MICROSTRUCTURE, MINERALOGY AND CHEMISTRY OF CAMBRIAN GLAUCONITE PELLETS AND GLAUCONITE, CENTRAL U.S.A.

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Abstraet~Glauconite pellets in the Cambrian of the central U.S.A. frequently contain two textural forms of glauconite--aggregate and oriented--which differ in both mineralogy and chemistry. The aggregate glauconite composes the bulk of most pellets and consists of crystals in a nearly random arrangement. The oriented glauconite occurs primarily as rims on the periphery of pellets. It has a honeycomb-like structure—the crystals are oriented with their c-axes tangent to the aggregate-textured cores. Scanning electron photomicrographs show that the aggregate and oriented textures grade one into the other.

The aggregate glauconite has a 1 M structure and less than 5% expandable layers, whereas the oriented form has a 1 Md structure and $\sim 10\%$ expandable layers. The aggregate glauconite contains 5-8% more total iron oxides and $2-3\frac{9}{2}$ less Al_2O_3 than the oriented glauconite. The b-cell dimension of individual samples increases nearly linearly with increasing octahedral $Fe^{3+} + F^{2+} + Mg$ content. Chemical and crystallographic variations among various samples are, for the most part, related to the ratio of aggregate to oriented glauconite.

The transition between the texture of the aggregate and oriented glauconite suggests that some glauconite pellets may form by concretionary growth. It is proposed that Cambrian glauconite pellets grew through the repetitive development of a smectite-like clay at the margin of pellets. The smectite was later altered, both chemically and texturally, first to the oriented and then to the aggregate-textured glauconite.

INTRODUCTION

ALTHOUGH glauconite pellets* in sedimentary rocks have been studied for more than 150 yr, it was not until systematic X-ray powder diffraction studies were made in the late 1950s and early 1960s that their mineralogical nature was clearly understood. Warshaw (1957), Burst (1958), and Hower (1961) showed that in many cases individual glauconite pellets are monomineralic---they often consist of an iron-rich illite smectite mixed-layer material. The percentage of illite layers in samples of various ages and in individual pellets from the same sample (Ehlman *et al.,* 1963), however, may range from more than 95% to only a few percent. Glauconite containing 95% or more illite layers is usually mineral glauconite. Mineral glauconite as a rule is much more common in Paleozoic than in younger sediments.

Although much data are available on the mineralogical nature of glauconite pellets and the chemistry of the glauconite which composes them, the origin of the pellets themselves is much less well understood. The major unresolved problems are the manner of their growth and the origin of the parent material.

The present study deals with the microstructure, mineralogy, and chemistry of glauconite pellets which occur prolifically in some of the Cambrian sandstones and dolostones of the Upper Mississippi Valley. The purposes of this investigation were to define the regional and stratigraphic mineralogical and chemical nature of this glauconite and to evaluate whether the microstructure of the glauconite pellets might reveal something of the nature of the parent material and of the growth mechanism of the pellets. The mineralogy of more than 200 samples from various geographic locations in Wisconsin, Minnesota, and Illinois were examined by X-ray powder diffraction methods, and the texture of many pellets was studied with the scanning electron microscope and thin sections. Seven samples were selected for detailed chemical analysis.

PELLET EXTERNAL MORPHOLOGY

The glauconite pellets present in the Cambrian sandstones and dolostones of the Upper Mississippi Valley show three types of external morphologies: (1) irregular (lobate); (2) smooth, rounded; and (3) vermicular. The irregular pellets are very abundant, whereas vermicular shapes are extremely rare. The smooth, rounded morphology is characteristic of pellets with rims or corona (Fig. la), and pellets of this nature are abundant. Both the irregular and smooth, rounded pellets are characterized by numerous microcracks believed to be caused by dessication.

^{*} In this paper the term "glauconite" is used in a mineralogical sense to indicate an iron-rich illite-smectite of all proportions of interlayering, and the term "glauconite pellets" is used to refer to the morphological occurrences of glauconite. The term "mineral glauconite" is used to indicate glauconite containing less than 5% expandable layers and a l M structure.

PELLET MICROSTRUCTURE

Based on microstructural characteristics observable in thin sections and in SEM photomicrographs, the glauconite composing the pellets studied can be segregated into two textural types--aggregate and oriented. The term oriented, as used herein, is synonymous with the textural forms previously called oriented microcrystalline and fibroradiating (Carozzi, 1960; Wermund, 1961; Triplehorn, 1966; and Zumpe, 1971).

