

## SOME FACTORS CONCERNING THE NATURE AND ORIGIN OF GLAUCONITE

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### ABSTRACT

The compositional variations of glauconite can be related to differences in mixed-layering involving "illite" (10 Å) and "montmorillonite" (expandable) layers. The interlayer cations potassium and rubidium and the octahedral cation iron decrease with increasing amounts of expandable layers. Strontium increases rapidly with increasing per cent expandable layers and because it is largely exchangeable is assumed to be present in the expandable layers as an exchange ion.

The relationships between structure and composition are used to examine Burst's model for glauconitization. Pellets that occur in clean sandstones, limestones and dolomites are almost exclusively monomineralic, consisting only of mixed-layer illite/montmorillonite with a low per cent expandable layers. Pellets that occur in argillaceous sandstones and marls frequently contain extraneous clay minerals and the illite/montmorillonite contains a high per cent expandable layers. Because of the well known observation that glauconite forms only at relatively low sedimentation rates it is concluded that the pellets occurring in argillaceous sandstones and marls represent less glauconitized material than those pellets occurring in clean sandstones, limestones, and dolomites. These observations fit Burst's model for glauconitization which assumes a degraded 2:1 layer-lattice structure as the parent material and the glauconitization process as a gradual substitution of iron for aluminum in the octahedral positions, a concomitant gradual increase in lattice charge (arising from the octahedral layer) and a consequent increase in interlayer potassium which results in the collapse of increasingly more layers to the non-expandable 10 Å type. It is also shown that potassium increases with octahedral charge and is independent of tetrahedral charge, a phenomenon predictable from Burst's model but no other.

Glauconites differ significantly in composition and structure with geologic age. Young glauconites are lower in potassium (and thus higher in per cent expandable layers) and are more frequently mineralogically heterogeneous than older glauconites. A large part of these age differences appears to be explainable on the basis of lithologic association. However, there is some evidence for late epigenetic gain of potassium.

Weaver has shown similar differences with geologic age in the clay mineral assemblages of shales. Because of this similarity and because a good case can be made for attributing most of the variations in the mineralogy of glauconite pellets to diagenetic effects, it is suggested that diagenesis may have played an important role in the formation of the clay mineral assemblages of shales.

### INTRODUCTION

Burst (1958*a*, 1958*b*) has recently shown that glauconite pellets are composed of mineralogically heterogeneous material. He has divided the pellets into four classes on the basis of *x*-ray diffraction data: (1) Ordered 10 Å structures, (2) Disordered 10 Å structures, (3) Interlayered structures, and (4) Mixed mineral pellets. The first three classes form a series of increasing potassium from class (3) to class (1). The fourth class includes glauconite pellets composed of more than one clay mineral. No relation was found between external morphology and mineralogical com-

position. Burst has shown clearly that since some pellets are mineral mixtures any interpretation of the chemical composition of glauconite must be aided by an  $x$ -ray diffraction determination of the mineralogical composition.

Investigations into the origin of glauconite previous to those of Burst were greatly handicapped by the lack of  $x$ -ray diffraction data. One of the major problems concerning the origin of glauconite has been the type of starting (parent) material. The conclusions of these previous investigations as to the nature of the glauconitization process have been colored by what appeared to be the parent material in a particular instance of glauconite formation. For this reason Galliher (1935, 1939) proposed that glauconitization involved the alteration of biotite, the chemical changes involved being: (1) oxidation of the iron already present, (2) partial loss of potassium, (3) "hydration," and (4) partial loss of aluminum. Takahashi (1929, 1939), on the other hand suggested that the parent material for glauconite formation was an amorphous gel of aluminates and silicates. This material, he assumed, was derived from a number of preexisting materials such as volcanic glass, mica, clays in fecal pellets, feldspar, etc., by hydration and consequent gelatinization. Subsequent recrystallization during diagenesis ("submarine metamorphism") along with compositional changes give rise to glauconite. The composition changes that Takahashi proposed include an increase in potassium and iron and a decrease in aluminum.

The model of glauconitization proposed by Burst assumes that the immediate starting material in the formation of glauconite can be any degraded (expandable) layer lattice mineral. The process of glauconitization according to this model consists of absorption of potassium and iron by the degraded layer lattice material under the proper environmental conditions. This model fits the known data on glauconites better than any previously proposed. The main purpose of the present study was to attempt to test the model for glauconitization with data supplementary to that provided by Burst. An additional purpose was to relate the compositional and structural variations in glauconite that are of interest to the use of this material in the radioactive dating of sedimentary rocks.

#### EXPERIMENTAL METHODS

##### *X-ray Diffraction Determinations*

Oriented specimens of the glauconites were prepared for the  $x$ -ray diffraction determinations. A sample was first disaggregated in distilled water, either by grinding or ultrasonics, and the suspension was then centrifuged through a porous porcelain plate. This technique was devised by Kinter and Diamond (1956).

The type and extent of interlayering was determined from diffraction patterns of treated samples. Patterns were obtained on untreated, glycol solvated, and potassium-treated (with a 1N KCl solution) samples. Most of the samples were also run after heat treatments in the range 500–600° C. for a period of  $\frac{1}{2}$  hour in order to detect the presence of chlorite layers. The per cent expandable layers was determined from the position of the combined 001/001 reflection following glycol solvation and also following potassium treatment. The per cent expandable layers was read from the curves of Brown and MacEwan (1951) and Weaver (1956) relating  $d$ -spacing to amount and type of interlayering, and is reported to the nearest five per cent.

Randomly oriented  $x$ -ray diffraction patterns were run on a number of glauconites to determine polymorphic type.

#### *Chemical Analyses*

Potassium was determined flame photometrically with a Perkin-Elmer instrument using lithium as the internal standard. The samples were taken into solution using a HF-HClO<sub>4</sub> attack. The standard deviation of the determinations is  $\pm$  three per cent of the amount present.

Strontium and rubidium were determined  $x$ -ray spectrographically using the method described by Hower (1959). Standards were prepared by mixing carbonates of Rb and Sr with Al<sub>2</sub>O<sub>3</sub>. Arsenic was used as the internal standard. The precision of trace element  $x$ -ray spectrographic techniques is best expressed in terms of absolute amount. The standard deviation of the Sr and Rb determinations is about  $\pm$  5 ppm. Therefore, the relative precision of the determination of Sr in some glauconites is quite poor.

Iron was determined for a few samples by a semi-quantitative  $x$ -ray spectrographic method. A one point working curve was constructed using an analyzed sample (the Bashi fm.) as the known point. The slope of the working curve was adjusted by calculating absorption coefficients for six additional analyzed glauconites relative to the Bashi sample. The standard deviation of the determinations is  $\pm$  2 per cent of the amount present. The accuracy is thought to be within  $\pm$  10 per cent. Iron is reported as Fe<sub>2</sub>O<sub>3</sub>.

