

NOTES ON THE MINERALOGY AND ORIGIN OF GLAUCONITE¹

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ABSTRACT

The variability in the physical and chemical properties of pure glauconite seems to be less than is generally believed. The observed spread is partly attributed to insufficient purity of the material studied. One of the major causes of the variation in properties is the occurrence of non-structural iron oxides, which was established by electron microscopy and by chemical analysis of free iron oxide. Formulae for glauconite reported in the literature should be recalculated accordingly. Interpretations based on the relationship between iron content and geologic age appear doubtful.

Very striking is the inverse relationship between the FeO- and Al₂O₃-contents of glauconite, which might indicate that part of the Fe²⁺ occurs in the tetrahedral layers. Part of the Mg²⁺ occupies vacant spaces in the octahedral layers. Titanium is the major trace element entering the glauconite structure.

The common alteration product of glauconite is goethite, and under special conditions, jarosite. On heating glauconite to temperatures above 1000°C. maghemite is formed.

The absence of glauconite in rocks older than late Precambrian is probably connected with the reducing character of the early atmosphere.

INTRODUCTION

In this paper the term "glauconite" is applied only to the mineral, while the term "glauconite pellets" describes green pellets which commonly consist of mineral mixtures.

Glauconite pellets are widespread in marine sedimentary formations from Early Paleozoic to Recent, and have also been found in the Upper Precambrian (Gulbrandsen, Goldrich, and Thomas, 1963).

In two parts of the stratigraphic column glauconite pellets are regionally widespread; that is, in the Lower Paleozoic and the Upper Cretaceous and Lower Tertiary. The characteristic environmental conditions in which glauconite is formed are shallow seas extending over large areas with a low rate of sedimentation, scarce supply of argillaceous material, and dominated by carbonate sediments.

Because of the variability in the physical appearance of glauconite pellets, many attempts have been made to classify them. These classifications developed historically in three stages:

- 1—Classifications based on macroscopic properties, for example color or morphology of the pellets;
- 2—Classifications based on chemical composition and microscopic properties;
- 3—Classifications based on structure.

Glauconite pellets were studied from outcrops in Israel of Lower Cretaceous to Mio-Pliocene

age. They were compared with glauconite pellets from the United States, kindly supplied by G. M. Friedman, which range in age from Lower Cambrian to Recent.

Glauconite pellets were separated from the sediment by hand picking under the binocular microscope. Dilute acid attacks the pellets and heavy liquids are partially adsorbed on the mineral and consequently cause errors in the determination of physical parameters and in the interpretation of X-ray diffraction patterns. The magnetic separator is not sufficiently powerful to eliminate partially oxidized pellets, or those in which cracks are filled with foreign minerals; therefore hand picking of the pellets is unavoidable.

DIAGNOSTIC PROPERTIES OF GLAUCONITE

Glauconite can be distinguished from other clay minerals by a number of physical methods, the most important of which are:

- 1) refractive index which on the average is higher than for the closely related mineral illite;
- 2) of all clay minerals glauconite has by far the highest magnetic susceptibility;
- 3) the X-ray pattern, although very similar to that of illite, differs in the d-values of the (060) reflections.
- 4) DTA-curves show a small characteristic exothermic peak around 330°C. due to oxidation of iron;
- 5) the loss of water, determined with the thermo-balance is relatively rapid with illites and occurs in the temperature range 370°-600°C.; with glauconite it proceeds more slowly at between 350° and 700°C.

¹ Manuscript received March 15, 1964; revised October 17, 1964.

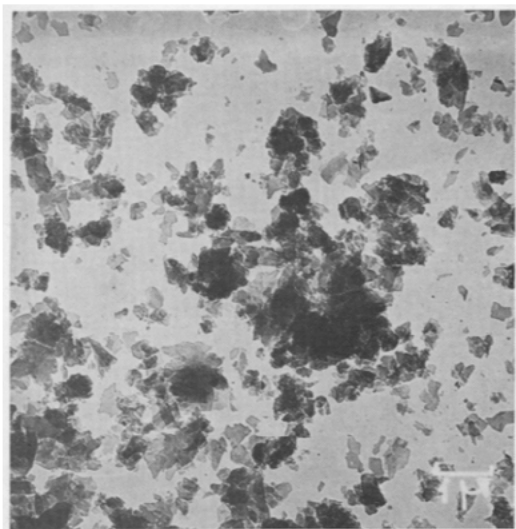


FIG. 1.—Glauconite (sample 6) 1M, Lower Cenomanian, Makhtesh Hathira, Israel

MORPHOLOGY OF GLAUCONITE

Glauconite occurs most frequently as pellets in a wide variety of shapes which bear no apparent relationship to the mineralogical composition of the specimen. Less common than pellets are fossil casts, single crystals (which may be mistaken as aggregates with unit extinction in polarized light), pigment glauconite, coatings on heavy minerals or quartz grains, and cement, most commonly between quartz grains. One of the samples studied consists of particles composed of alternating laminae of calcite and glauconite, 0.1 mm and 0.2–0.3 mm wide respectively. Glauconite replaces other minerals such as feldspars.

The micromorphology of the mineral glauconite was examined by electron microscopy and found to be lath-shaped or plate-like, (figs. 1 and 2).

PHYSICAL PROPERTIES OF GLAUCONITE

Some physical properties of the mineral glauconite determined in this study, are:

Average specific gravity: 2.79 ± 0.02 gr/cm³

Average magnetic susceptibility: $(32.6 \pm 1.5) \times 10^{-6}$ c.g.s.

In pure glauconite higher values of the specific gravity and magnetic susceptibility are due to extensive substitution of iron for aluminum in the lattice. In glauconitic pellets additional causes are: 1) partial internal oxidation of pelletal glauconite (fig. 3), 2) nonstructural iron oxide on glauconite laths or plates (see p. 8) and 3)

admixture of minerals with higher magnetic susceptibility, for example, iron oxides, or higher specific gravity, as, apatite.

