THE NATURE OF ILLITE

by

H. E. GAUDETTE, J. L. EADES, and R. E. GRIM

University of Illinois, Urbana, Illinois

ABSTRACT

CHEMICAL composition, X-ray diffraction and other analytical data of a series of samples of clays that are composed essentially of illite are presented. The physical properties of these samples are given and related to variations in the composition and character of the illites.

Data indicate that these illites have less potassium than well-crystallized micas and some of them are not essentially mixed-layer structures. It is concluded, therefore, that illite is not necessarily a mixed-layer material.

INTRODUCTION

THE NAME *illite* was proposed by Grim, Bray and Bradley in 1937 for the mica-type mineral occurring in argillaceous sediments. It was specifically stated that "the term is not proposed as a specific mineral name, but as a general term for the clay mineral constituent of argillaceous sediments belonging to the mica group".

Abundant research has shown that many soils, clays and shales contain a mineral with a 10Å spacing that does not expand on treatment with glycol. Commonly, because of the complex association of the 10Å mineral with other clay minerals, its relatively low degree of order and its small particle size, the polymorphic form of the mineral may not be absolutely determined in all cases. Neither can its precise chemical composition be determined. However, chemical data indicate that this 10Å mineral has a variable but substantially lower potassium content than well-crystallized micas and that its tetrahedral and octahedral cation population is variable. Experience, it is believed, has shown that it is desirable to apply a general name *illite* to such clay minerals rather than to call them simply micas or hydro-micas, since this does not distinguish them from well-crystallized micas that may have somewhat different chemical compositions and whose polymorphic form can be definitely determined.

Some of the illites described in the literature are undoubtedly mixed-layer assemblages. Other illites give X-ray diffraction data that do not suggest any mixed layering. Consequently, the lower potassium content of illite cannot be ascribed universally to mixed-layer assemblages.

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The present paper presents analytical data for several clay-mineral assemblages ranging from illite without any mixed layering to illite–mixed-layer structure. In the case of the mixed-layer assemblages, the evidence indicates that the 10Å component has less potassium that well-crystallized micas. Such assemblages may then be best described as illite–montmorillnoite, illite–vermiculite, etc, mixed-layered structures.

EXPERIMENTAL
Sample Description

The samples of this study range from Ordovician to Pennsylvanian in age. They include Beavers Bend illite, from near Broken Bow, Oklahoma; illite from Fond du Lac County, Wisconsin, called Marblehead illite in this study; Rock Island illite, from near Geneseo, Rock Island County, Illinois; Fithian illite from Vermillion County, Illinois, which has been previously described as API reference clay mineral no. 35; and an illitic material from the Goose Lake area, Grundy County, Illinois, which is marketed at present under the trade name "Grundite".

The Beavers Bend sample is composed of a well-crystallized illite of exceptional purity, with minor amounts of chlorite as a mechanical mixture reported from some samples. It is a fine-grained dark olive-gray clay that is found in layers in the Blaylock formation of Silurian age. This illite has been described in detail by Mankin and Dodd (1963) and, owing to its exceptional purity, has been proposed for use as a reference clay mineral.

The Marblehead illite, a gray laminated clay, which occurs in pockets in a Silurian dolomite at the Western Lime and Cement Company Quarries near Marblehead, Wisconsin, is also an exceptionally pure illite containing no detectable quantities of any other clay minerals (Gaudette, 1965).

The Rock Island illite was collected from pockets in an Ordovician limestone at the Cleveland Quarries near Geneseo, Illinois. This illite is light gray, well-crystallized, and, like the Beavers Bend illite, contains a mechanical mixture of small amounts of chlorite in some samples. The description of this material is now reported for the first time.

Both Fithian illite and "Grundite" are from Pennsylvanian underclays. Fithian illite from Vermillion County, Illinois, was first described by Grim, Bray and Bradley in 1937 and was one of the bases for the proposal of the term *illite* as a general term for the clay-mineral constituent of argillaceous sediments belonging to the mica group. More recently, Molloy and Kerr (1961) have described Fithian illite as Illite no. 35 in the A.P.I. project on reference clay minerals.

The light-green, nonbedded, underclay from the Goose Lake area, Illinois, was first described by Grim and Bradley (1939). Production of this underclay at that time and up to the present has been made under the trade name "Grundite", the name by which this material will be designated in this study.