Aggregate texture

SEM photomicrographs show the aggregate texture consists of crystals in a crude edge to face arrangement. Many crystals are bent and curled (Fig. lb) forming numerous micropores that are not interconnected. Some variation in microporosity exists among pellets from different locations and even in the same sample. This variation in microporosity may be a partial cause for the previously observed differences in specific gravity among similar glauconite pellets (Shutov *et al.,* 1973).

Although this paper is concerned with glauconite. pellets of Cambrian age, it should be pointed out that the aggregate texture is present in other glauconite pellets examined ranging in age from Mississippian to Recent. An aggregate-like texture was also shown by Hein, Allwardt and Griggs (1974) in two glauconite pellets from Monterey Bay, California.

Oriented texture

The oriented glauconite occurs mainly as rims partially or completely surrounding aggregate glauconite cores, but it also frequently occurs in patches, as arcuate zones, and lining cracks within the aggregate texture (Fig. 2a). In polarized light, the rims exhibit high birefringence and wavy extinction (Figs. 2a and b). The tendency toward unit extinction has been considered by others to be indicative of parallel crystal orientation. Zoning within the rims is evident. In plane light (Fig. 2c), the zones grade from a dark to a light green color toward the margin of the rims. In polarized light (Fig. 2b), the birefringence increases toward the margin. These variations in color and birefringence suggest that the rims vary slightly in both composition and texture. Chemical data presented later show that iron content is lower in the rims, and SEM photomicrographs confirm that the aggregate and oriented textures are gradational.

In SEM photomicrographs it can be readily observed that the glauconite crystals composing the rims are indeed oriented. Their c -axes are tangent to the pellet surface and to the underlying core characterized by the aggregate texture (Fig. 3a). The rims are layered and tend to separate along layer boundaries (Fig. 3b).

Even though the glauconite crystals composing the rims are oriented, all crystals do not have a common orientation. On the surface of the rims, the crystals are in a face to edge arrangement around tubular pores, giving the appearance of a honeycomb (Figs. 3b and 4a). The honeycomb-like structure is interrupted by many dessication cracks (Fig. 3b). In spite of the fact that the boundary between the aggregate and oriented textures appears to be sharp in thin sections (Fig. 2), the SEM photomicrographs show this boundary is consistently gradational (Fig. 4b).

These rims are similar in structure to those described by Zumpe (1971) on Cenomanian age pellets from the Isle of Wight, England, but internally they lack the subjacent cryptocrystalline and c-radial layers he observed. Perhaps the lack of a cryptocrystalline layer is due to a greater age and higher degree of mineralogic maturity, but a reason for the absence of crystals oriented with their c-axes radial is not apparent.

MINERALOGY AND CHEMISTRY

Samples

As previously indicated, the mineralogical character of more than 200 samples from Wisconsin, Minnesota and Illinois was examined by X-ray powder diffraction methods. In addition, a thin section was prepared for each whole rock sample. The thin sections were used to study over-all texture and structure and to estimate the percentage of aggregate vs oriented glauconite present. Bulk samples of the glauconite pellets were obtained by magnetic separation.

Glauconite characteristic of the oriented texture (rims) was obtained for detailed X-ray analysis from several samples in which most pellets contained thick rims (Fig. la). To separate the oriented glauconite, the pellets were first washed in distilled water until all fines were removed. A 5 g split was then placed in distilled water and gently rubbed with the thumb in a porcelain mortar for 3 min, after which the disaggregated glauconite was decanted. The same routine was then repeated on separate 5 g splits until sufficient material was obtained,

Six bulk samples were selected for detailed wet chemical analysis based on the estimated amount of oriented glauconite present $(0-25)$ %). Each of these samples was completely disaggregated by rubbing the pellets with the thumb as described above, and 3-4 g of each was submitted for analysis. One 4 g sample, estimated to contain at least 80% oriented glauconite, also was submitted for chemical analysis. Wet chemical analyses were done by the Mineral Constitution Laboratory, The Pennsylvania State University, under the direction of Mr. Norman Suhr.

Mineralogy

The mineralogy of greenish pellets called glauconite has been studied in detail by Smulikowski (1954), Burst (1958), Hower (1961), Benton and Kastner (1965), and others. An excellent summary of work on glauconite previous to 1972 has been published by McRae. Another comprehensive paper on the mineralogy of glauconite was recently published by Thompson and Hower (1975), so that no detailed review of this literature is included herein.