Conversely, specific gravity and magnetic susceptibility values lower than average are due to a low degree of substitution of iron for aluminum in the glauconite lattice. In pellets additional causes are: 1) high water content; 2) presence of pellets composed of interlayered glauconite, and 3) admixture of other minerals such as calcite. This geochemical and mineralogical variability is also responsible for the range in refractive indices of the mineral glauconite as shown in table 1.

Figure 4 illustrates the relationship between specific gravity and chemical composition. The low sp.g. of sample 4 is apparent only and caused by its high porosity.

Figure 5 illustrates the relationship between refractive index, magnetic susceptibility and total iron content.

X-RAY CLASSIFICATION

Glauconite has been indexed by Warshaw (1957). She assumed that glauconite is a mica and that it is monoclinic with pseudohexagonal symmetry. The pseudohexagonal symmetry has been confirmed in this study by electron diffraction (fig. 6).

On the basis of X-ray analyses made in this study and in accordance with Warshaw, four

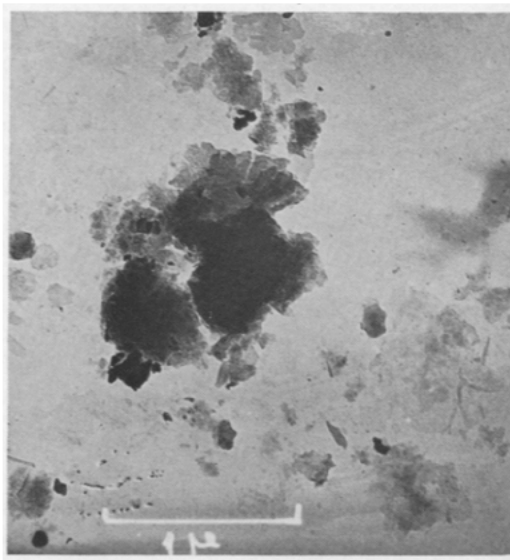


FIG. 2.—Glauconite (sample 1) Lower Cretaceous, "2nd intercalation (yellow cuesta)," Makhtesh Hatsera, Israel.

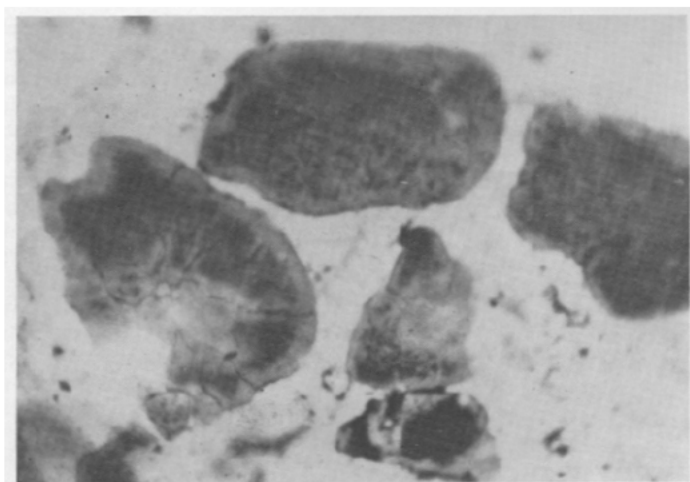


FIG. 3.—Photomicrograph of internally oxidized glauconite pellets, Lower Cretaceous, Makhtesh Hatsera, Israel. ($\times 40$, crossed nicols)

classes of pellets are distinguished similar to those proposed by Burst (1958b):

Class 1. Mineral glauconite

- a. Well-ordered 1M, with symmetric and sharp diffraction at 10.1, 4.53, 3.3 Å. Reflections (112) and (112) are always present.
- b. Disordered 1Md, with asymmetric basal diffractions broadened at the base. Reflections (112) and (112) are absent.

Class 2. Interlayered glauconite, $d(001) > 10.15 \text{ Å}$.

Class 3. Mixed mineral

- a. Two or more clay minerals.
- b. Mixture of clay with non-clay minerals.

Class 4. Green pellets containing no glauconite.

No relationship has been found between the four classes of glauconite and their geological age. Glauconite pellets from the Gros Ventre Formation, Middle Cambrian, Wyoming, are of class 2; sample 6 of the Lower Cenomanian, Makhtesh Hathira, Israel, is of class 1a; sample

7 of the Lower Cenomanian, Makhtesh Ramon, Israel, is of class 1b; and sample 10 of Upper Campanian or Lower Maastrichtian, Tarshiha, Israel, is of class 3b. There is, however, a close relationship between the different classes and the lithology of the samples (see p. 19).

STRUCTURAL AND NON-STRUCTURAL IRON IN GLAUCONITE

Although glauconite is characterized by a high iron content within its lattice, not all the iron oxide is structural even in pure glauconite. Electron microscope photographs of pure glauconite invariably show small black spots (fig. 7), which were assumed to be free iron oxides. The method of Jackson (1958) was therefore applied to distinguish chemically between free iron oxide and structural iron in the lattice; it was shown that sample 3 contains 2.09% and sample 5, 3.85% free iron oxides.

CHEMISTRY

The present discussion is based on nine full and three partial chemical analyses, carried out on small quantities of material (table 2).

TABLE 1

	Index of refraction		$\gamma - \alpha$	Optic sign and 2V	Pleochroism	
	α	γ			X	Z
Glauconite	1.608–1.616	1.626–1.636	0.018–0.020	—small	green yellow	dark green
Glauconite pellets	1.578–1.616	1.592–1.636	0.014–0.020	—small	yellow green	dark green

