THE AMERICAN MINERALOGIST, VOL. 52, JULY-AUGUST, 1967

X-RAY AND CHEMICAL STUDY OF WEATHERING GLAUCONITE[1]

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Abstract

In the outcrop of the Aquia Greensand west of Annapolis, Maryland, the weathering of glauconite does not follow the reverse of the normally accepted formation process. Chemical, mineralogical, and morphological data indicate that weathering results in the formation of goethite pseudomorphs after glauconite. The presence of a well-disseminated, white coating composed of kaolinite, and probably a mixed-layered assemblage, suggests that reprecipitation accompanies the pseudomorphic replacement.

Introduction

Burst (1958b) and Hower (1961) suggest that glauconite may form from any degraded, layer-lattice silicate provided a plentiful supply of potassium and iron is available in a favorable environment. Porrenga (1966, p. 227) has observed conditions of apparent glauconite formation which essentially conform to this suggestion. The present study reports the results of an investigation at a site where macroscopic field relations suggested that the reverse of this reaction may be occurring under natural conditions.

Site Description

When viewed at a distance, the Aquia Greensand (Eocene) (Clark and Martin, 1901, p. 58) outcrop, 1–1/4 miles west of Bay Bridge, Maryland, on Highway 50, appears to be a relatively uniform red color. From the base of the outcrop, a definite mottling of green and red is evident. On closer inspection, it appears that the staining results from weathering and that the weathering stages can be followed by the color changes.

The patches of green range from minute to several feet in diameter. Some of these patches are encased by a goethite-cemented quartz crust, Figure 4, which varies to 2 inches in thickness. Other green areas are gradational with the more common red material.

Mineralogically, the outcrop consists primarily of quartz and glauconite with very minor amounts of other heavy minerals and feldspar. As measured in thin section, less than 5 percent of the grains are feldspar. The glauconite generally occurs as foraminiferal casts or as vermicular and globular pellets. The particle-size distribution, viewed under a binocular scope, is fine to medium sand with the quartz varying from angular to well rounded (for more detailed petrology, see Drobnyk, 1965).

In addition, the samples have a "sugary" coating on many grains. This coating, which also acts as a cementing agent, is best seen in the green

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[1] Publication authorized by Director, U. S. Geological Survey.

samples where its white color has not been stained. It will be discussed in detail later.

Figure 1 is a diagrammatic sketch of the sampling sequence on a vertical exposure of the outcrop. As shown, samples A-1 through A-5 are a suite of samples taken along a gradational change from green to red material, respectively. A-6 is a green sample isolated from the red material by a goethite crust. A-7 is a red sample taken immediately outside the crust.

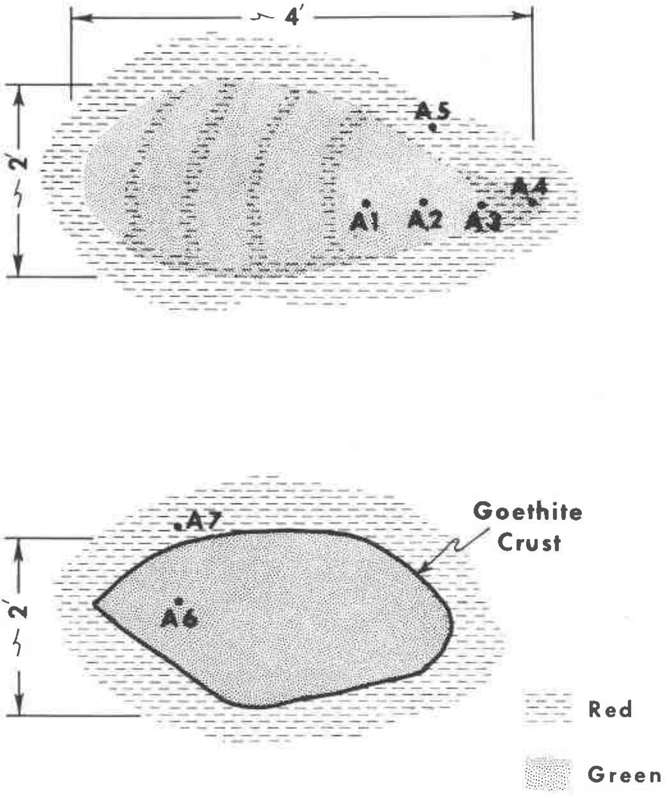

FIG. 1. Schematic sketch of outcrop relations and sampling locations.