## RESULTS AND DISCUSSION

### *Relationship Between Glauconite Composition and Structure*

As discussed in the previous section, the method of sample preparation for  $x$ -ray diffraction determinations was different from that employed by Burst (1958*a*, 1958*b*). The more vigorous orientation technique results in a lack of patterns showing the 448 Å peak exhibited by

Burst's "disordered" type of glauconite. A comparison of the results of both methods can be briefly made as follows. All glauconites are interlayered to a certain extent. The interlayering is almost exclusively between expandable (montmorillonitic) layers and non-expandable 10 Å layers. Patterns obtained from glycolated, potassium-treated, and heat-treated samples show no appreciable amount of chlorite or vermiculite layers in any glauconite. Burst (personal communication, 1960) has detected chlorite in some glauconites and has pointed out that the heat treatment used in this study would destroy some sedimentary chlorites. Glauconites exhibit a continuous series from <5 per cent to approximately 40 per cent expandable layers. A comparison with Burst's first three classes can be related to the amount of expandable layers. An approximate comparison is that "ordered" glauconites contain  $\leq 10$  per cent expandable layers, "disordered" glauconites 10–20 per cent expandable layers, and "interlayered" glauconites  $\geq 20$  per cent expandable layers. Figure 1 shows the diffraction patterns of glauconites that cover the range from <5 per cent to approximately 30 per cent expandable layers.



FIG. 1. Examples of monomineralic glauconite pellets composed of mixed-layer illite/montmorillonite. The samples are glycol solvated. (upper left) Tonto Fm., Cambrian, 5% expandable layers, 6.7% K; (upper right) Bonne Terre Fm., Cambrian, 10% expandable layers, 6.9% K; (lower left) Gros Ventre Fm., Cambrian, 15% expandable layers; (lower right) Colorado shale, Cretaceous, 25% expandable layers, 4.2% K.

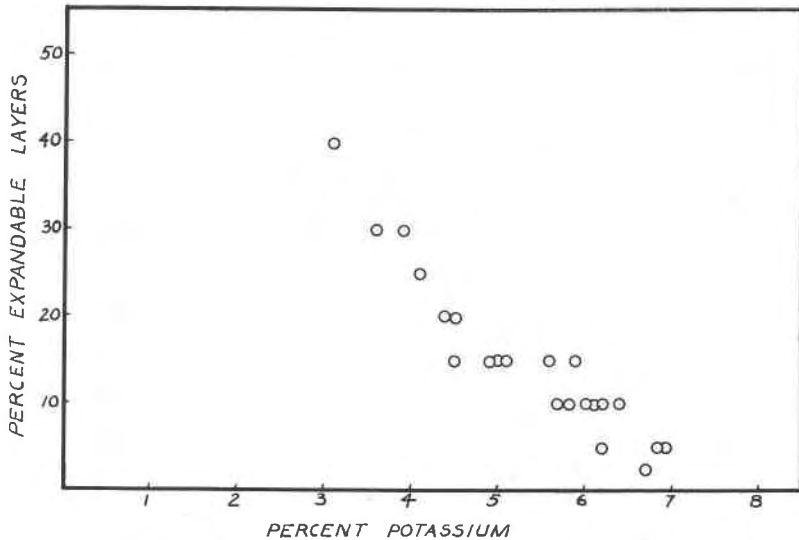


FIG. 2. The relationship between weight per cent potassium and per cent expandable layers in monomineralic mixed-layered illite/montmorillonite glauconite pellets.

Randomly oriented diffraction patterns gave the same results as those reported by Burst (1958*b*). Glauconites with a low per cent of expandable layers are the  $1M$  polymorph; glauconites with a high per cent of expandable layers are the  $1Md$  polymorph.

Table I is a summary of the structural and some of the compositional data on glauconites for which  $x$ -ray diffraction data are available. A portion of the diffraction data was obtained during the present study. The remaining diffraction data were obtained from Burst (1958*a*, 1958*b*) and Warsaw (1957). The sources for data of all types are noted in the table. The values reported of per cent expandable layers from the Burst sources were roughly estimated from his patterns of untreated samples. None of these estimated values are used in the plots relating compositional and structural changes which follow.

The samples are listed in Table I in order of increasing amounts of expandable layers. Some relationships between structure and chemical composition can be noted. Potassium decreases with increasing per cent expandable layers. This is the same trend noted by Burst for his first three classes. Figure 2 is a plot of weight per cent potassium against per cent expandable layers for glauconites that are not clay mineral mixtures. The plot indicates a continuous series in glauconites that covers a wide range of potassium content.

Other elemental variations can be related, at least in part, to structural variations. Figure 3 is a plot of strontium against per cent expand-

TABLE I. SUMMARY OF GLAUCONITE STRUCTURAL AND COMPOSITIONAL DATA

Sample	Age	Lithology	Per cent Expandable	Burst Class	Mixed Mineral	Per cent K	ppm Rb	ppm Sr	Per cent Fe <sub>2</sub> O <sub>3</sub>	Sample No.
Tonto Fm.	Cambrian	clean ss	5 (1)	—	none	6.7 (1)	300	10 (1)	19.4 (1)	1
Birkmose Mem. (Franconia Fm.)	Cambrian	clean ss	5 (1)	—	none	6.9 (1)	290	20 (1)	24.9 (1)	2
Bonne Terre Fm.	Cambrian	dolomite	5 (1)	Ordered	none	6.9 (2)	—	—	22.9 (2)	3
Stenbrottet ls.	Ordovician	limestone	5 (1)	—	none	6.2 (4)	307	13 (4)	—	4
Ceratopyge ss	Ordovician	? ss	10 (5)	Ordered	none	6.0 (2)	—	—	15.1 (2)	5
Reno Mem. (Franconia Fm.)	Cambrian	clean ss	10 (1)	Ordered	none	6.4 (1)	265	15 (1)	21.5 (1)	6
Mt. Whyte Fm.	Cambrian	calc. ss	10 (1)	—	none	—	180	116 (4) (calcite)	—	7
Tyner Fm.	Ordovician	limestone	10 (3)	—	—	—	—	—	—	8
Vidoto Fm.	Cretaceous	chert	10 (3)	—	—	5.7 (3)	—	—	18.7 (3)	9
H & S #1	Cret./Tert.	—	10 (3)	—	—	6.2 (3)	—	—	17.2 (6)	10
Mahele Fm.	Paleocene	clean ss	10 (3)	—	—	—	—	—	—	11
Bashi Fm.	Eocene	marl	10 (1)	Disordered	none	5.8 (1)	290	40 (1)	22.7 (2)	12
San Saba Mem. (Wilberns Fm.)	Cambrian	limestone	10 (1)	—	none	6.1 (4)	244	10 (4)	—	13
Gros Ventre Fm.	Cambrian	arg. ss	15 (1)	—	kaolinite	—	275	25 (1)	—	14
Riley Fm.	Cambrian	? xx	15 (1)	—	none	5.6 (4)	—	—	—	15
Murray sh	Cambrian	arg. ss	15 (1)	—	none	5.9 (4)	171	28 (4)	—	16
Carlisle Cent. Fm.	Devonian	arg. silt	15 (1)	—	none	4.9 (4)	309	39 (4)	—	17
Navesink Fm.	Cretaceous	marl	15 (1)	Ordered	none	5.1 (1)	—	—	22.3 (1)	18
Warsaw #8	Cretaceous	? ss	15 (3)	—	—	—	—	—	—	19
Temblador Fm.	Cretaceous	arg. ss	15 (3)	—	—	—	—	—	—	20
H & S #4	Cret./Tert.	—	15 (3)	—	—	5.0 (3)	—	—	24.8 (6)	21
H & S #4	Cret./Tert.	—	15 (3)	—	—	5.0 (3)	—	—	24.9 (6)	22
Warsaw #9	Cretaceous	ark. ss	15 (3)	—	—	4.5 (3)	—	—	20.6 (6)	23
Pierson Fm.	Eocene	—	15 (5)	Disordered	none	5.1 (2)	—	—	19.3 (2)	24
Wilcox Fm.	Eocene	marl	10-20 (5)	Mixed Mineral	—	—	—	—	—	25