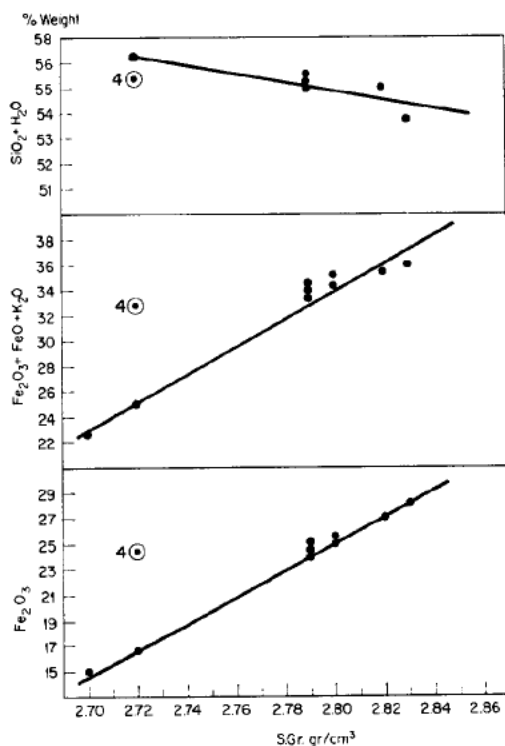


FIG. 4.—Relationship between specific gravity and chemical composition of glauconite

Brochert & Braun (1963) list 78 analyses, which vary greatly, collected from the literature. Their dissimilarity is probably caused by the

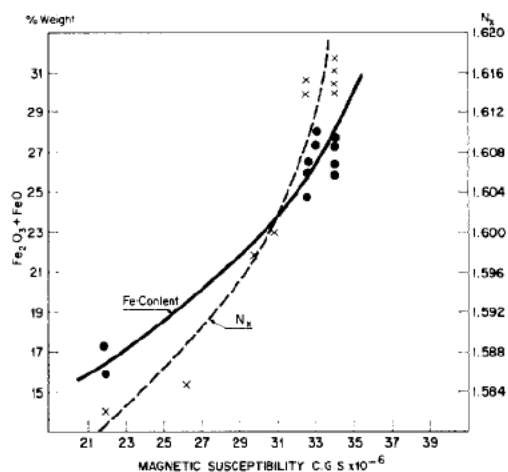


FIG. 5.—Relationship between magnetic susceptibility, total iron content and index of refraction in glauconite

difficulty in extracting pure glauconite from a sediment, and many of the samples listed certainly contain contamination from the host rock. Even chemical analyses of hand picked pellets are subject to error. Clean hand picked pellets which superficially resemble glauconite, frequently contain non-glauconitic material and belong to classes 2 or 3. A chemical analysis of these pellets is meaningless, unless X-ray examination reveals the identity of the contaminating mineral, and the analysis can be recomputed to allow for the impurities. X-ray analyses of the nine samples for which complete chemical analyses are presented show that six (analyses 2, 4, 5, 6, 10, 11) contain minor non-glauconitic inclusions; these analyses were recalculated accordingly (table 3). Analyses 2, 4, 5, and 6 contain minor amounts of calcite, 10 and 11, calcite and apatite. The sample of analysis 12, although it is morphologically a glauconite pellet, is in fact a mixture of calcite, apatite and an unidentified mineral (fig. 8); thus, it belongs to class 4.

The possibility remains that illite, which cannot be detected in glauconite pellets by X-ray methods, may be present in minor amounts in some of the samples studied.

Green pellets of glauconite which have undergone partial oxidation cannot always be recognized under the binocular microscope, and thin sections are necessary to establish the fact. Chemical analyses of such samples may be misleading. Moreover, correction must be made for non-structural iron oxide, nearly always present in glauconite pellets.

Table 4 presents these recalculated analyses for the two samples in which the amount of free

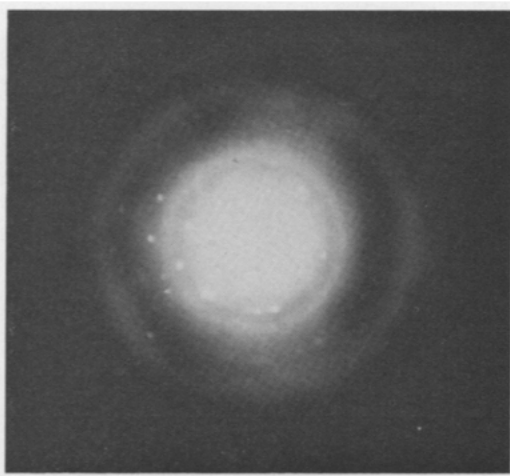


FIG. 6.—Glauconite (sample 5), pseudohexagonal symmetry, Lower Cenomanian, Makhtesh Hatsera, Israel

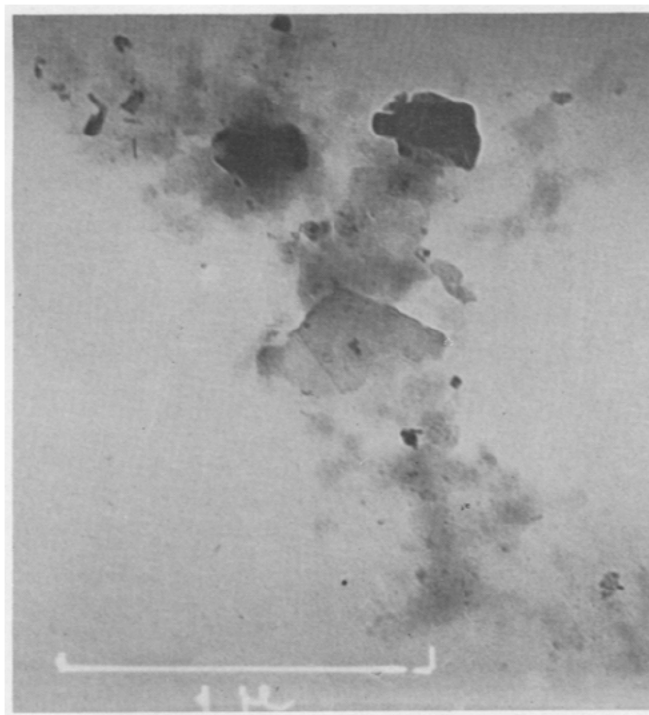


FIG. 7.—Sample 1, Lower Cretaceous "2nd intercalation (yellow cuesta)," Makhtesh Hatsera, Israel.