PROCEDURE AND RESULTS

Separation of glauconite from the quartz and other minerals was accomplished by passing samples through a Franz isodynamic separator several times. The glauconite was further purified by handpicking.

The iron stain was essentially removed from a red sample by soaking the sample (A-5) in 0.1 N HCl for 16 hours, after which the sample was repeatedly washed with distilled water.

TABLE 1. CHEMICAL ANALYSES IN PERCENT

	A-1	A-2	A-3	A-4	A-5	A-6	A-7	HA-1[1]	HA-5[1]	Normal glauconite[2]
SiO_2	42.1	41.3	41.6	40.4	41.7	40.9	36.7	44.1	44.2	47 to 5
Al_2O_3	10.2	9.9	10.0	9.7	9.3	9.1	7.9	9.7	9.4	5 to 10
Fe_2O_3	28.2	29.1	29.1	29.7	31.0	30.1	37.9	27.0	27.6	5 to 22
FeO	0.33	0.31	0.24	0.24	0.16	0.24	0.16	0.32	0.32	2 to 4
MgO	2.7	2.4	2.5	2.5	2.1	2.2	1.5	2.6	2.5	3 to 4
CaO	0.04	0.12	0.00	0.07	0.28	0.28	0.22	0.04	0.07	0 to 0.8
Na_2O	0.16	0.14	0.14	0.13	0.15	0.13	0.11	0.10	0.14	0 to 0.5
K_2O	5.2	5.3	5.2	5.2	4.9	4.8	3.9	5.9	6.0	6 to 8
H_2O	10.5	10.8	10.7	11.5	9.8	11.5	10.2	9.6	9.6	7 to 9
TiO_2	0.37	0.34	0.32	0.34	0.34	0.42	0.44	0.22	0.26	
P_2O_5	0.24	0.26	0.31	0.24	0.29	0.35	0.73	0.20	0.20	
MnO	0.03	0.03	0.04	0.05	0.07	0.04	0.07	0.03	0.05	
CO_2	<.05	<.05	<.05	<.05	<.05	<.05	<.10	<.05	<.05	

[1] Acid-treated equivalents of A-1 and A-2.

[2] Most often encountered analyses, after Smoluchowski (1954).

As a check on the structural and chemical effect of the treatment, the same treatment was accorded a green sample (A-1). The acid-treated samples are designated HA-5 and HA-1.

Chemical analyses of these glauconite samples, Table 1, were performed by the Geochemistry and Petrology Branch, U. S. Geological Survey, in accordance with the methods described by Shapiro and Brannock (1962). For comparison, a normal range of values for chemical analyses of glauconites, as given by Smulikowksi (1954), is presented in the last column.

Chemical formulae, based on the above analyses, are presented in Table 2. These formulae were calculated according to the half-cell method

TABLE 2. CHEMICAL FORMULAE OF SAMPLES SHOWN (HALF-CELL METHOD)