The bulk material for each of these samples was disaggregated by gentle stirring in distilled water. Fractionation of the $<2\mu$ material was accomplished by settling in distilled water, with the suspension containing the $<2\mu$ clay drawn off and consolidated by drying. This $<2\mu$ fraction was then utilized for all the analytical procedures.

Chemical Analyses

The chemical analyses of the illite samples (Table 1) show a restricted range of silica and alumina contents, with the most prominent relative variation occurring in the iron and magnesia. The potash content, which ranges from 5.90 per cent for Fithian illite to 7.98 per cent for the Marblehead sample, is of special interest and is significantly below the theoretical potash content for the ideal muscovite structure.

TABLE 1. CHEMICAL ANALYSES OF ILLITES

Oxide	Beavers Bend Illite	Marblehead Illite	Rock Island Illite	Fithian Illite	"Grundite"
SiO_2	47.00	52.87	54.09	43.95	47.08
Al_2O_3	23.30	24.90	26.30	21.12	28.05
Fe_2O_3	7.74	0.78	1.50	7.90	8.16
FeO	3.20	1.19	1.49	3.42	nd
MgO	1.70	3.60	2.00	1.50	2.33
CaO	0.17	0.69	0.49	0.84	nil
Na_2O	0.14	0.22	0.22	0.32	0.32
K_2O	6.69	7.98	6.87	5.90	6.48
H_2O+	8.24	6.73	6.89	8.25	nd
H_2O-	0.64	2.56	1.32	2.08	nd
Ign Loss	6.64	6.36	5.79	12.44	7.73
TiO_2	0.66	1.02	0.68	0.62	nd
P_2O_5	—	—	—	0.70	nd
Total	97.24	99.61	99.43	98.69	100.15

Samples 1–4 : Analyst, J. Witters, Illinois State Geological Survey
Sample   5 : Analyst, C. Koger, Southern Cement Co.

Calculation of the ionic populations of the illite structures, according to the methods and procedures of Marshall (1949), has allowed assignment of the various atoms to the unit cell for each sample. Table 2 shows that the potassium content, which is assumed to be present exclusively in the interlayer position of the illite structure, varies from 1.1 to 1.4 per unit cell; again, this is well below the theoretical number of 2, which is assumed for the ideal muscovite structure. Aluminum assigned to the tetrahedral layer ranges from 0.9 to 1.6 per unit cell, a range of aluminum substitution in the tetrahedral layers of from 11.0 to 19.5 per cent. The average value of the aluminum

TABLE 2. ASSIGNMENT OF ATOMS TO UNIT CELL*

		Beavers Bend Illite	Marblehead Illite	Rock Island Illite	Fithian Illite	"Grundite"
Non-exchangeable alkalis	K+	1.2130	1.3615	1.1567	1.1411	1.1418
	Na+	0.0372	0.0554	0.0549	0.0935	0.0858
	Ca++	0.0263	0.0989	0.0686	0.1360	—
	Total	1.2765	1.5158	1.2802	1.3706	1.2276
Tetrahedral layers	Si++++	6.6833	7.0724	7.1364	6.6605	6.4359
	Al+++	1.3167	0.9276	0.8636	1.3395	1.5641
	Total	8.0000	8.0000	8.0000	8.0000	8.0000
	Al+++	2.5886	2.9974	3.2272	2.4339	2.9564
Octahedral layer	Fe+++	0.8278	0.0789	0.1487	0.9014	0.8394
	Fe++	0.3804	0.1334	0.1640	0.4330	—
	Mg++	0.3607	0.7174	0.3938	0.3391	0.4745
	Ti++++	0.0706	0.0955	0.0678	0.0707	—
	Total	4.2281	4.0266	4.0015	4.1781	4.2703

* Calculated according to the procedure of Marshall, 1949.

substitution in the tetrahedral layers for all illites of this study is 15.0 per cent, which correlates closely to the postulated 16.7 per cent adopted by Grim (1953). The constituents of the octahedral layer of the illite structures vary, with aluminum present as a major constituent in each of the illite samples. The amount of ferrous and ferric iron and magnesium varies from sample to sample and substitution of these atoms in the octahedral layer causes an increase from the ideal dioctahedral condition; the more highly aluminous illites thus approach the true dioctahedral character. As the amount of iron and magnesium in the octahedral portion of the structure increases, the illite correspondingly tends toward a mixed or transitional dioctahedral–trioctahedral character.