TABLE 2.—*Glauconite pellets—chemical analyses (weight %)*

	1	2	3	4	5	6	7	8	9	10	11	12
SiO ₂	43.45	45.56	46.52	47.17	47.28	47.03				46.57	42.11	23.68
Al ₂ O ₃	8.22	5.53	4.61	7.95	6.70	6.12				11.24	6.00	4.03
Fe ₂ O ₃	28.80	27.07	24.76	24.82	25.19	24.49	25.09	24.01	25.96	16.68	15.06	10.08
FeO	0.96	0.66	2.02	1.31	1.18	1.66	2.59	2.67	2.52	0.67	0.67	—
TiO ₂	0.26	—	—	0.12	0.14	0.12				—	—	0.25
CaO	0.14	0.56	0.51	0.56	1.12	0.28				1.35	8.60	27.90
MgO	2.92	4.43	4.65	4.42	4.03	4.23				4.02	4.42	2.12
K ₂ O	6.42	7.89	7.65	6.99	7.89	7.90	6.73	8.00	6.73	7.70	6.79	2.25
Na ₂ O	0.68	0.31	0.19	0.57	0.13	0.61	0.29	0.66	0.46	0.38	0.37	0.26
P ₂ O ₅	0.15	0.05	0.08	0.13	0.09	0.09				1.56	4.86	3.96
MnO	0.08	0.04	—	0.03	—	0.04				—	—	—
CO ₂	—	0.15	—	0.28	0.24	0.26				0.48	0.60	17.96
—H ₂ O	4.25	3.50	3.20	2.14	2.34	3.28				3.77	3.68	4.02
+H ₂ O	6.07	6.23	5.83	6.01	5.28	5.03				6.03	5.40	3.85
Total	102.40	101.98	100.02	102.50	101.61	101.14				100.45	98.56	100.36

Analyses by M. Gaon, Geological Survey of Israel

No. of analysis

1. Lower Cretaceous, "2nd marine intercalation (yellow cuesta)," Makhtesh Hatsera, Israel.
2. Lower Cretaceous, Makhtesh Ramon, Israel.
3. Lower Cenomanian, Makhtesh Ramon, Israel.
4. Lower Cenomanian, Wadi Siq, Israel.
5. Lower Cenomanian, Makhtesh Hatsera, Israel.
6. Lower Cenomanian, Makhtesh Hathira, Israel.
7. Lower Cenomanian, Makhtesh Ramon, Israel.
8. Lower Cenomanian, Makhtesh Hathira, Israel.
9. Lower Cenomanian, Wadi Tsaft, Israel.
10. Upper Campanian or Lower Maastrichtian, Tarshiha, Israel.
11. Middle Eocene, Ein-Yahav, Israel.
12. Lower Eocene (Ypresian), near Nazareth, Israel.

TABLE 3.—Recalculated chemical analyses of glauconite (weight %)

	1	2	3	4	5	6	10	11
SiO ₂	42.43	44.82	46.51	46.31	46.78	46.76	47.52	49.00
Al ₂ O ₃	8.03	5.44	4.61	7.80	6.63	6.08	11.47	6.98
Fe ₂ O ₃	28.12	26.63	24.75	24.37	24.92	24.34	17.02	17.52
FeO	0.94	0.65	2.02	1.28	1.17	1.65	0.68	0.78
TiO ₂	0.25	—	—	0.12	0.14	0.12	—	—
CaO	0.14	0.37	0.51	0.20	0.81	—	—	1.68
MgO	2.85	4.36	4.65	4.34	3.99	4.20	4.10	5.15
K ₂ O	6.27	7.76	7.65	6.86	7.81	7.85	7.86	7.90
Na ₂ O	0.66	0.31	0.19	0.56	0.13	0.61	0.39	0.43
P ₂ O ₅	0.15	0.05	0.08	0.13	0.09	0.09	0.96	—
MnO	0.08	0.04	—	0.03	—	0.04	—	—
CO ₂	—	—	—	—	—	—	—	—
H ₂ O—	4.15	3.44	3.20	2.10	2.31	3.26	3.85	4.28
H ₂ O+	5.93	6.13	5.83	5.90	5.22	5.00	6.15	6.28
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

iron oxide was determined.

The variation diagram (fig. 9), based on table 3, shows: 1) The variation in the amount of silica is considerable; 2) Fe₂O₃ is the most important variant. This is due to non-structural iron and partial oxidation of the pellets, as well as to a varying degree of substitution within the lattice; 3) The percentages of MgO and K₂O are nearly constant; 4) No relationship was detected between MgO and FeO, similar to that found in many other silicates; and 5) There is inverse relationship between FeO and Al₂O₃, which seems to indicate that Fe²⁺ substitutes for Al³⁺ in the tetrahedral layers. The theoretical aspect of this assumption is discussed in the following section.

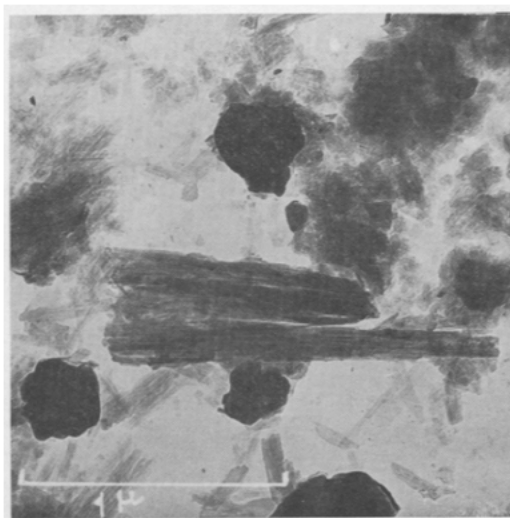


FIG. 8.—Electron micrograph of sample 12, unidentified fibrous mineral, Lower Eocene (Ypresian), near Nazareth, Israel.