Sample Number	Formula
A-1	$(Al_{0.17}Ti_{0.02}Fe'''_{1.63}Fe''_{0.02}Mg_{0.31})(Si_{3.25}Al_{0.75})O_{10}(OH)_2(K_{0.5}Na_{0.02})$
A-2	$(Al_{0.15}Ti_{0.02}Fe'''_{1.70}Fe''_{0.02}Mg_{0.28})(Si_{3.2}Al_{0.8})O_{10}(OH)(K_{0.5})$
A-3	$(Al_{0.14}Ti_{0.02}Fe'''_{1.70}Fe''_{0.02}Mg_{0.29})(Si_{3.2}Al_{0.8})O_{10}(OH)_2(K_{0.51}Na_{0.03})$
A-4	$(Al_{0.08}Ti_{0.02}Fe'''_{1.76}Fe''_{0.02}Mg_{0.29})(Si_{3.2}Al_{0.8})O_{10}(OH)_2(K_{0.52}Na_{0.02})$
A-5	$(Al_{0.06}Ti_{0.02}Fe'''_{1.80}Fe''_{0.01}Mg_{0.24})(Si_{3.22}Al_{0.78})O_{10}(OH)_2(K_{0.48}Na_{0.02}Ca_{0.02})$
A-6	$(Al_{0.06}Ti_{0.02}Fe'''_{1.78}Fe''_{0.02}Mg_{0.26})(Si_{3.2}Al_{0.8})O_{10}(OH)_2(K_{0.48}Na_{0.02}Ca_{0.02})$
A-7	$(Ti_{0.05}Fe'''_{2.99}Fe''_{0.01}Mg_{0.18}P_{0.05})(Si_{2.95}Al_{0.75}Fe'''_{0.30})O_{10}(OH)_2(K_{0.40}Na_{0.02}Ca_{0.02})$
HA-1	$(Al_{0.38}Ti_{0.01}Fe'''_{1.47}Fe''_{0.02}Mg_{0.28})(Si_{3.2}Al_{0.8})O_{10}(OH)_2(K_{0.51}Na_{0.01})$
HA-5	$(Al_{0.34}Ti_{0.01}Fe'''_{1.51}Fe''_{0.02}Mg_{0.27})(Si_{3.2}Al_{0.8})O_{10}(OH)_2(K_{0.55}Na_{0.02})$