Calculation of the ionic populations according to the procedures of Brown and Norrish (1952) based upon the assumption that H_3O^+ ions are included as interlayer occupants resulted in essentially the same atomic distribution within the silicate portion of the illite structure (Table 3). The presence of the hydronium ions in the interlayer positions, however, resulted in interlayer occupants totalling significantly greater than 2.0 and in octahedral occupancy generally less than dioctahedral as derived from the chemical analyses available for the materials of this study. Therefore, the structural formulae derived from the assignment of various atoms to their respective structural positions in the unit cell, according to Marshall (1949), are more in accord with the chemical data available for the samples of this study and are chosen

TABLE 3. ASSIGNMENT OF ATOMS TO UNIT CELL*

		Beavers Bend Illite	Marblehead Illite	Rock Island Illite	Fithian Illite	"Grundite"
	K+	1.1781	1.3410	1.1387	1.1062	1.1058
	Na+	0.0361	0.0554	0.0547	0.0911	0.0836
Interlayer positions	Ca++	0.0246	0.0974	0.0679	0.1325	——
		1.2388	1.4938	1.2613	1.3298	1.1894
	H_3O+	1.2041	0.6657	0.6598	1.3620	0.9672
	Total	2.4429	2.1595	1.9211	2.6918	2.1566
		4 (OH)	4 (OH)	4(OH)	4 (OH)	4 (OH)
		20 O	20 O	20 O	20 O	20 O
Tetrahedral layers	Si	6.5009	6.9645	7.0299	6.4541	6.2964
	Al	1.4991	1.0355	0.9701	1.5459	1.7036
	Total	8.0000	8.0000	8.0000	8.0000	8.0000
	Al	2.2989	2.8307	3.0592	2.1097	2.7180
Octahedral layer	Fe+++	0.8051	0.0776	0.1468	0.8727	0.8213
	Fe++	0.3705	0.1314	0.1617	0.4198	——
	Mg	0.3500	0.7069	0.3874	0.3287	0.4645
	Ti	0.0690	0.1013	0.0664	0.0687	——
	Total	3.8935	3.8479	3.8215	3.7996	4.0038
Al substitution in tetrahedral layers		18.7%	12.9%	12.1%	19.3%	21.3%

* According to Brown and Norrish, 1952.

TABLE 4. STRUCTURAL FORMULAE*

BEAVERS BEND ILLITE

$(Al_{1.29}Fe^{+++}_{0.41}Fe^{++}_{0.19}Mg_{0.18}Ti_{0.04})$ $(Si_{3.34}Al_{0.66})O_{10}(OH)_2(K^+_{0.61}Na^+_{0.02}Ca^{++}_{0.01})$

MARBLEHEAD ILLITE

$(Al_{1.50}Fe^{+++}_{0.04}Fe^{++}_{0.07}Mg_{0.36}Ti_{0.05})$ $(Si_{3.54}Al_{0.46})O_{10}(OH)_2(K^+_{0.68}Na^+_{0.03}Ca^{++}_{0.05})$

ROCK ISLAND ILLITE

$(Al_{1.61}Fe^{+++}_{0.07}Fe^{++}_{0.08}Mg_{0.20}Ti_{0.03})$ $(Si_{3.57}Al_{0.43})O_{10}(OH)_2(K^+_{0.58}Na^+_{0.03}Ca^{++}_{0.03})$

FITHIAN ILLITE

$(Al_{1.22}Fe^{+++}_{0.45}Fe^{++}_{0.22}Mg_{0.15}Ti_{0.04})$ $(Si_{3.33}Al_{0.67})O_{10}(OH)_2(K^+_{0.57}Na^+_{0.05}Ca^{++}_{0.07})$

"GRUNDITE"

$(Al_{1.5}Fe^{+++}_{0.40}Mg_{0.20})$ $(Si_{3.20}Al_{0.80})O_{10}(OH)_2(K^+_{0.57}Na^+_{0.04})$

* From the calculations of Table 2, according to Marshall, 1949.

for Table 4 to summarize the variations in the character of the illite samples in the octahedral and tetrahedral positions. These formulae are noted for one-half unit cell in each case and are an illustration of the variation that may occur in representative clay samples of 10Å material.

X-RAY DIFFRACTION ANALYSIS

In all cases, X-ray diffraction analysis was made on the $<2\mu$ sized fraction of the samples. Oriented aggregates were prepared on glass slides by air drying and on porous plates by the centrifuging process of Kinter and Diamond (1956). Powder diffraction patterns of the $<2\mu$, <200 mesh material were run for determination of polymorphic type. Use of extremely well-oriented aggregates resulted in diffraction from twelve basal orders for the illite samples. Integrated intensity counts for each of the basal reflections were made and one-dimensional Fourier summations calculated to provide one-dimensional structural plots of the illite structures.