The mineralogy of selected samples of the Cambrian glauconite described herein has been studied by others, and in each instance it has been classified as mature ("true"), mineral glauconite. Burst (1958) proposed that the glauconite in the Cambrian Franconia and Bonne Terre Formations be adopted as a neotype for mineral glauconite. This study confirms that on the whole the glauconite throughout the Cambrian of the Upper Mississippi Valley clearly fits the currently accepted definition of mineral glauconite; that is, it has a 1 M structure with less than 5% expandable layers. There are, however, significant structural and chemical differences between the glauconite composing aggregate and oriented textural forms.

Figure 5 shows powder patterns of two samples of predominantly aggregate glauconite and one sample of predominantly oriented glauconite. Sample 7 contains nearly 100% aggregate glauconite, whereas sample 2 contains approximately 75% aggregate and 25% oriented glauconite. Sample 1 represents the oriented glauconite which was removed from pellets constituting sample 2 and chemically analyzed. It is estimated to consist of at least 80% oriented glauconite.

The sharp 112 and $11\overline{2}$ reflections from both samples composed of predominantly aggregate glauconite indicate that it has an ordered 1 M structure. In the case of the oriented glauconite, the 112 and $11\overline{2}$ reflections are considerably broadened and several other reflections are less well defined. These diffraction characteristics indicate a disordered structure (1 Md).

Fig. 5. X-ray powder diffraction patterns of glauconites with aggregate (a and b) and oriented (c) textures.

The structural difference between the aggregate and oriented glauconites is also evident in diffraction patterns from oriented aggregates (Fig. 6). The oriented glauconite (sample 1) is estimated to contain 10% expandable layers compared to less than 5% in the aggregate glauconite (sample 7). This is shown by a subtle broadening of the 001 reflections from the oriented glauconite after ethylene glycol treatment compared to the width of the same reflections from the aggregate glauconite. SEM photomicrographs show that particle size in both samples is similar, thus is not a factor in the broadening of the 00l reflections.

The b-cell dimensions of mineral glauconites are intermediate between those of dioctahedral muscovite and trioctahedral biotite, but glauconite is considered to be dioctahedral. In the case of the Cambrian mineral glauconite, the b-cell dimension, as determined from the 060 reflection, varied from 9.054 to 9.132 Å. Variations in the b -cell dimensions undoubtedly reflect some chemical differences but are mostly

Fig. 6. X-ray diffraction patterns of oriented aggregates of glauconites with aggregate (a and b) and oriented (c) textures after ethylene glycol treatment.

due to the ratio of aggregate to oriented glauconite present.

Chemical composition

Table 1 shows the composition and structural formula of the six samples (Nos. 2-7) that were selected on the basis of the relative percentage of aggregate and oriented glauconite they contained and the sample of predominantly oriented glauconite (No. 1), Note that sample 5 is from the Deadwood Formation, a Cambrian stratigraphic unit in the Black Hills, South Dakota, which is roughly equivalent in age to the Cambrian of the Upper Mississippi Valley. The chemical formulas are based on an idealized half-cell containing 12 oxygens and 22 cationic valences.

The chemical compositions are in good agreement with the mineralogy and structure. The lowest K_2O (7.34%) and highest absorbed H₂O contents occur in the oriented glauconite (sample 1), which supports the previous statement that it contains approximately 10% expandable layers. This sample contains the highest A1 and lowest total Fe. Conversely, samples which consist largely of aggregate glauconite (Nos. 5-7) contain the highest total Fe, the lowest AI and approximately 8% K₂O. The sum of the octahedral cations per three octahedral sites is within 0.05 of the ideal value of 2 in all cases, which attests to the dioctahedral character of this glauconite. The net lattice charge of these glauconites is similar to that reported by Benton and Kastner (1965). The net negative charge not balanced by interlayer cations may be balanced by hydronium ions.

Relation of the b-cell parameter to chemical composition

Figure 7 shows a scatter diagram of the relation of weight percent $Fe₂O₃$, FeO, $Al₂O₃$ and total iron oxides +MgO to the 2θ value of the 060 line for each sample chemically analyzed (Table 1). The b-cell dimension clearly increases with increasing content of the larger ions; namely, Fe^{+3} , Fe^{+2} and Mg. Also, the K_2O increases with increasing total Fe plus Mg and with decreasing net negative charge. There is no obvious relation between the amount of A1 substitution in tetrahedral sites and the b parameter.