CRYSTAL STRUCTURE

Formulae for glauconite are listed in table 5; they are computed from the total analyses of tables 3 & 4 according to the usual methods (Hendricks and Ross, 1941; Kelley, 1955).²

Although it is possible to arrive at a balanced structural formula in each case, the results reveal some systematic peculiarities. Glauconite is normally considered to be a dioctahedral mineral. All the samples studied contain, however, appreciable amounts of Mg and some Fe²⁺. By placing all these ions into the octahedral layers, a high charge should result. In fact, as table 7 shows, the charge of the octahedral layers is generally not higher, and frequently much lower, than that of the tetrahedral layers. Furthermore, the inverse relationship between Fe²⁺ and Al³⁺, expected within the octahedral layers, is absent. Adding the fact that Cloos, Gastuche and Croe-

² Analysis 11 was not used, as it was made on only 400 mg and contains an unexplained excess of CaO.

TABLE 4.—Glauconite, recalculated chemical analyses (weight %)

	3	5
SiO ₂	47.51	48.64
Al ₂ O ₃	4.71	6.89
Fe ₂ O ₃	23.15	21.96
FeO	2.06	1.21
TiO ₂	—	0.14
CaO	0.52	0.83
MgO	4.75	4.15
K ₂ O	7.81	8.12
Na ₂ O	0.19	0.13
P ₂ O ₅	0.08	0.09
—H ₂ O	3.27	2.41
+H ₂ O	5.95	5.43
Total	100.00	100.00

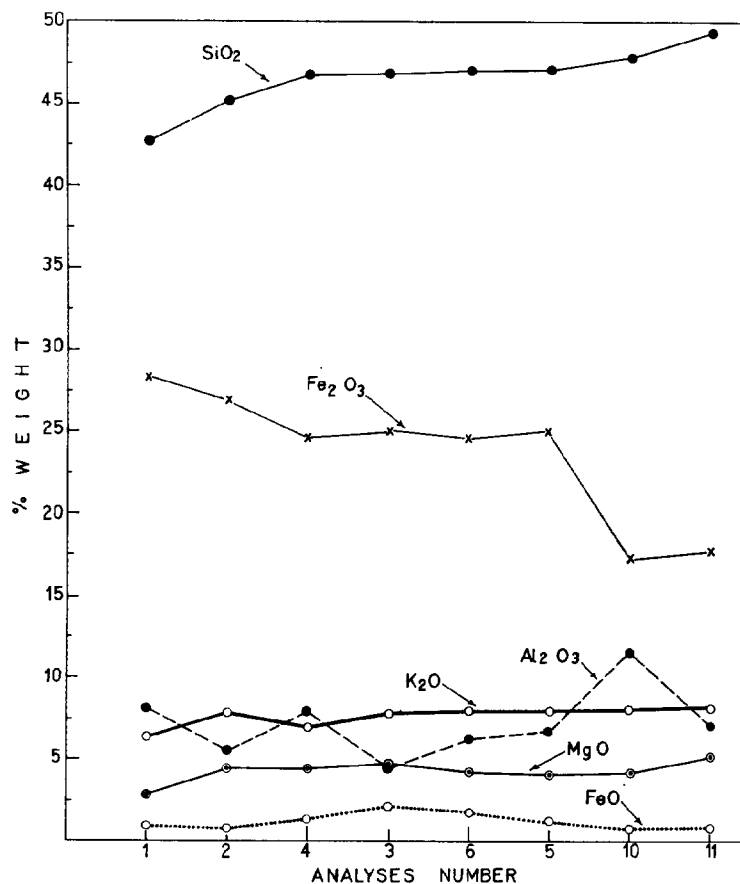
FIG. 9.—Variation diagram according to increasing SiO₂ content.

TABLE 5.—Formulae of glauconite*

1:	$K_{0.42}(Ca_{0.01}Na_{0.10})(Al_{0.06}Fe'''_{1.66}Fe''_{0.07}Mg_{0.33})(Si_{3.32}Al_{0.58})O_{10}(OH)_2$
	$b_0 = 9.189 \text{ \AA}$ $a_0 = 5.305 \text{ \AA}$ $c_0 = 10.15 \text{ \AA}$
2:	$K_{0.77}(Ca_{0.03}Na_{0.06})(Fe'''_{1.43}Fe''_{0.04}Mg_{0.50})(Si_{3.45}Al_{0.49}Fe'''_{0.06})O_{10}(OH)_2$
	$b_0 = 9.191 \text{ \AA}$ $a_0 = 5.307 \text{ \AA}$ $c_0 = 10.10 \text{ \AA}$
3:	$K_{0.76}(Ca_{0.04}Na_{0.03})(Al_{0.06}Fe'''_{1.33}Fe''_{0.13}Mg_{0.54})(Si_{3.64}Al_{0.36})O_{10}(OH)_2$
	$b_0 = 9.194 \text{ \AA}$ $a_0 = 5.307 \text{ \AA}$ $c_0 = 10.10 \text{ \AA}$
4:	$K_{0.65}(Ca_{0.02}Na_{0.03})(Al_{0.16}Fe'''_{1.37}Fe''_{0.03}Mg_{0.49})(Si_{3.47}Al_{0.53})O_{10}(OH)_2$
	$b_0 = 9.184 \text{ \AA}$ $a_0 = 5.302 \text{ \AA}$ $c_0 = 10.09 \text{ \AA}$
5:	$K_{0.77}(Ca_{0.07}Na_{0.02})(Al_{0.23}Fe'''_{1.24}Fe''_{0.08}Mg_{0.46})(Si_{3.62}Al_{0.38})O_{10}(OH)_2$
	$b_0 = 9.155 \text{ \AA}$ $a_0 = 5.286 \text{ \AA}$ $c_0 = 10.08 \text{ \AA}$
6:	$K_{0.83}(Na_{0.09})(Al_{0.07}Fe'''_{1.39}Fe''_{0.11}Mg_{0.47})(Si_{3.54}Al_{0.46})O_{10}(OH)_2$
	$b_0 = 9.184 \text{ \AA}$ $a_0 = 5.302 \text{ \AA}$ $c_0 = 10.08 \text{ \AA}$
10:	$K_{0.74}(Na_{0.06})(Al_{0.59}Fe'''_{0.96}Fe''_{0.04}Mg_{0.45})(Si_{3.59}Al_{0.41})O_{10}(OH)_2$
	$b_0 = 9.129 \text{ \AA}$ $a_0 = 5.271 \text{ \AA}$ $c_0 = 10.12 \text{ \AA}$

* Formulae 3 and 5 are based on table 4; the others on table 3.