The X-ray diffraction powder patterns indicate that the Beavers Bend, Marblehead, and Rock Island illites are of the $2M_1$ polymorphic type. Fithian illite gave diffuse prism reflections in the 18° to 40° 2θ range. On the basis of these diffuse reflections, the Fithian illite is apparently a mixture of types 2M, and 1Md as has been previously described by Yoder and Eugster (1955). The X-ray powder patterns of Grundite also showed diffuse prism reflections in the 18° to 40° 2θ range and, as a result, the determination of the Grundite polymorph could not be made.

One oriented aggregate of the $< 2\mu$ material for each of these samples was analyzed in the natural state, then subjected to an ethylene glycol atmosphere for 72 hr, and X-rayed immediately upon removal. A second oriented aggregate was heated at 550°C for 1 hr and then subjected to X-ray analysis. Responses to these analytical techniques accentuate the modulation of diffraction effects consequent to the presence of any mixed-layer material in the illite samples. The diffraction traces of the $<2\mu$-oriented aggregates are shown in Fig. 1 for comparison of each of the illite samples before treatment of any kind. The samples are arranged from top to bottom in order of apparent decreasing conformity to monomineralic character as disclosed by the X-ray diffraction traces. The apparent abundance of mixed-layer material increases from little or none in Beavers Bend and Marblehead illite through the obvious presence in the Grundite sample. Diffraction traces of each of the illite samples in the untreated, heat-treated, and glycol-treated states are shown in Figs. 2 through 6 for determination of the amount of mixed-layer material present in each sample.

The diffraction traces of Beavers Bend illite in Fig. 2 show that the sample is exceptionally pure and well-crystallized, and contains no mixed-layer material as disclosed by heat and glycol treatments. The basal reflections are symmetrical and intense, and the relative intensities indicate dioctahedral occupation of the octahedral layer.
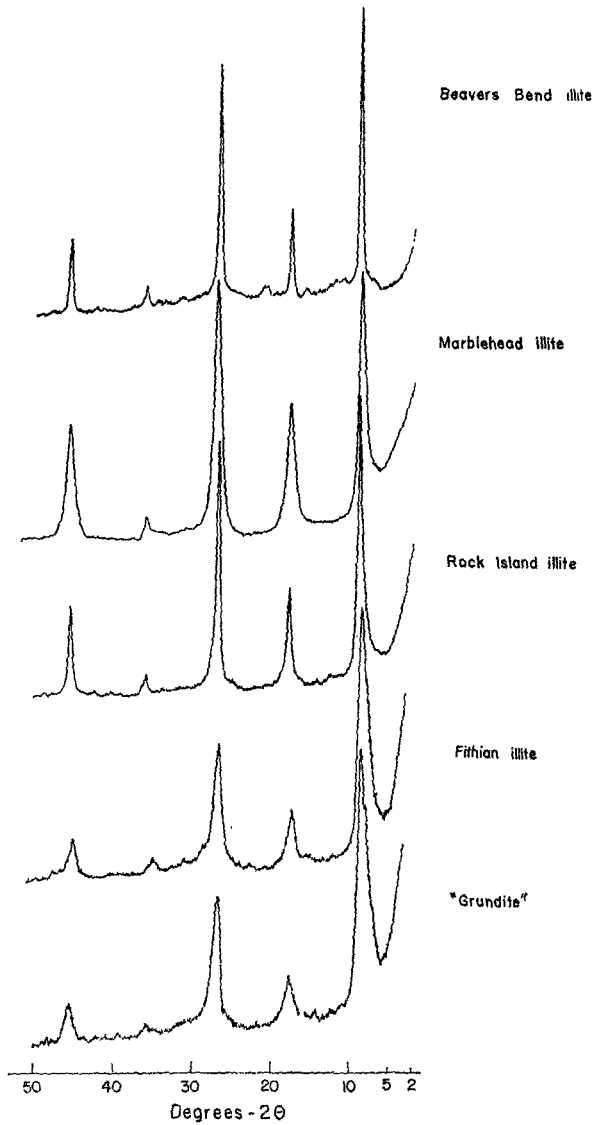
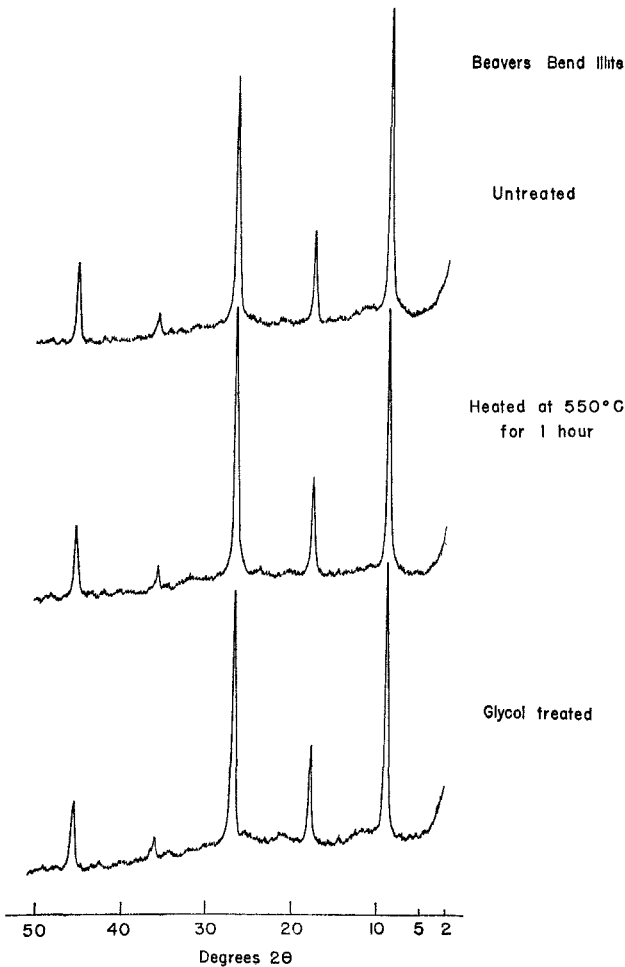FIG. 1. Diffraction traces, $< 2\mu$-oriented aggregates, natural state.