TABLE I (continued)

Sample	Age	Lithology	Per cent Expandable	Burst Class	Mixed Mineral	Per cent K	ppm Rb	ppm Sr	Per cent Fe <sub>2</sub> O <sub>3</sub>	Sample No.
Gatchell Fm.	Eocene	?	10-20 (5)	Mixed Mineral	—	—	—	—	—	26
Martinez Fm.	Paleocene	ark. ss	20 (3)	—	—	4.5 (3)	—	—	22.5 (3)	27
Morrow Fm.	Pennsylv.	sandy sh.	20 (5)	Mixed Mineral	—	—	—	—	—	28
Burditt marl	Cretaceous	marl	20 (5)	Disordered	none	5.3	—	—	16.9 (2)	29
"Subsurface"	Eocene	?	20 (5)	Disordered	none	4.0 (2)	—	—	14.1 (2)	30
H., New Jersey	?	?	20 (1)	—	none	4.4 (1)	—	—	—	31
Matalani Fm.	Eocene	chert	20 (3)	—	—	—	—	—	—	32
Domengine Fm.	Eocene	arg. ark ss	20 (3)	—	—	—	—	—	—	33
Colorado sh.	Cretaceous	arg. ss	25 (1)	—	none	4.2 (1)	320	100 (1)	9.4 (1)	34
Carrizo Fm.	Eocene	marl?	25 (1)	—	none	—	—	—	—	35
Panoche Fm.	Cretaceous	arg. ss	20-30 (5)	Interlayered	none	—	—	—	—	36
Euaw Fm.	Cretaceous	—	20-30 (5)	Interlayered	none	—	—	—	—	37
Ripley Fm.	Cretaceous	calc. arg ss	20-30 (5)	Interlayered	none	—	—	—	—	38
Prairie Bluff Fm.	Cretaceous	marl	20-30 (5)	Mixed Mineral	—	—	—	—	—	39
Lodo Fm.	Paleocene	?	20-30 (5)	Interlayered	none	—	—	—	—	40
Reklaw Fm.	Eocene	arg. ss	20-30 (5)	Mixed Mineral	—	—	—	—	—	41
Sundance Fm.	Jurassic	arg. ss	30 (1)	—	kaolinite	3.9 (1)	240	115 (1)	8.9 (1)	42
Moody's Branch Fm.	Eocene	marl	30 (1)	—	none	3.6 (1)	150	170 (1)	14.2 (1)	43
Winona Fm.	Eocene	arg. ss	30 (5)	Interlayered	none	—	—	—	—	44
Mathews Ldg.	Paleocene	marl	30-40 (5)	Interlayered	none	—	—	—	—	45
Weches Fm.	Eocene	arg. ss	30-40 (5)	Mixed Mineral	—	—	—	—	—	46
Byram Fm.	Oligocene	marl	40 (1)	Interlayered	none	3.1 (1)	165	245 (1)	—	47

(1) This investigation.

(2) Burst (1958b).

(3) Warshaw (1957).

(4) Hurley, P. M., Fairbairn, H. W., Pinson, W. H., and Winchester, J. (1958), Age study of Lower Paleozoic glauconites: Sixth Annual Progress Report, USAEC Contract AT (30-1)-1381, pp. 53-62.

(5) Burst (1958a).

able layers for glauconites which are not clay mineral mixtures and contain no detectable calcite. The strong positive correlation suggests that Sr is an exchange ion present in the expandable layers. Table II compares the Sr contents of glauconites that have been treated with a one normal  $\text{NH}_4\text{Ac}$  solution with untreated samples. It is apparent that most of the Sr in these glauconites is easily exchangeable. The conclusion is that most of the Sr present in glauconite pellets is indigenous to the glauconite and is adsorbed on the basal plane surfaces of the expandable layers. This

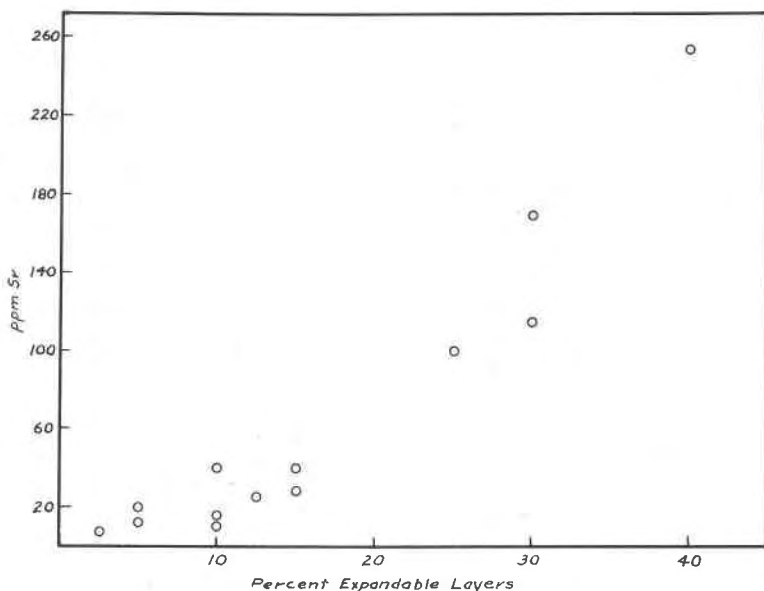


FIG. 3. The relationship between strontium and per cent expandable layers in carbonate-free glauconite pellets.

conclusion differs from that of Herzog et al (1958), who determined Sr in glauconites in the course of Sr/Rb dating studies, and attributed the strontium variations in glauconite wholly to calcite contamination. Their HCl treatment to remove calcite would also remove exchangeable Sr held by the glauconite. However, addition of "common" Sr to glauconite samples by calcite contamination could undoubtedly be significant for glauconites that are intrinsically very low in Sr. An example is sample number 8 in Table I (Mt. Whyte Fm.) which contains only 10 per cent expandable layers and 116 ppm. Sr. Calcite is readily detectable in this sample by *x*-ray diffraction.