Excess P₂O₅ was added to SiO₂; TiO₂ to Fe₂O₃ and MnO to FeO.

The amount of exchangeable Mg⁺⁺ was determined separately and considered in the calculation of the formulae, but turned out to be too small to influence the result.

TABLE 6.—Cation population of octahedral layer

Sample	1	2	3	4	5	6	10
Number of octahedral cations	2.11	2.06	2.06	2.10	2.01	2.04	2.03

TABLE 7.—Relationship between lattice charge of glauconite and chemical composition

Sample No.	Net octahedral charge	Net tetrahedral charge	Per cent K ₂ O
1	0.07	0.68	6.27
2	0.36	0.52	7.76
3	0.49	0.36	7.65
4	0.31	0.53	6.86
5	0.51	0.38	7.81
6	0.46	0.46	7.85
10	0.40	0.41	7.86

garet (1960) found some chemical evidence that Fe²⁺ might be present within the tetrahedral layers, a case can be made for this assumption. However, replacement of Si⁴⁺ by Fe²⁺, even in restricted amounts, is difficult to conceive in view of the large difference in ionic size.

Although this possibility should be investigated there seems to be an alternative explanation. As already suspected by Yoder (1957),

glauconite might not be a true dioctahedral mineral; Fe²⁺, and even more so Mg²⁺, might partly fill vacant spaces within the octahedral layer. This assumption would explain the charge relationship of octahedral versus tetrahedral layers, and the fact that in all the formulae given in table 5 the total of the octahedral cations is greater than 2 (table 6).

Only under the assumption that part of the Mg²⁺ in the octahedral layers is not replacing Al³⁺, but is additional to it, can the negative lattice charges be balanced by the amounts of K⁺ and adsorbed cations present. The proportion of this "excess" Mg²⁺ is 2%–33% of the total Mg²⁺ present.

There seems to be, moreover, some independent evidence for this hypothesis. The (002) reflections are very weak, a feature more characteristic of tri- than of dioctahedral minerals, and the values of the (060) reflections of the mineral glauconite vary between 1.51–1.52 Å, that is, they are intermediate between those of pure dioctahedral and pure trioctahedral minerals.

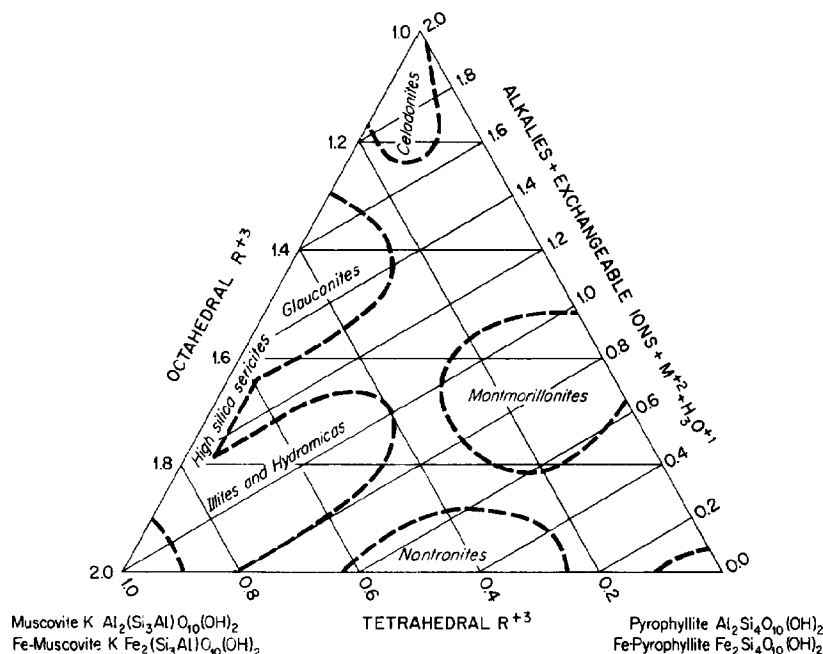


FIG. 10.—Plot of tetrahedral R^{+3} and octahedral R^{+3} in atom proportions of dioctahedral micas and related minerals (from Yoder & Eugster 1955).

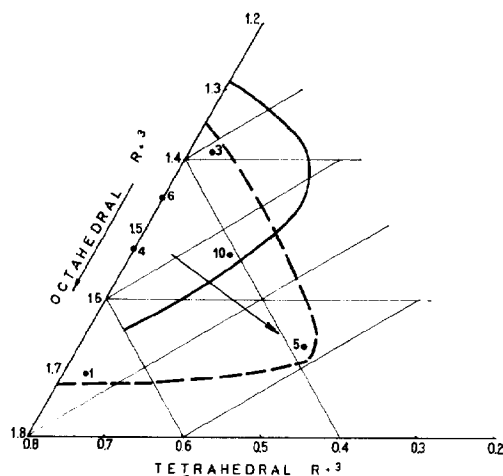


FIG. 11. ——— Yoder and Eugster field of Glauconite
 --- revised field of glauconite.

Figure 10 is a plot of tetrahedral R^{+++} and octahedral R^{+++} ($R^{+++} = Al^{+++}, Fe^{++}$) in atomic proportions in dioctahedral micas and related minerals, taken from Yoder and Eugster (1955). They delimited the field of glauconite on the basis of chemical analyses from the literature. These analyses, however, are partly those of glauconite pellets (classes 2 and 3 of this study) and not of pure glauconite. Formulae computed in the present study suggest that the field of glauconite, as presented by Yoder and Eugster (1955), should be modified. The revised field for glauconite is approximated in figure 11, where projection points based on the formulae of table 5 are also shown. If it is assumed that part of the Fe^{++} is in the tetrahedral layer, the field would shift even further in the direction of the arrows in figure 11. One analysis (no. 2) lies outside this field, possibly because of the presence of some illite, not detected in the sample.