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FIG. 2. Diffraction traces, Beavers Bend-oriented aggregates.

In the Marblehead sample (Fig. 3), the purity of the material can be ascertained from the diffraction trace of the oriented bulk sample. No contaminant clay minerals or other minerals appear to be present. The $<2\,\mu$ oriented slide shows relatively sharp basal reflections that are sharpened slightly upon heat treatment. The glycol-treated slide produces a slight asymmetry in the first basal reflection on the higher "d" value side. These diffraction effects may then be attributed to the presence of a small amount of expandable material present in the Marblehead sample, probably as little as 5 per cent. The presence of about 8 per cent potash in this sample as
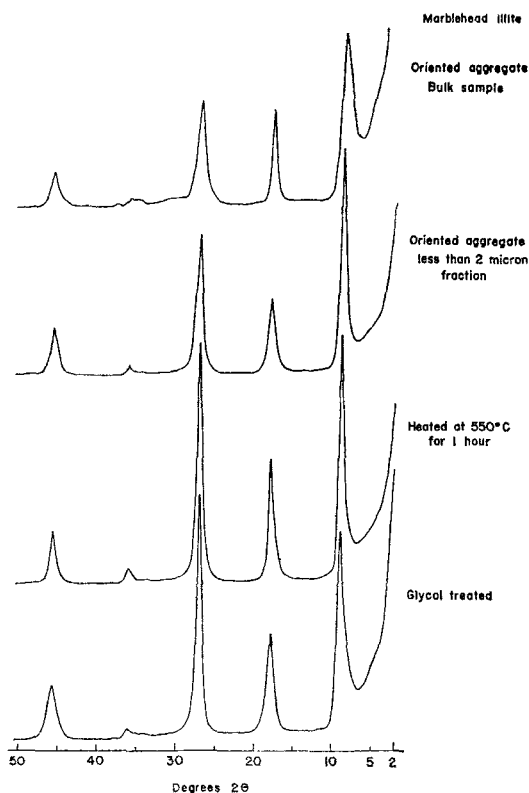
FIG. 3. Diffraction traces, Marblehead illite.

determined from chemical analysis is a further indication that the amount of mixed-layer material present is slight.

The Rock Island traces (Fig. 4) indicate an essentially pure well-crystallized 10Å material. Heat treatment does not affect the relative intensities or positions of the basal reflections. Glycol treatment produces only a slight feathering on the low-angle side of the first basal reflection. This may be attributed to only a slight amount of expandable mixed-layer material present, also probably as little as 5 per cent.