Rubidium decreases roughly with increasing amounts of expandable layers (Fig. 4). Rubidium does not decrease as rapidly as potassium,



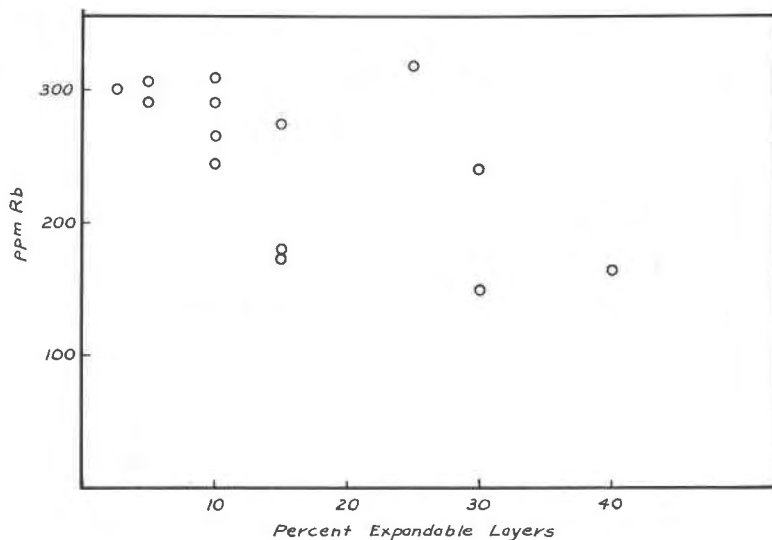


FIG. 4. The relationship between rubidium and per cent expandable layers in glauconite pellets.

probably because it is preferentially adsorbed in the expandable layers. On the basis of the most limited data shown in Table II, the Rb is non-exchangeable. Most of the Rb is undoubtedly held in the non-expandable layers.

Potassium, rubidium, and strontium are interlayer cations in glauconite and would thus be expected to show some relationship with the per cent expandable layers. Iron is octahedrally coordinated in the

TABLE II. EFFECT OF  $\text{NH}_4\text{Ac}$  TREATMENT ON THE STRONTIUM CONTENT OF GLAUCONITES

Sample	% Expandable	Sr		Rb	
		Untreated	$\text{NH}_4$ treated	Untreated	$\text{NH}_4$ treated
Tonto Fm.	< 5	~ 10	~10	310	295
Birkmose Fm.	5	20	~10	290	—
Bashi Fm.	10	40	~10	290	—
Franconia Fm.	10	~ 15	~10	265	265
Gros Ventre Fm.	15	25	~10	275	—
Colorado Fm.	25	100	25	320	330
Sundance Fm.	30	115	40	245	235
Moody's Branch Fm.	30	170	60	145	150
Byram Fm.	40	245	25	165	175

glaucanite structure and would therefore not necessarily show any relation with the nature of inter-layering. Figure 5 is a plot of total iron, reported as  $\text{Fe}_2\text{O}_3$ , against per cent expandable layers. There appears to be a rough correlation, the possible significance of which will be discussed in a later section.

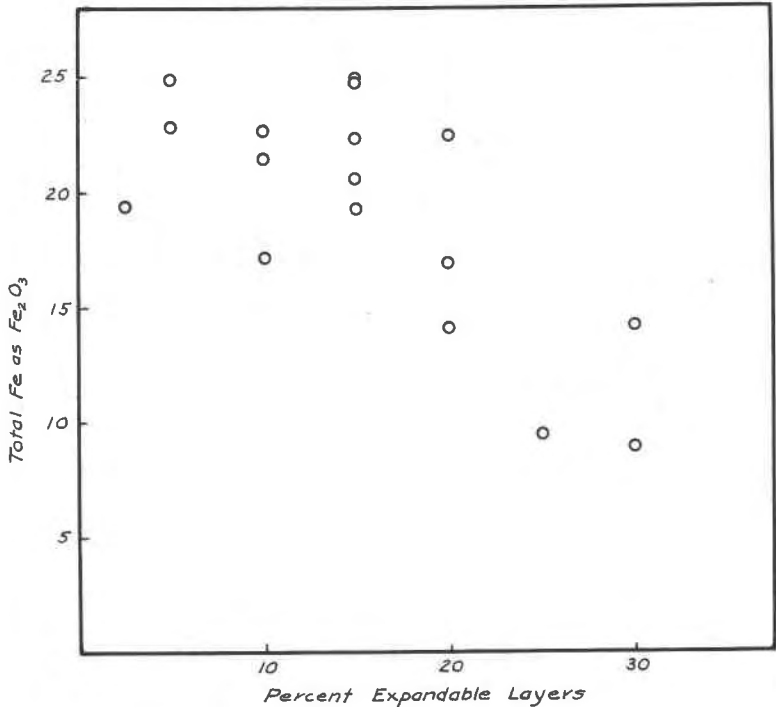


FIG. 5. The relationship between total iron as  $\text{Fe}_2\text{O}_3$  and per cent expandable layers in glauconite pellets.

#### RELATION BETWEEN LITHOLOGIC TYPE OF ENCLOSING SEDIMENT AND GLAUCONITE STRUCTURE

Warshaw (1957) has pointed out a relationship between glauconite structure and the lithologic nature of the rock type in which the pellets occur. For twelve occurrences she found the following relationships: Glaucanites equivalent to Burst's "ordered" and, in part, "disordered" type occurred in a dolomite, a chert, and sandstones in which the detrital grains are mostly quartz, quartzite, or chert and the cement is silica and/or carbonates; glaucanites of Burst's "disordered" type occurred in a subarkosic sandstone and a bentonitic shale; "mixed-layer" type

glaucconites occurred in sandstones containing large amounts of feldspar, clay minerals other than glauconite, and mica.

Included in Table I is, when known, the general nature of the lithologic type of the enclosing sediment in which the glauconite sample occurs. The lithologic description is generalized and simplified—it is hoped not oversimplified. Table III is a summary of these data, dividing glauconites into two groups, those with  $\leq 10$  per cent expandable layers and those with  $\geq 15$  per cent expandable layers. Glauconites with  $\leq 10$  per cent expandable layers occur predominantly in non-argillaceous quartzose sandstones and “normal” carbonate rocks (limestones and dolomites). Glauconites with  $\geq 15$  per cent expandable layers occur predominantly in argillaceous sandstones and marls.