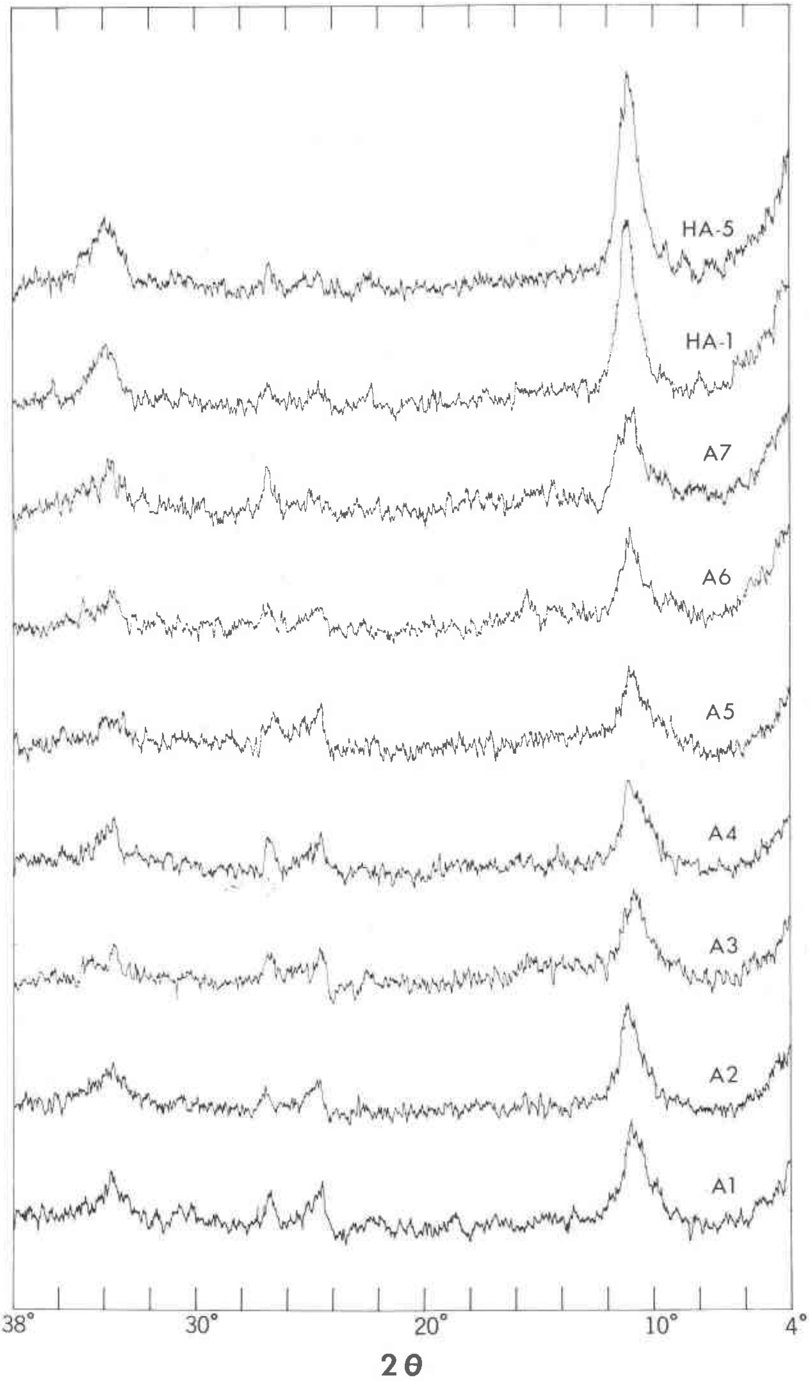

FIG. 2. X-ray diffractograms of samples indicated using FeKα, Mn filtered radiation (1° and 1/2"/min.).

of Foster (1960) assuming no impurities were present. As shown, the ferric/ferrous iron ratio increases as the sample color becomes redder. However, as shown by the similarity of this ratio in the acid-washed samples, the change is apparently due to an iron oxide coating of the grains and not to oxidation of structural ferrous iron.

Diffractograms for the glauconite samples described above are presented in Figure 2. All of these samples were prepared for X-ray diffraction analysis by hand grinding the glauconite grains. This material was suspended in distilled water and sedimented onto ceramic slides. The details of radiation and mechanical settings are presented with the diffractograms.

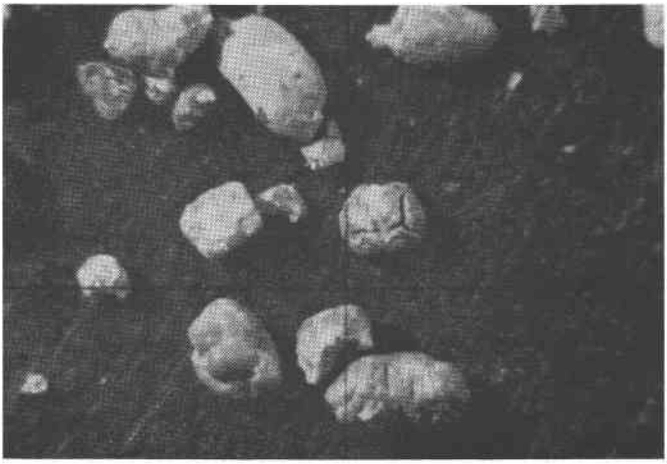

FIG. 3. Goethite pseudomorphs after glauconite. (magnification$\sim$×24).

As can be seen in Figure 2, the X-ray diffraction patterns of the various colored samples are not sufficiently distinctive to permit any correlation of structural changes with color changes.

Burst (1958*a*, p. 491), using chemical formulae and X-ray diffraction patterns, separated glauconite into two categories, ordered and disordered. Using the same criteria, the glauconites examined in this study are definitely in the disordered group. This accounts, at least in part, for the lack of resolution of the X-ray diffractograms.