Fithian illite, which has been described as A.P.I. reference clay no 35, contains a greater amount of expandable mixed-layer material (Fig. 5). The asymmetry of the first basal reflection, the definite sharpening of the basal reflections upon heat treatment and the development of an expandable phase upon saturation with ethylene glycol indicate about 10–15 per cent mixed-layer material in the Fithian illite sample. The decreased crystallinity of the material appears to be indicated by the more diffuse nature of the basal reflections.
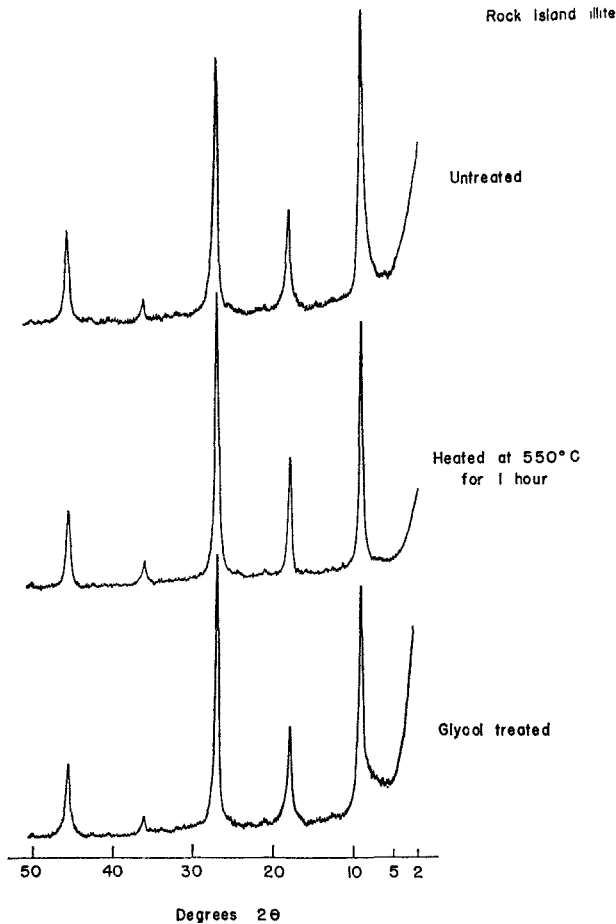
FIG. 4. Diffraction traces, Rock Island–oriented aggregates.

The X-ray diffraction traces of untreated, heat-treated, and glycol-saturated "Grundite" (Fig. 6) show the presence of illite and mixed-layer material. Sharpening of the basal reflections upon heating and the appearance of an expandable component upon exposure to ethylene glycol show the presence of approximately 25–30 per cent of mixed-layer material in the sample.

In summary, the diffraction traces of the $<2\mu$-oriented aggregates, both in the natural state and after undergoing heat and glycol treatments, indicate that the 10Å clay materials investigated may vary considerably in crystallinity and the amount of mixed-layer material that may be present. Beavers Bend
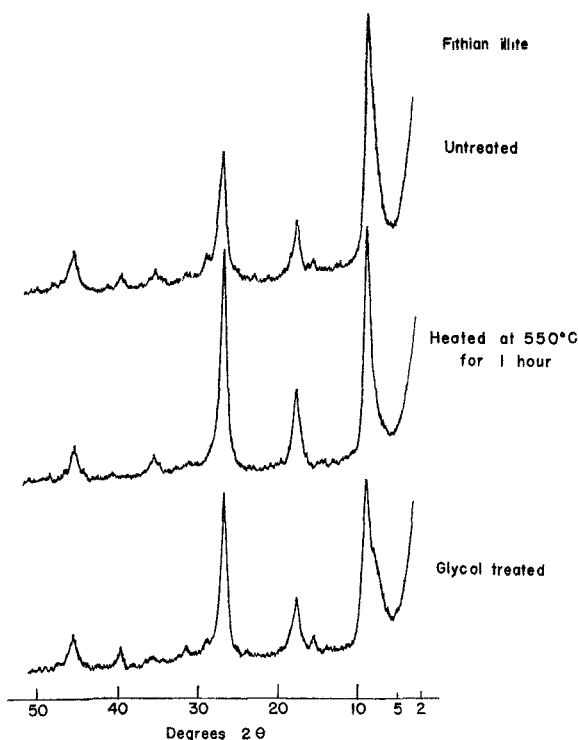
FIG. 5. Diffraction traces, Fithian–oriented aggregates.

illite has no mixed-layer material that can be ascertained by X-ray diffraction. The Marblehead and Rock Island samples have only slight amounts of mixed layering present—on the order of 5 per cent or less. Fithian illite appears to be transitional in that the amount of mixed layering is moderate, with most of the diffraction apparently produced by the 10Å component. As an extreme in this series of samples, "Grundite" has approximately 25–30 per cent of mixed layering apparent. Again, however, most of the diffraction intensity may be attributed to the 10Å component, and even in this case there are substantial packets consisting of 10Å members only.