#### THE ORIGIN OF GLAUCONITE

Burst (1958*a*, 1958*b*) has proposed, on the basis of his investigations, a model for the origin of glauconite that reconciles many of the older proposals. He suggests that the process of glauconitization requires simply (1) a degraded silicate layer lattice, (2) a plentiful supply of iron and potassium, and (3) a suitable redox potential. The redox potential is frequently supplied by a locally reducing environment associated with decaying organic matter, in a generally oxidizing environment. The locally reducing environment can be present in fecal pellets, inside foraminiferal tests, etc., hence the frequent glauconitization of these materials. Other factors, such as sedimentation rate, water temperature, water depth and parent material can have an influence on the specific nature (type) of glauconite that forms. Burst further suggests that the chemical changes involved in glauconitization are “the adjustment by absorbing iron and potassium into . . . impoverished clay lattices in amounts controlled, in part, by the surrounding sea-water chemistry. . . .” By impoverished is meant degraded; that is, a layer-lattice structure consisting largely or wholly of loosely bonded (expandable) layers. This expandable material could also include the montmorillonoids as well as degraded originally non-expandable layer-lattices. Presumably, given the proper chemical conditions and enough time the material would approach the composition and structure of Burst’s “mineral glauconite.” Burst has defined the “mineral glauconite” on the basis of his “ordered” glauconites—those which have few expandable layers, ordered stacking, and are high in potassium.

The data reported in previous sections can be profitably used to test the model for glauconitization proposed by Burst. First, however, it would be well to attempt to describe the mechanism of chemical change in more detail. The “absorption of potassium and iron” would involve

TABLE III. RELATION BETWEEN GLAUCONITE STRUCTURE AND  
 LITHOLOGIC TYPE OF ENCLOSING SEDIMENT

Sample	Age	Lithology
<i>a.</i> Glauconites with $\leq 10$ per cent expandable layers		
Tonto Fm.	Cambrian	clean quartzose ss
Birkmose Mem.	Cambrian	clean quartzose ss
Reno Mem.	Cambrian	clean quartzose ss
Park Fm.	Cambrian	clean quartzose ss
Mahele Fm.	Paleocene	clean quartzose ss
Mt. Whyte Fm.	Cambrian	calcareous ss
Stenbrottet ls.	Ordovician	limestone
San Saba Mem.	Cambrian	limestone
Tyner Fm.	Ordovician	dolomite
Bonne Terre Fm.	Cambrian	dolomite
Vidono Fm.	Cretaceous	chert
Bashi Fm.	Eocene	marl
<i>b.</i> Glauconites with $\geq 15$ percent expandable layers		
Lion Mt. Mem.	Cambrian	limestone
Gros Ventre Fm.	Cambrian	argillaceous ss
Murray sh.	Cambrian	argillaceous ss
Carlisle Cent. Fm.	Devonian	argillaceous silt
Temblador Fm.	Cretaceous	argillaceous ss
Warshaw #9	Cretaceous	argillaceous felds. ss
Domengine Fm.	Eocene	argillaceous felds. ss
Colorado Fm.	Cretaceous	argillaceous ss
Panoche Fm.	Cretaceous	argillaceous ss
Ripley Fm.	Cretaceous	calc. argillaceous ss
Reklaw Fm.	Eocene	argillaceous ss
Sundance Fm.	Jurassic	argillaceous ss
Winona Fm.	Eocene	argillaceous ss
Weches Fm.	Eocene	argillaceous ss
Navesink Fm.	Cretaceous	marl
Wilcox Fm.	Eocene	marl
Burditt Marl	Cretaceous	marl
Carrizo Fm.	Eocene	marl
Prairie Bluff Fm.	Cretaceous	marl
Moody's Branch Fm.	Eocene	marl
Mathews Ldg.	Paleocene	marl
Byram Fm.	Oligocene	marl
Martinez Fm.	Paleocene	felds. ss
Morrow Fm.	Pennsylvanian	arenaceous sh.
Matalani Fm.	Eocene	chert

the adsorption and subsequent fixation of these ions in the lattice and the simultaneous release of other ions that were either exchanged on or fixed in the lattice of the parent material. During the glauconitization process iron would have to make its way into the octahedral layer of the parent layer lattice mineral, where it would commonly take the place of aluminum. The replacement mechanism would most easily be accomplished in parent material of a degraded nature consisting largely of expandable layers—the parent material suggested by Burst. The iron ions could migrate into the expandable layers, be adsorbed there, and eventually diffuse into the octahedral layer, replacing aluminum ions. Most likely the rate of supply of iron ions would not be high considering the low concentration of soluble iron compounds in the ocean. Also, the replacement process would probably be slow. Once the material being glauconitized was buried very far below the sediment-sea water interface (where the proper chemical environment is present) the process would stop.

A few observations can now be made relating this proposed mechanism of glauconitization to the known facts of glauconite formation.

A low or negative sedimentation rate has been recognized as a condition necessary for the formation of glauconite (Cloud, 1955). If the rate of sedimentation is too high, glauconite does not form. In terms of the proposed model this means that the rate of supply of degraded argillaceous material must be low and that the material being glauconitized would remain at the sediment-sea water interface a long time. There would, of course, be a range of sedimentation rates—other factors being constant—over which glauconite could form. The glauconitization process would not proceed as far when the sedimentation rate was at the high end of the range as toward the lower. Therefore, the glauconitization process under more rapid sedimentation would be arrested somewhere along the series “degraded [layer] lattice mineral”—“mineral glauconite.” This is here proposed as the reason for the relationship between glauconite structure and lithologic type of the enclosing sediment shown in Table III. Glauconites containing  $\geq 15$  per cent expandable layers are found dominantly in argillaceous sandstones and marls in which the rate of supply of argillaceous material is high. In contrast, glauconites with  $\leq 10$  per cent expandable layers occur dominantly in clean quartzose sandstones and normal carbonate rocks in which the rate of supply of argillaceous material is low.

Burst (1958*b*) has shown a similar effect of sedimentation rate on the glauconite type that forms. In a group of glauconites he has studied from the Tertiary, glauconites occurring at unconformities approach his “ordered” type in contrast to glauconites occurring in conformable sedi-

ments that tend to be of his "disordered" and "interlayered" types. Presumably the glauconites occurring at unconformities had a longer time to approach the ordered potassium-rich (low per cent expandable layers) end product and remained near the sediment-sea water interface longer.

Since the rate of formation of glauconite is slow, it can be concluded that degraded or expandable material with a high lattice charge would probably not be easily glauconitized. Weaver (1958c) has shown that such material rapidly adsorbs potassium from sea water and collapses to a non-expandable lattice. Once the layers collapse it would be difficult for iron to make its way into the octahedral layers and glauconitization would proceed only slowly, if at all. Therefore, if the parent material for glauconite formation is a degraded layer lattice mineral, its susceptibility to glauconitization should be greatly enhanced if the lattice charge were relatively low. This means, then, an increase in net lattice charge and therefore a consequent increase in the number of interlayer cations (mainly potassium) as glauconitization proceeds. This fits the model suggested by Burst. If this model is at least approximately correct, potassium and iron should be directly proportional to each other and both should be inversely proportional to the per cent expandable layers. The model, however, does not require a one to one correlation between the parameters. It means only that potassium (which depends on net lattice charge) and iron increase—though not necessarily at the same rate—together during glauconitization. Figure 5, presented previously without a suggested explanation, shows that iron is roughly inversely proportional to per cent expandable layers. Figure 6 shows that iron is proportional to potassium. These relationships conform with the predictions made above and based on Burst's model for glauconitization. These relationships would not be predicted by other proposed mechanisms of glauconitization such as crystallization from amorphous material or the alteration of biotite.