Electron microprobe analysis confirms that the aggregate and oriented forms of glauconite are chemically different. The microprobe data indicate that the oriented glauconite contains $5-8 \text{ wt}_{\alpha}^{\circ}$ less iron oxides and about 2-3 wt $\%$ more Al₂O₃ than the aggregate glauconite. The fact that the oriented glauconite has the smallest b parameter, while samples containing mostly aggregate glauconite have the largest b parameters suggests that the variations in the b parameter from sample to sample may be largely related to the relative amounts of the two chemically different forms of glauconite present in each sample rather than to octahedral ionic content alone. Mössbauer studies (in press) of iron in these glauconite samples show that an additional factor which might cause the

Table 1. Chemical composition and formulas of glauconites from the Cambrian of the central U.S.A. Sample 1 is representative of the glauconite with oriented texture. Samples 2–6 range from 25 to $\langle 5\% \rangle$ oriented glauconite, whereas sample 7 is almost entirely aggregate glauconite

	Sample 1 $R - 90 - 45 - 20$	Sample 2 $C - 90 - 45 - 20$	Sample 3 $4 - 91 - 20 - 27$	Sample 4 $4 - 91 - 3 - 10$	Sample 5 Deadwood	Sample 6 Vermillion Franconia	Sample 7 Vermillion Eau Claire
Si0 ₂	47.46	48.99	49.68	48.53	47.76	47.29	46.83
$A1_20_3$	10.89	9.03	8.67	9.33	8.78	7.72	7.85
Ti0 ₂	0.39	0.11	0.13	0.14	0.13	0.18	0.14
Fe ₂ O ₃	15.34	17.13	18.31	18.86	20.31	20.82	21.30
Fe0	1.55	1.99	2.55	2.43	2.43	3.98	4.23
Mg0	3.77	4.02	3.58	2.98	2.82	2.70	2.53
Mn0	0.04	0.03	0.04	0.03	0.03	0.03	0.03
CaO	1.90	1.40	0.51	0.42	0.37	0.40	0.54
Na ₂ 0	0.24	0.12	0.02	0.02	0.02	0.04	0.03
K ₂ 0	7.34	7.57	7.71	8.04	7.96	8.02	7.94
P_2O_5	0.96	0.66	0.05	0.10	0.04	0.06	0.15
C ₁	۰	\blacksquare	$\qquad \qquad \blacksquare$	\blacksquare	$-.01$		
H_20^{+*}	5.50	5.38	5.40	5.32	5.20	5.56	5.40
$H20-$	4.36	3.56	3.10	3.31	3.96	3.13	2.61
C.	۰		0.27	0.21	0.14	0.14	0.14
Total	99.74	99.99	100.02	99.72	99.95	100.09	99.72

*Water determined indirectly by loss on ignition at 1000^0 C.

Structural Formula of Glauconite Specimens

b-cell dimensions to be larger than that expected for a dioctahedral mica is that the octoahedral cations are disordered.

POSSIBLE ORIGIN OF ORIENTED AND AGGREGATE TEXTURES

The occurrence of oriented glauconite as rims (corona) **as well as within glauconite pellets ranging in age from Cambrian to at least Tertiary age has been** reported by many workers. This oriented glauconite may have a previously unrecognized importance in the genesis of glauconite and in the origin of many types of glauconite pellets. Of the many mechanisms proposed for the genesis of the various mineralogical forms of glauconite, the most widely accepted is the "layer lattice" theory proposed by Burst (1958) and further developed by Hower (1961). They describe a glauconitization process which involves the absorption of potassium and iron by any degraded layer

Fig. 7. Relationship of the b-cell dimension to $Fe₂O₃$ + FeO + MgO, $Fe₂O₃$, Al₂O₃, and FeO contents. Sample 1 consists of at least 80% oriented glauconite. Samples 2-6 range from 25 to $\langle 5\frac{6}{9} \rangle$ oriented glauconite, whereas sample 7 is almost entirely aggregate glauconite.

structure material under suitable chemical and physical conditions. This process causes a reduction of expandable layers and mineral glauconite may be an end product after considerable time. In some cases, however, mineral glauconite apparently can develop quite rapidly.

Mechanisms previously suggested for the origin of the various morphologies of glauconite and glauconite pellets include: (1) the alteration of internal fillings in foram tests, (2) the conversion of fecal pellets, (3) the transformation of biotite flakes, (4) the agglomeration of clay-sized material, (5) the precipitation on or the alteration of mineral surfaces, and (6) the direct replacement of certain minerals (e.g. amphiboles). These proposed origins are based largely on empirical observations of the occurrences of glauconite.