Because of the scarcity of non-structural iron determinations, it seems too early to study a

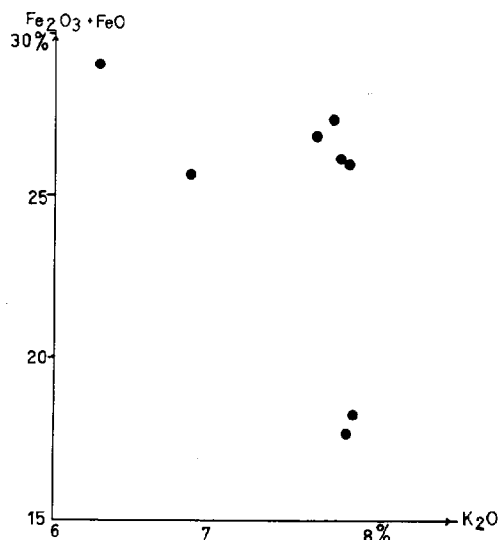


FIG. 12.—Relationship $Fe_2O_3 + FeO/K_2O$ in glauconite.

possible relationship between chemical composition and calculated parameter b , as has been attempted by Warsaw (1957).

DEFINITION OF GLAUCONITE

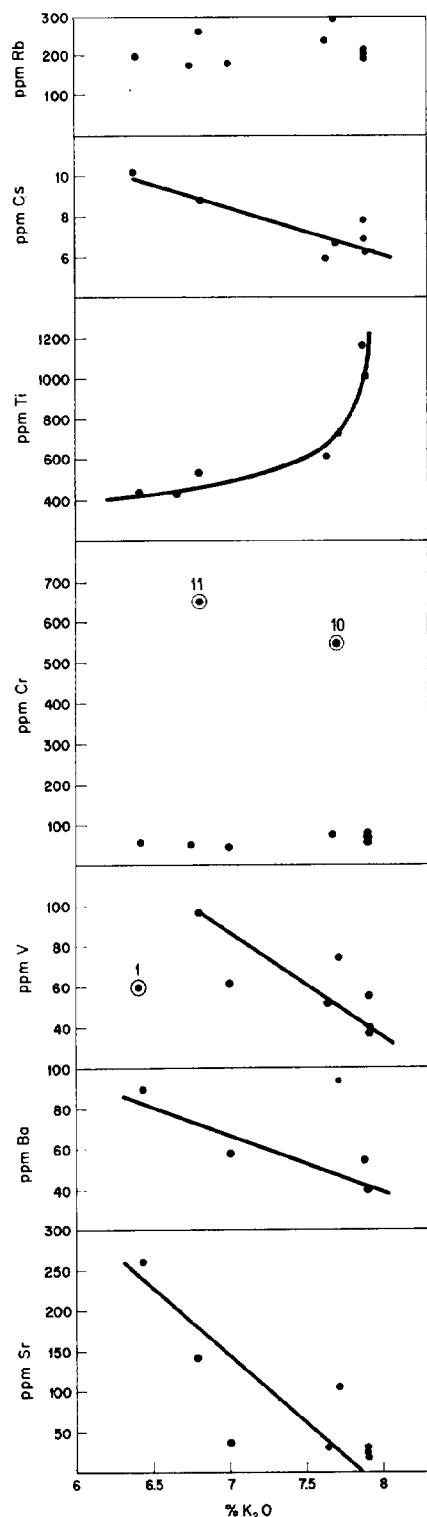
Glauconite is an independent IM or IMd potassium phyllosilicate, nearly but not quite dioctahedral, which contains more iron than aluminum in the octahedral layer and in which the net charge of the lattice is due to a considerable part to substitutions within the tetrahedral layer.

ALTERATION OF GLAUCONITE

The common alteration product of glauconite is goethite. In sample No. 4 jarosite has been detected. The sediment from which this sample has been taken, is rich in gypsum, anhydrite and oyster shells and also contains goethite pseudomorphous after pyrite cubes. Oxidation of pyrite

TABLE 8.—*The relationship between class, lithology and geologic age of glauconite*

Sample No.	Class in the X-ray classification	Geologic Age	Lithology	Per cent clay ($<2\mu$)	Per cent sand ($>62\mu$)
1	2	Lower Cretaceous	calcareous argillaceous sandstone	20.77	63.00
2	2	Lower Cretaceous	calcareous argillaceous sandstone	19.17	71.13
3	1b	Lower Cenomanian	calcareous sst.	20.28	55.69
5	1a	Lower Cenomanian	sandstone	4.90	79.34
6	1a	Lower Cenomanian	sandstone with small amount of carbonate	3.87	84.67
7	1b	Lower Cenomanian	calcareous	9.03	69.20



resulted in the formation of sulphuric acid which attacked the shells and glauconite pellets. Most of the acid reacted with the dissolved Ca⁺⁺ to form gypsum, the remainder with potassium and iron released from glauconite formed jarosite.

If glauconite is heated in the laboratory above 1000°C., maghemite is formed. Normally this mineral inverts to hematite at temperatures between 200°–700°C. (Deer, Howie and Zussman 1962). The formation of maghemite at a temperature above its normal stability field might be due to contaminations of the maghemite lattice by cations which prevent the inversion to the stable polymorph. It is well known that many vacant positions occur in the lattice of maghemite.

ORIGIN OF GLAUCONITE

According to Takahashi and Yagi (1929) and Takahashi (1939), the parent material of glauconite is an amorphous gel of silicates and aluminates which has been derived by hydration of various silicates and consequent gelatinization. The diagenesis includes recrystallization and compositional changes, the most important of which are an increase in iron and potassium and a decrease in aluminum. Smulikowski (1954) suggests a mixed ferri-alumino-siliceous hydrogel with adsorbed potassium as starting material. He emphasizes that such an origin of glauconite as an absorptive rather than purely chemical compound, might explain the variability of its chemical composition which may be due to two principal causes: a. physical conditions and concentration of chemical elements in the depositional environment; b. diagenetic changes.