Another question which arises is that of the structural position of the increase in net lattice charge during glauconitization. Again following the proposed model, one would conclude that the increase in charge takes place in the octahedral layer—for it is in this layer that extensive ionic substitution takes place. It is also possible, of course, that some substitution takes place in the tetrahedral layer—of iron for aluminum or silicon—as suggested by Hoebeke and Dekeyser (1955). However, the presence of iron in tetrahedral coordination has yet to be proved (Warsaw, 1957). Assuming that the increase in net charge takes place by substitutions in the octahedral layer, it can be predicted that the total number of interlayer cations would increase with the net octahedral charge and that no specific relationship would be expected between the

number of interlayer cations and the net tetrahedral charge. Figures 7 and 8 indicate a confirmation of this prediction. Figure 7 shows an increase in potassium with increasing octahedral charge. Figure 8 shows no obvious relationship between potassium and tetrahedral charge. The data plotted in these figures were obtained from structural formulas calculated by Hendricks and Ross (1941), Burst (1958*b*) and Warshaw (1957). The relationships are somewhat open to question for they may result, in part, from the method of calculation of a structural formula.

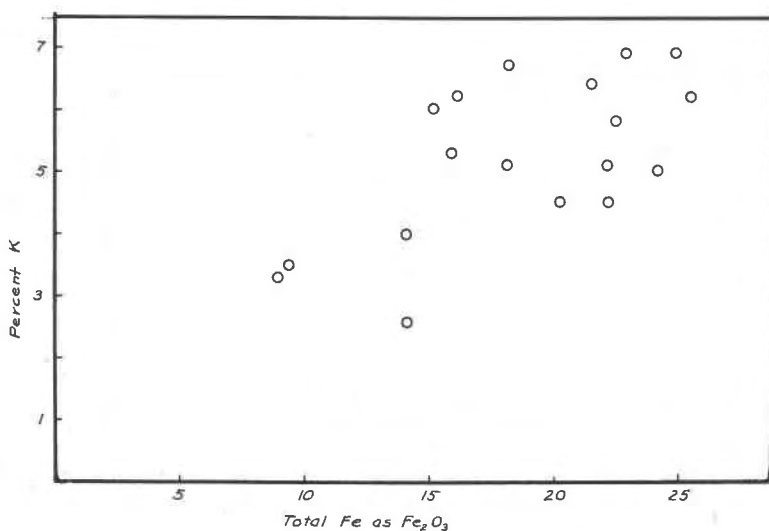


FIG. 6. The relationship between potassium and iron in glauconite pellets.

However, if the structural formulas are close to reality, the relationships are valid. Another feature that suggests that the increase in lattice charge is predominantly in the octahedral layer is that the mean octahedral charge ( $-0.92$ ) in glauconite is higher than for any other 2:1 clay mineral.

To summarize, the data reported in the previous section lend support to Burst's model for glauconitization. The model is as follows: (1) the parent material can be any degraded 2:1 layer lattice mineral (except those with a high net lattice charge); (2) the material must be subjected to locally reducing conditions in a generally oxidizing environment—this usually occurs in fecal pellets, foraminiferal fillings, etc.; (3) an abundant supply of K and Fe must be present. This condition is met in the marine environment and not in fresh water environments; (4) glauconitization proceeds by the slow substitution of iron in the octahedral

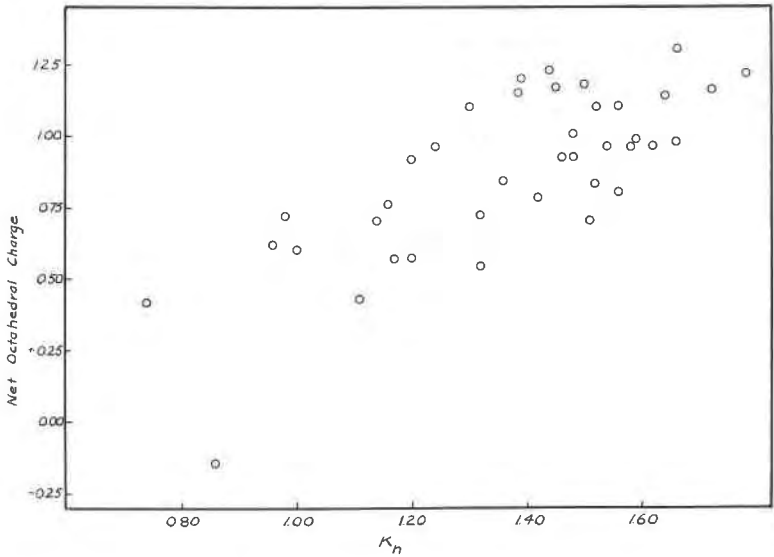


FIG. 7. The relationship between net octahedral charge and the number of potassium ions per unit cell in glauconites.

layer, usually displacing aluminum. Along with this substitution there is a gradual increase in the lattice charge with the consequent uptake of more potassium and the eventual collapse of increasing amounts of layers to 10 Å. The end product is high in iron and potassium and the structure consists mainly of non-expandable 10 Å layers.

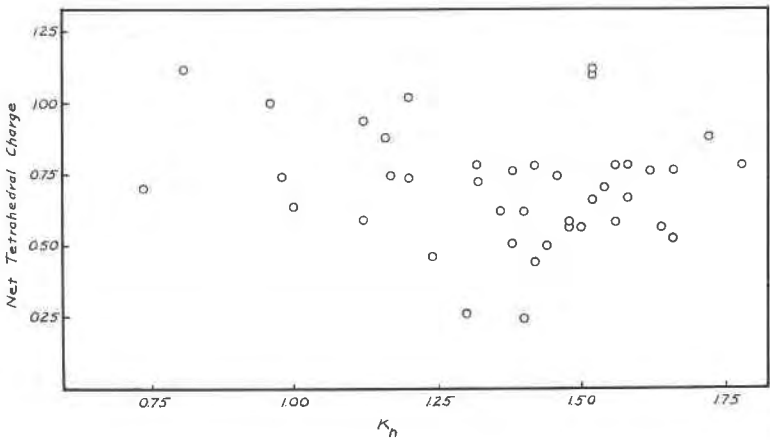


FIG. 8. The relationship between net tetrahedral charge and the number of potassium ions per unit cell in glauconites.



Other factors such as temperature and sedimentation rate will control the rate of the chemical reactions and also determine how far the reaction proceeds before it is stopped. This gives rise to the serial relation in composition and structure found in glauconites. One end of this series approaches a 2:1 layer lattice low in iron and potassium and high in aluminum and has a high percentage of expandable layers; the other end reaches the "mineral glauconite" which is high in iron and potassium, low in aluminum, and has a low percentage of expandable layers.