In addition to the samples described above, a small group of particles retaining "typical" glauconite morphology but reddish in color (not stained) were carefully handpicked. These are pictured in Figure 3. The fragility of these grains resulted in some fragmentation as shown. The X-ray diffractogram for this sample is presented in Figure 4. Within the limits of detection (X-ray diffraction), these grains appear to be composed of pure goethite.

The sugary white material mentioned earlier is an evenly disseminated coating occurring on most of the grains. Attempts to handpick a sufficient quantity for powder diffraction were discouraging because of the difficulty of removing the thin coating from the quartz and glauconite without including some of the host. One such handpicked sample gave X-ray diffraction spacings (FeK-Mo radiation):10.1 (s), 7.2 (w), 4.49 (s), 4.30 (m), 3.33 (s, sharp) 2.57 (ms, b), 2.41 (vw, vb), 1.53 (vvw), and 1.507 Å (w, b).

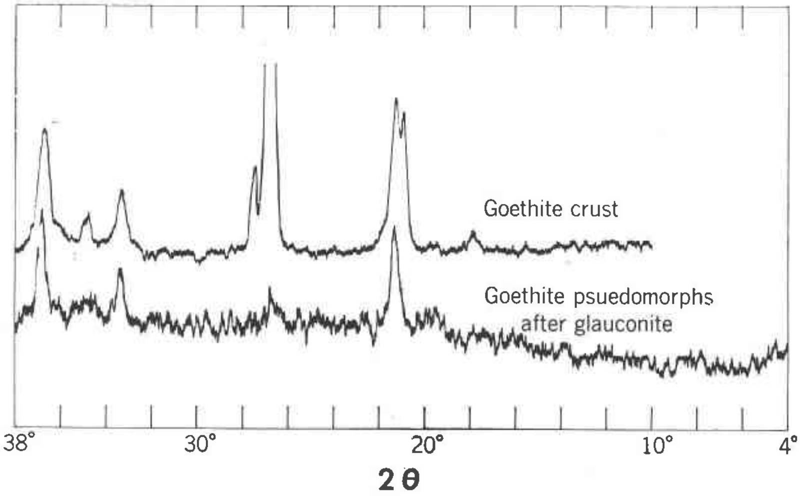

FIG. 4. X-ray diffractograms of samples indicated using Cu Kα, Ni filtered radiation (1° and 1/2"/min.).

Another attempt to identify the mineralogy of the white material consisted of collecting a large sample of the green material which appeared to be relatively rich in white coating material. Small quantities of this sample were ultrasonically disaggregated. The less than 0.5μ size fraction resulting from this procedure was sedimented onto glass slides. X-ray diffractograms of this material are presented in Figure 5.

