	1, 000	283	106	93	389
11-----	1, 000	225	179	97	404
12-----	1, 000	262	133	98	395

<sup>13</sup> Searle, Alfred B., The chemistry and physics of clays, pp. 263-269, Ernest Benn, Ltd., London, 1924.

<sup>14</sup> Svedberg, Theo, Chemical Review, vol. 1, 1924, p. 629.

<sup>15</sup> Hallimond, A. F., Mineralogical Magazine, vol. 19, No. 98, pp. 332-333, 1922.

The proportion of alkalis is remarkably constant, and there is clearly no evidence of the substitution of these by water, or, as was assumed by Clarke, by the magnesia group. There is, however, considerable replacement of potash by soda, \* \* \* , and it may be suggested that the name "soda-glaucouite" should be used to distinguish these varieties.

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. The total for these two groups combined is given in the last column of Table II, and it will be seen that, with the exception of Nos. 4, 6, and 7, the total is constant and in simple ratio to the silica. The ratios so obtained lead to the simple formula



the ratio of bases to silica being 1 : 2.

There exists a certain justification for regarding the above substitution as possible, for the only definite hydrate of  $Fe_2O_3$  known to exist is the monohydrate, which may be written  $OFeOFe(OH)_2$  resembling  $Fe(OH)_2$ . The extent of this substitution is not great, the ratio of  $R_2O_3$  to RO lying between the limits 3:1 and 1:1.

As regards the water, apart from the observation that it does not substitute the solid constituents, there is no information as to the extent to which it is present in definite combination; detailed work on the dehydration would be necessary to throw light on this question, and it has been thought best to omit this from the present paper.

The writer is in substantial agreement with Hallimond as to the chemical composition of glaucouite. In fact, most of the present paper was prepared before the publication of Hallimond's paper, and so we have come independently to substantially similar conclusions.

#### CELADONITE

Only a few analyses of celadonite are available and the mineral appears to be even more difficult to obtain in the pure state than glaucouite. For these reasons no trustworthy interpretation of the chemical relations of celadonite can be attempted at the present time. If the analyses are plotted they all seem to fall near the composition curves of glaucouite when extended far to the left in Figure 1. Therefore celadonite may possibly be made up of the same or a closely related chemical series.

Celadonite of unusual purity has been collected in Cuba by Hewett and kindly placed at the disposal of the writer for examination. This material has indices of refraction that are nearly the same as those of glaucouite, but the habit is fibrous, rather than micaceous as in glaucouite. The optical character is very difficult to determine as the acute bisectrix is parallel to the thin fibers, but it is probably (+) rather than (-) as in glaucouite. This indicates that celadonite may be distinct from glaucouite although it is closely related to it in chemical composition.