#### VARIATIONS IN GLAUCONITE STRUCTURE AND COMPOSITION WITH GEOLOGIC TIME

Several writers (Warshaw, 1957, Conway, 1942, and Smulikowski, 1954) have commented on the variations of glauconite composition with geologic times. Warshaw found no apparent changes. However, both Conway and Smulikowski noted a potassium "deficiency" in Tertiary

TABLE IV. SUMMARY OF THE STRUCTURE AND COMPOSITION OF GLAUCONITES OF DIFFERENT GEOLOGIC AGES

Geologic age	No. of samples	Per cent expandable layers		Per cent K		No. of K Anal.
		Mean	Range	Mean	Range	
Early Paleozoic	14	<10	< 5-15	6.1	4.9-6.9	11
Late Paleozoic and Mesozoic	17	~20	10-30	4.8	3.3-6.2	8
Cenozoic	19	~25	10-40	4.3	2.3-6.2	9

and Recent glauconites. Table IV is a summary taken from the data in Table I, of the means and ranges of per cent expandable layers and per cent potassium for different portions of geologic time. The potassium analyses are reported only for non-mixed-mineral glauconites. Quite apparent differences in structure and composition occur between Early Paleozoic (Cambrian through Devonian) and all younger glauconites. Glauconites younger than Devonian average considerably less potassium and consequently have a more expandable structure. These data substantiate a potassium "deficiency" in young glauconites. Both Conway and Smulikowski have proposed explanations for this potassium deficiency. Smulikowski interprets it as the result of changes in the chemical environment of the ocean; Conway further proposes that this difference in environment is a result of a potassium deficiency in Tertiary and Recent seas. There is, however, an alternate, simpler, explanation based on the relationship between glauconite type and lithology of the

enclosing sediment, pointed out in a previous section. Most Early Paleozoic glauconites that have been sampled occur in orthoquartzites and normal carbonate rocks; most Mesozoic and younger glauconites occur in argillaceous sandstones and marls. Hence the structural and compositional relationship with geologic time.

Even though the relationship between glauconite structure and composition and lithologic type seems to provide an adequate explanation for the potassium deficiency in young glauconites, the possibility of epigenetic gain of some potassium in Lower Paleozoic glauconites cannot be excluded. Some data indicate the possibility of epigenetic gain of potassium: (1) Four of the eleven Lower Paleozoic glauconites analyzed for potassium are higher in potassium than any younger glauconite; (2) Three Lower Paleozoic glauconites were sampled from argillaceous

TABLE V. FREQUENCY OF OCCURRENCE OF MIXED-MINERAL GLAUCONITES AS RELATED TO GEOLOGIC AGE

Geologic	No. of Samples	No. of Mixed-Mineral Glaucon.	Frequency	Lithologic Types
Lower Paleozoic	14	1	0.07	arg. ss
Upper Paleozoic and Younger	23	8	0.35	4 arg. ss 4 marls

sandstones (sample numbers 14, 16, and 17), and have the least amount of expandable layers (15 per cent) of all glauconites occurring in argillaceous sandstone.

Another interesting mineralogical feature of glauconites is the frequency of occurrence of the "mixed-mineral" type of glauconite pellets (Burst's type four) in different portions of geologic time. Table V is a summary of the known data from Lower Paleozoic and from Upper Paleozoic (Mississippian on up) and younger glauconites. The frequency of occurrence of mixed mineral glauconites in Lower Paleozoic glauconites is strikingly lower than the frequency in younger glauconites. Assuming a  $\chi^2$  distribution, this has one degree of freedom and  $\chi^2 = 3.94$  and a relationship can be rejected at the 0.05 level.

Kaolinite and chlorite appear to be the usual extraneous clay minerals present in glauconite pellets (Burst, 1958a). However, it is possible that many glauconites contain illite as a "contaminant." The structure of illite is the same as that of glauconite, hence the detection of illite contamination is difficult or impossible. It is possible that some "aluminous" glauconites with a low per cent of expandable layers are actually illite contaminated. On the other hand, it can be pointed out that the relationship

between the iron and aluminum content of glauconite and the per cent expandable layers indicates that the effect of illite contamination, if any, is masked.

Though the data are limited, it can be seen from Table V that, as with the variability in per cent expandable layers, the occurrence of mixed-mineral pellets appears to be related to the lithologic type of the enclosing sediment. All the mixed-mineral glauconites occur either in argillaceous sandstones or marls. No mixed-mineral pellets have been found to occur in orthoquartzites or normal carbonate rocks. Also, extraneous clay minerals occur only in pellets in which the interlayered illite-montmorillonite-type structure contains  $\geq 15$  per cent expandable layers. The relationship could be explained in two possible ways: (1) The mixed-mineral pellets were formed from a different (more heterogenous) source material from non-mixed-mineral pellets; (2) The extraneous clay minerals are eliminated in some manner during the glauconitization process, leaving a simpler mineralogy. It would also seem likely, because of their sympathetic variation, that the differences in interlayering and the presence or absence of extraneous clay minerals have a common cause.

The problem of the variations in the chemical composition and structure of glauconite pellets with geologic age is a very interesting one, especially in the light of the fact that the temporal variations are very similar to the changes that have been found for clay mineral assemblages in shales. Weaver (1958*a*) has shown abundant evidence indicating that a change in the clay mineral composition of shales takes place within the Mississippian Period. Illite is the dominant clay mineral of pre-Upper Mississippian sediments. Post-Lower Mississippian clay mineral assemblages tend to be more complex; illite is less abundant and kaolinite and expandable clays (including mixed-layer illite/montmorillonite) are more abundant.

The relation between the clay mineralogy of glauconite pellets and geologic age is as follows. The clay mineral assemblages of glauconite pellets in the Lower Paleozoic are almost always monomineralic interlayered illite-montmorillonite structure averaging less than 10 per cent expandable layers. The mineralogy of Upper Paleozoic and younger glauconite pellets is more complex in that the pellets frequently contain extraneous clay minerals and significantly more expandable material (20-25 per cent). A summary of the comparison of clay mineral suites and glauconite pellet mineralogy of different geologic ages is shown in Table VI.

Weaver (1958*b*) has shown quite convincingly that the clay mineral composition of Recent sediments strongly reflects the source material. He has further argued that this relationship can be applied to all sedi-

ments since the beginning of the Paleozoic. In other words, he has concluded that clay minerals have a detrital origin and owe little of their character to diagenetic changes. The chemical changes that Weaver agrees can take place involve only the interlayer cations and not the ions present in the basic lattice—those in octahedral and tetrahedral coordination.