The degree of crystallinity of the illite appears to decrease with an increase in the amount of mixed layering present in the samples. This can be assumed to result directly from the increase in disordering, which occurs as mixed layering increases. The polymorphic type, which was noted previously for the samples, also follows the same trend; as disorder increases, determination becomes more difficult and apparently progresses from $2M_1$ toward 1Md.

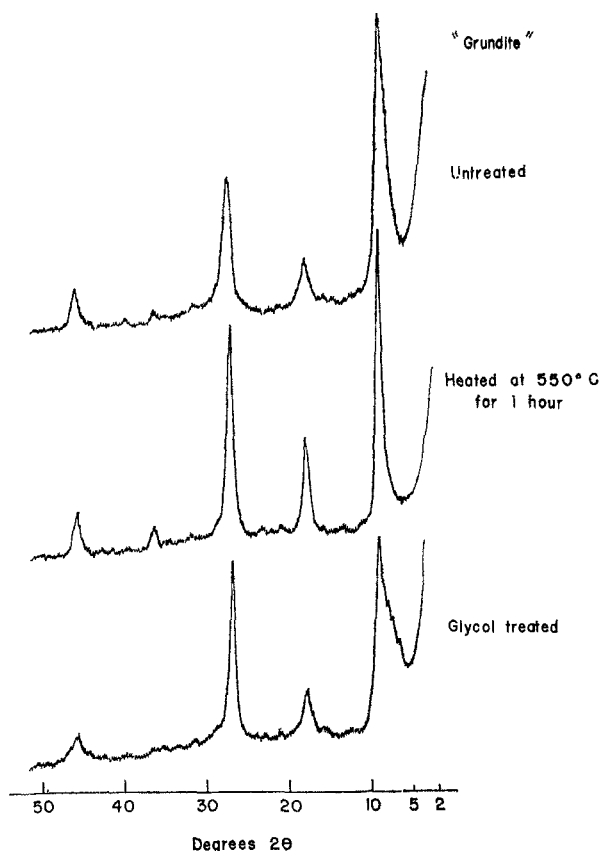The presence of twelve basal reflections in the X-ray analyses of extremely

FIG. 6. Diffraction traces, "Grundite"–oriented aggregates.