The only detailed study to date of glauconite pellets containing oriented glauconite was made by Zumpe (1971). He proposed that the corona (rims) present on some pellets of Cretaceous age initially began as a metacolloidal, cryptocrystalline precipitate around the periphery of pre-existing pellets and that the precipitated material subsequently recrystallized. Three characteristics of the oriented glauconite associated with the Cambrian pellets studied indicate that it did not form epigenetically by the recrystallization of a colloidal material. First, the oriented texture of the

rims is gradational with the aggregate texture characteristic of the pellet cores (Fig. 4b). Second, the oriented glauconite is not confined to peripheral areas of pellets or to the lining of cracks in the aggregate texture. It also occurs as isolated patches and as arcuate zones within the aggregate texture (Fig. 2a). Third, the oriented glauconite often occurs as detached fragments that were broken from pellets during sediment reworking which shows that the oriented texture of the rims formed at a very early stage.

These characteristics, on the contrary, suggest that the oriented glauconite is primary. Both Burst and Hower argue convincingly that the initial material from which mineral glauconite may eventually form is a mixed-layer or smectite-type clay material. Studies made of several occurrences of Tertiary age glauconite pellets show that where they contain large amounts of expandable-type clay usually a significant amount of glauconite is present with an oriented texture. The presence of large amounts of oriented glauconite in Tertiary glauconite pellets was also noted by Tripplehorn (1966).

Based on the foregoing discussion, it is proposed that the oriented glauconite initially formed by direct crystal growth of a smectite-type clay containing primarily A1, Fe, and Mg in octahedral cation positions---compositionally intermediate between montmorillonite and nontronite. The primary smectite crystals grew with their pseudo-c axes roughly aligned parallel to each other. Due to an initial structural charge, the smectite immediately would have begun to fix K in interlayer sites. The absorption of K naturally would lead to the expulsion of some interlayer water which in turn would cause shrinkage and decrease in volume. This contraction is thought to initiate the development of the honeycomb structure characteristic of the oriented glauconite.

The diffusion of $Fe³⁺$ into the octahedral cation sites with time would initiate more K absorption, additional water expulsion and further shrinkage. The concomitant decrease in interlayer water, shrinkage, and thickness of the oriented glauconite would undoubtedly cause internal stress within the honeycomb structure. This internal stress is believed to cause bending, curling, and collapse of the honeycomb structure leading to the formation of the aggregate texture. It is believed that the oriented texture still preserved in the form of rims and elsewhere was not altered to the aggregate texture because of its thinness and peripheral location; thus internal stresses were greatly reduced.

In summary, it is suggested that lobate and probably other morphological forms of glauconite pellets grow by the development of smectite in successive stages (layers) which then become oriented glauconite and then aggregate glauconite—the textural modifications being caused by a combination of chemical change, shrinkage and internal stress. Pellet development would be akin to the growth of concretions with the initial growth of smectite probably being related to decaying (animal) organic material in an environment with favorable pH, Eh, and physical conditions. The chemical composition of the developed smectite and the rate of its development during successive stages of growth might be somewhat variable in different environments.

This proposed mechanism for the growth of glauconite pellets supports the concept that glauconite develops from a smectite-like layer structure material which subsequently undergoes certain chemical and physical changes. A crystallizing rather than a detrital smectite-like starting material would alleviate many of the problems inherent in forming glauconite from just any degraded layered material. For example it would explain why oriented textural forms of glauconite are seemingly abundant in pellets having large amounts of expandable clay material. The development of pellets by crystal growth would also permit a more satisfactory explanation of the common occurrence of (1) glauconite as internal fillings in forminifera shells without requiring that the shells first contain a detrital (degraded) clay, (2) the frequently observed perfect reproduction of the internal mold of these shells, and (3) the instances where a lobe of a glauconite pellet is observed to protrude through a hole in a foram shell. This explanation would not, however, preclude the previously observed alteration of iron-rich aluminosiliates to glauconite or the precipitation of glauconite on the surface of certain substrates as has previously been described.

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Fig. l. Electron micrographs showing (a) the smooth, rounded shape of a glauconite pellet containing a rim (corona) and (b) the arrangement of glauconite crystals in the aggregate-type texture.

Fig. 2. Photomicrographs showing the structure of glauconite pellets with rims and of the appearance of the aggregate and oriented textures in polarized (a and b) and plane light (c).

Fig. 3. Electron micrographs showing the texture and structure of oriented- and aggregate-textured glauconite.

Fig. 4. Electron micrographs showing (a) the honeycomb structure of a rim and (b) the gradation of oriented glauconite (rim) to aggregate glauconite (core).