Alteration of biotite to glauconite has been described by Galliher (1935). As biotite changes to glauconite it loses aluminum, potassium and magnesium, and gains water, while most of the iron is oxidized.

Triplehorn (1961) states that glauconite forms by direct chemical replacement of minerals, such as feldspars or pyroxenes, without explaining the process.

Burst (1958a) and Hower (1961) suggest any degraded 2:1 layer lattice with a relatively low lattice charge as the starting material. The process of glauconitization involves a gradual increase in the charge (mainly of the octahedral layer) and a consequent increase in interlayer potassium which results in the collapse of successive layers to the nonexpandable 10Å type.



FIG. 13.—Relationship between trace elements and percent K₂O content in glauconite.

If this model is at least approximately correct, the following results would be expected:

- Potassium and iron should be proportional to each other and inversely proportional to per cent expandable layers;
- The increase in lattice charge arises from the octahedral layer;
- The degree of glauconitization depends on the lattice charge of the original degraded material.

To check the first point, the contents of $\text{Fe}_2\text{O}_3 + \text{FeO}$ were plotted against K_2O (fig. 12). There is no obvious relationship between these oxides, but as the presence of non-structural iron obscures the true chemical composition of the mineral, Hower's interpretation may still be correct. Moreover, variations in the composition and charge of the original material which changed to glauconite may be responsible for the lack of correlation between iron and potassium. Hower's second point is not supported in this study, as evidenced by table 7, which shows that the lattice charge of glauconite is caused in a large measure by the charge of the tetrahedral layer, and no correlation exists between the K_2O content and the octahedral charge. Neither can the K_2O -content be correlated with the charge on the tetrahedral layer.

RELATIONSHIP BETWEEN COMPOSITION AND CRYSTAL CHEMISTRY OF GLAUCONITE AND LITHOLOGY

In the evolutionary sequence proposed by Hower, the glauconitization process can be arrested anywhere along the trend "degraded layer lattice mineral" to "mineral glauconite". This is obviously the reason for the existence of different glauconite classes which are partly not true glauconite. Table 8 summarizes data illustrating the relationship between the different glauconite classes and the lithology of the rock in which they occur.

The class of glauconite pellets present in a rock is related to the amount of non-glaucinitic argillaceous matter. Mineralogically pure glauconite (class 1) occurs in sandstone and limestone poor in argillaceous matter, while inter-layered glauconite and glauconite with included clay minerals (classes 2 and 3 a) are formed in predominantly argillaceous rocks.

The relationship between lithology and glauconite class is also reflected in the trace element content of the pellets. Figure 13 shows the correlation between the K_2O -content of glauconite pellets and the trace elements Sr, Ba, V, Cr, Ti, Cs, and Rb. The amount of K_2O is an indicator of the mineralogical purity of the glauconite, val-

TABLE 9.—*Relationship between geologic age and chemical composition of glauconite*

No.	Geologic Age	% K_2O	Fe''/Fe''' -ratio
1	Lower Cretaceous	6.27	0.037
2	Lower Cretaceous	7.76	0.027
3	Lower Cenomanian	7.65	0.091
4	Lower Cenomanian	6.86	0.058
5	Lower Cenomanian	7.81	0.052
6	Lower Cenomanian	7.85	0.075
10	Upper Campanian or Lower Maastrichtian	7.86	0.045
11	Middle Eocene	7.90	0.049

ues from 7.5 to 8.0 indicating pure glauconite. Lower values attest to the presence of clay mineral admixtures, that is, glauconite pellets of classes 2 and 3. The inverse approximately linear relationship between K_2O and Sr, Ba, V, and Cs, is easily understood as these elements do not enter the glauconite structure; their concentration in glauconite pellets increases with the quantity of argillaceous non-glaucinitic matter. Sample 1, which is slightly oxidized, shows an exceptionally low V-content. No relationship seems to exist between K_2O , Rb and Cr. For Ti a clear correlation is indicated: with increasing K_2O -content the Ti-content in the samples studied increases rapidly following a quadratic regression equation; this obviously indicates that Ti enters the glauconite lattice.

Several authors (Smulikowski, 1954; Hower, 1961) have suggested that glauconites of different geologic age differ in their K_2O -content and Fe''/Fe''' ratio. The present study does not support this suggestion, as shown by the figures of table 9, although the Fe''/Fe''' -ratio of the oldest samples is somewhat lower than that of the younger ones.

Glauconite has been reported only from the Upper Precambrian onward. In older rocks two other but related minerals, greenalite and stilpnomelane, occur; but these have not been reported in post-Precambrian rocks except as accessories. According to the structural formulae of greenalite and stilpnomelane given by James (1954), their Fe''/Fe''' ratio exceeds 1, while it is much less than 1 in glauconite. The high Fe''/Fe''' ratio of greenalite and stilpnomelane may correlate with a reducing atmosphere in the earlier Precambrian, and this would explain why glauconite was formed only later.

CONCLUSIONS

1. Classes of glauconite pellets based on mineralogical differences can be used to explain the variability in physical properties and chemical composition.

2. Chemical analyses of the mineral glauconite are meaningful only if allowance is made for the presence of non-structural iron oxide and if glauconite has not undergone partial oxidation.

3. Part of the Fe²⁺ in glauconite might occur in the tetrahedral layer; part of the Mg²⁺ fills vacancies in the octahedral layer. Glauconite is, thus, intermediate between di- and tri-octahedral, although nearer to the first.

4. Correlations between chemical composition of glauconite and geologic age are doubtful.

5. A relationship exists between glauconite class and lithology.

ACKNOWLEDGMENTS

We wish to express our thanks to Dr. G. M. Friedman who supplied a number of glauconite samples and contributed his constructive criticism of the manuscript; to Dr. W. Bodenheimer for helpful suggestions concerning the thermal analyses; to Dr. L. Heller and Z. Kalman for their valuable comments on the X-ray analyses; to M. Gaon, who performed the difficult chemical analyses and to C. A. Key who carried out the spectrographic work; finally to Dr. R. Freund and E. Sass with whom we had many instructive discussions.

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