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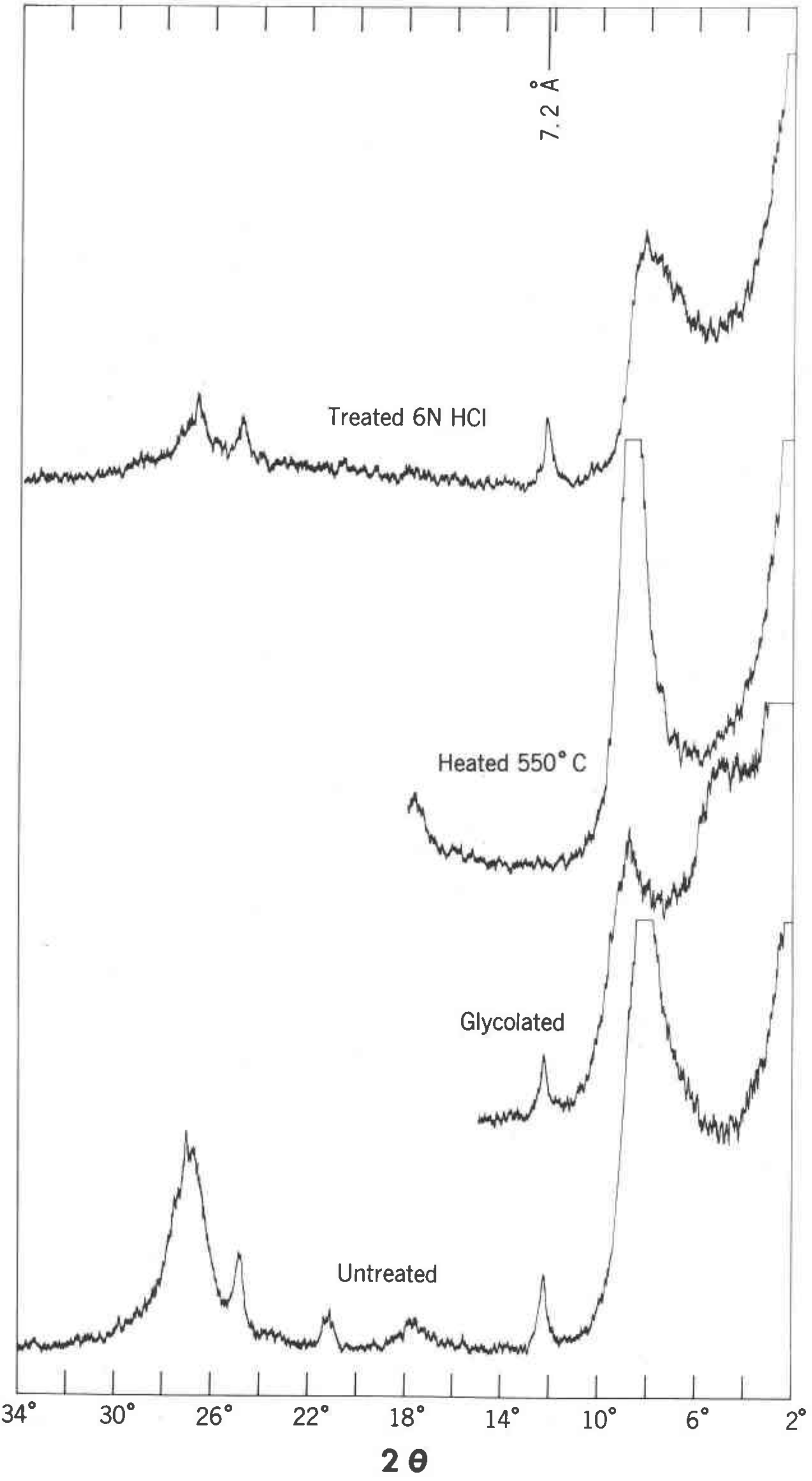
FIG. 5. X-ray diffractograms of the $<0.5\mu$ sonically disaggregated material using Cu Kα, Ni filtered radiation (1° and 1/2"/min.). (Treatment times: HCl—60 hr.; 550°C—1 hr.)


7.2 Å
Treated 6N HCl
Heated 550° C
Glycolated
Untreated
34°
30°
26°
22°
18°
14°
10°
6°
2°
2 θ