Weaver (1958*b*) has also concluded that source material determines the mineralogical character of glauconite pellets. It cannot be denied that the mineralogical character of glauconite pellets reflects, in part, the source material. For example, it seems quite certain that the tetra-

TABLE VI. COMPARISON OF THE MINERALOGY OF GLAUCONITE PELLETS AND THE CLAY MINERAL ASSEMBLAGES OF SHALES OF DIFFERENT GEOLOGIC AGES

Geologic Age	Abundance of Expandable Material		Complexity of Clay Mineral Assemblage	
	Clay Mineral Suites	Glauconite Pellets	Clay Mineral Suites	Glauconite Pellets
Pre-Upper Mississippian	illite the dominant clay; little expandable material	Ave. <10% expandable layers in interlayered illite/montmorillonite	Generally simple	Frequency of occurrence of mixed-mineral pellets 0.07
Post-Lower Mississippian	illite less abundant; expandable clays more abundant	Ave. 20-25% expandable layers in inter-layered illite/montmorillonite	More complex, containing more kaolinite and expandable clays	Frequency of occurrence of mixed-mineral pellets 0.35, kaolinite and chlorite the extraneous clays

hedral charge and composition of the interlayered illite-montmorillonite clay in glauconite pellets—that material of which most pellets are exclusively composed—is inherited from the source. However, striking changes do take place in the basic lattice involving ions in the octahedral layer. The present writer believes that the evidence given by Burst (1958*a*, 1958*b*) and in this paper shows that the nature of the interlayered illite-montmorillonite in glauconite pellets is determined overwhelmingly by diagenetic changes and the resulting mineralogy reflects little of the original character of the source material. The conclusions concerning the reason for the presence or absence of extraneous clay minerals cannot be stated so strongly. However, since most glauconite pellets (regardless of geologic age) are monomineralic it appears quite likely that the glauconitization process tends to eliminate these clays. Monomineralic pellets frequently occur in matrix of heterogeneous clay minerals. As Burst (1958*a*) has pointed out, “to prescribe . . . a ‘detrital’ background for the argillaceous material in fecal pellets would be to prescribe an organism which is capable of selecting only single-layer, monoclinic, dioctahedral crystal fragments from among the innumerable diet possi-

bilities on the ocean floor." Additional evidence that points to the probability that extraneous clay minerals are eliminated during glauconitization is that extraneous clays occur only in pellets in which the interlayered illite/montmorillonite contains  $\geq 15$  per cent expandable layers—those pellets which have undergone the least glauconitization. Of course, it is possible that both processes have been operative; i.e., younger sediments have more heterogeneous sources and thus the glauconitization process has not been able to eliminate extraneous clay minerals from pellets as efficiently as in the Lower Paleozoic.

#### CONCLUSIONS

To summarize, it seems that glauconitization—which is a diagenetic process—determines the bulk of the chemical and structural properties of the clay minerals in glauconite pellets. Glauconitization involves large chemical changes in the basic lattice and interlayer cations of the predominant illite/montmorillonite clay that occurs in glauconite pellets and appears to eliminate extraneous clay minerals. The mineralogy of glauconite pellets is changed radically from the mineralogy of the source material. Therefore, since the clay mineralogy of glauconite pellets shows changes with geologic time that are very similar to those changes exhibited by the clay mineral suites of shales, it is tempting to suggest that Weaver has not given enough credit to the effect of diagenesis in the formation of clay mineral assemblages.

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#### REFERENCES

- BROWN, G., AND MACEWAN, D. M. C. (1951) X-ray diffraction by structures with random interstratification: in Brindley, G. W., *X-ray identification and crystal structure of clay minerals*, Chap. XI, 266–284, *Mineral Soc. Great Britain Mono.*
- BURST, J. F. (1958a) "Glauconite" pellets: their mineral nature and applications to stratigraphic interpretations: *A.A.P.G. Bull.*, **42**, 310–327.
- (1958b) Mineral heterogeneity in "glauconite" pellets: *Am. Mineral.*, **43**, 481–49.
- CLOUD, P. E. (1955) Physical limits of glauconite formation: *A.A.P.G. Bull.*, **39**, 484–492.
- CONWAY, E. J. (1942) Mean geochemical data in relation to oceanic evolution: *Proc. Royal Irish Acad.*, **48**, 119–212.

- GALLIHER, E. W. (1935) Glauconite genesis: *Bull. Geol. Soc. Amer.*, **46**, 1351-1366.
- (1939) Biotite-glauconite transformation and associated minerals: *Recent Marine Sediments*, A.A.P.G., 513-515.
- HENDRICKS, S. B., AND ROSS, C. (1941) Chemical composition and genesis of glauconite and celadonite, *Am. Mineral.*, **26**, 683-708.
- HERZOG, L. F., PINSON, W. H., AND CORMIER, R. F. (1958) Sediment age determination by Rb/Sr analysis of glauconite: *A.A.P.G. Bull.* **42**, 717-733.
- HOEBEKE, F., AND DEKEYSER, W. (1955) La glauconite: *Comptes Rendus de Recherches, IRSIA*, **14**, 102-121.
- HOWER, J., (1959) Matrix corrections in the x-ray spectrographic trace element analysis of rocks and minerals: *Am. Mineral.*, **44**, 19-32.
- HURLEY, P. M., FAIRBAIRN, H. W., AND PINSON, W. H. (1959) Variations in isotopic abundances of strontium, calcium, and argon and related topics: *Seventh Annual Prog. Rept., USAEC Contract AT(30-1)*—1381, 11-22.
- JOHNS, W. D., AND GRIM, R. E. (1958) Clay mineral composition of recent sediments from the Mississippi River Delta: *Jour. Sed. Petrol.*, **28**, 186-199.
- KINTER, E. B., AND DIAMOND, S. (1956) A new method for preparation and treatment of oriented-aggregate specimens of soil clays for x-ray diffraction analysis: *Soil Science*, **81**, 111-120.
- REYNOLDS, R. C. (1959) Geochemical method for determining paleosalinity: *Eighth Nat. Conf. Clays and Clay Min.*, abstract.
- SMULIKOWSKI, I. (1954) The problem of glauconite: *Polska Akad. Nauk Kom. Geol. Arch.-Mineral*, **18**, 21-120.
- TAKAHASKI, J., AND YAGI, T. (1929) Peculiar mud grains and their relation to the origin of glauconite: *Econ. geol.*, **24**, 838-852.
- (1939) Synopsis of glauconitization: *Recent Marine Sediments*, A.A.P.G., 503-512.
- WARSHAW, C. M. (1957) The mineralogy of glauconite: unpublished Ph.D. thesis, Penn. State Univ.
- WEAVER, C. E. (1956) The distribution and identification of mixed-layer clays in sedimentary rocks: *Am. Mineral.*, **41**, 202-221.
- (1958a) The clay petrology of sediments: *Proc. Sixth Nat. Conf. Clays and Clay Min.*, Pergamon Press, 154-187.
- (1958b) Geologic interpretation of argillaceous sediments: *A.A.P.G. Bull.*, **42**, 254-309.
- (1958c) The effects and geologic significance of potassium "fixation" by expandable clay minerals derived from muscovite, biotite, chlorite, and volcanic material: *Amer. Mineral.*, **43**, 839-861.

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