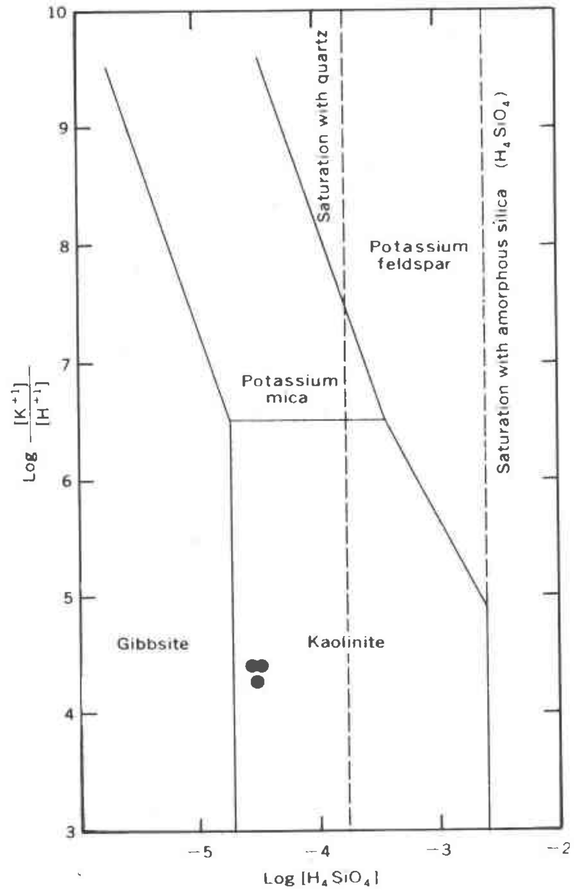


FIG. 6. Plot of Aqui greensand water compositions in the stability field of some of the phases in the system K_2O–Al_2O_3–SiO_2–H_2O at 25°C and 1 atmosphere as presented by Feth and others (1962, p. 62). The potassium activity was determined using the method given by Hem (1961).

INTERPRETATION OF RESULTS

If the formation of glauconite is reversible, *i.e.*, if the weathering of glauconite results in the release of ferrous iron and potassium leaving a degraded layer lattice silicate behind, it is conceivable that this process is signified by a color change accompanying the release and oxidation of the iron. Based on the chemical analyses, Table 1; the resultant formulae, Table 2; and the X-ray diffraction patterns, Figure 2, this reverse reaction does not occur within the limits of detection used in the area chosen for study.

The pseudomorphs of goethite after glauconite indicate that by some method the weathering of glauconite results in the formation of goethite, which is in agreement with the results reported by Bentor and Kostner (1965, p. 163). If this is a leaching process which removes everything from the glauconite except the iron oxides and hydroxides, it would be expected that the ground water would be relatively high in silica and alumina or that reprecipitation occurs. The available water analyses from wells screened in the Aquia sand do not show unusual levels for silica or alumina. Plotting these water compositions in the K_2O-Al_2O_3-SiO_2-H_2O stability diagram given by Feth and others (1964, p. 62), Figure 6, the water appears to be in equilibrium with kaolinite.

X-ray powder diffraction results of the white pellet (see above) and the less than 0.5μ material (Fig. 5) indicate that the clay minerals present are a mixed-layer material and kaolinite. The possible presence of a detectable amount of iron-rich chlorite is ruled out by the persistence of the 7.2 Å peak after 60-hour treatment with 6N HCl (Brindley, 1961, p. 85). This conclusion is further fortified by the disappearance of the 7.2 Å peak after heating to 550°C.

Assuming that the breakdown of the minute quantity of feldspar present is insufficient to account for the quantity of sugary material observed, a possible schematic reaction sequence for the glauconite is:

$$H_2O + \text{glauconite} \rightarrow \text{goethite} + \text{dissolved material} + H_2O$$

$$\xrightarrow{\text{precipitation}} \text{kaolinite} + \text{dissolved material} + H_2O$$

This schematic sequence assumes pure glauconite for starting material and does not include consideration of a possible intermediary mixed-layer phase. The less than 0.5μ fraction of the disordered glauconite, which is undoubtedly present as a contaminant in the material used for diffraction, probably accounts for the majority of the mixed layer material. However, based on the observations by Rex (1966), it is conceivable that authigenic mica is also present as a component in the mixed-layer material.

CONCLUSIONS

In the area studied, the chemical, mineralogical, and morphological data cited suggest that the end products of the weathering of glauconite are pseudomorphs of goethite and authigenic kaolinite.

The staining and goethite-quartz crust formation apparently result from the breakdown of the goethite pseudomorphs. Inherent permeability differences in the formation probably control deposition or precipitation of the goethite. In zones of lowest permeability, this process has resulted in the thick crusts observed.

ACKNOWLEDGMENTS

The comments and discussion by Ivan Barnes, Blair Jones, and Kenneth Towe are gratefully acknowledged.

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Manuscript received, November 22, 1966; accepted for publication, May 10, 1967.