well-oriented aggregates of $<2\mu$ material for each sample allowed the calculation of one-dimensional Fourier summations. The one-dimensional structural plots derived from these calculations are shown in Fig. 7. These structural plots are based upon the structural formulae calculated from chemical analyses of these materials; the agreement index for each sample has been computed as a test of validity for each structural determination. In all cases, the agreement indices of the structural plots of the illite samples range from 0.10–0.15 for calculated structures based upon the Marshall (1949) procedures with the addition of sufficient H_2O in interlayer space to equal 2.0 per unit cell. When the calculated structure derived from computation of the structural formulae according to Brown and Norrish (1952) was used for the determination of agreement indices, the resultant values ranged from 0.19–0.27 for the illite samples. Comparison was, therefore, made on the basis of the adjusted
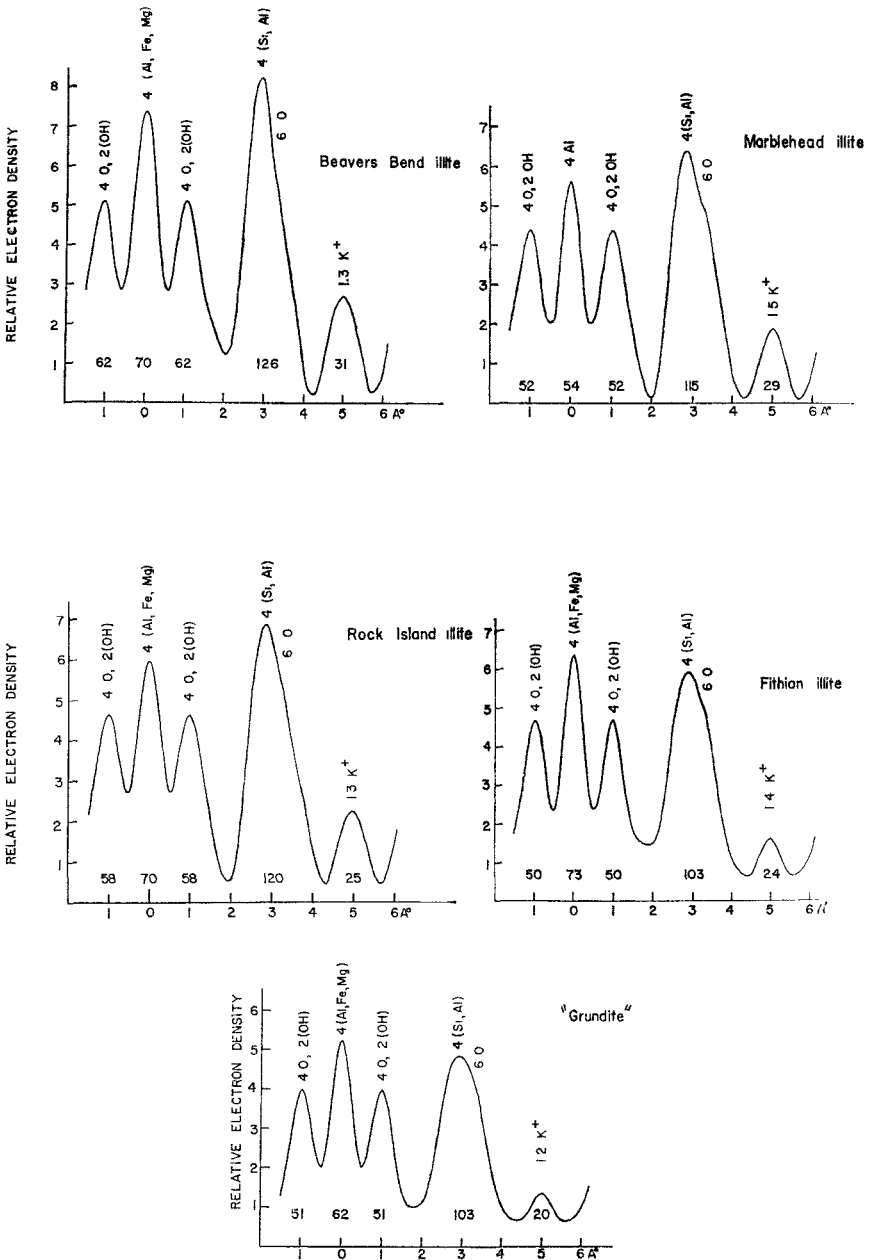
FIG. 7. One-dimensional structural projections.

Marshall calculations for structural representation of the illite samples of this investigation.

In Fig. 7, the one-dimensional plots show well-resolved maxima that appear to be representative of the atomic constituents at each structural position in the silicate portion of the structure. The electron density maximum resulting from the scattering power of the hexagonal or ditrigonal oxygen plane is less prominently resolved for "Grundite" than the other samples.

The density maxima corresponding to the interlayer constituents in each of the samples correlate with the occupation of these interlayer sites as determined from chemical analysis. In each structural projection, the cationic total for the interlayer sites has been expressed in terms of potassium.

It would appear that the most prominent feature of these electron density projections is the relationship of the interlayer maxima for each of the samples analyzed to a similar interlayer maximum for well-crystallized dioctahedral muscovite. The relative values of the interlayer occupants for all the samples show a variation in the abundance of cations present in interlayer co-ordination and confirm the deficiency of potassium in illite in respect to well-crystallized muscovite. The structural analyses and the agreement indices computed as a comparison to the calculated structures of the illite samples according to Marshall (1949) or Brown and Norrish (1952) have not been adequate to prove the presence of water or of hydronium ions in interlayer positions in the samples in this investigation. They denote only that the 10Å material, whether in a pure sample or in one in which mixed layering is present, is, in fact, deficient in potassium when compared to well-crystallized dioctahedral muscovite, but they do not permit observation on whether the interlayer electron densities ever clearly exceed those commensurate with the potassium contents.

DIFFERENTIAL THERMAL ANALYSES

Differential thermal analyses were made using the fractionated $<2\mu$ material of each of the clays studied. The clay, which had been dried at 80°C, was ground to pass a <200 mesh for analysis.

All five samples (Fig. 8) show an initial endothermic reaction between 100°–200°C, generally considered to be the result of loss of interlayer water.

Both the Beavers Bend and Rock Island samples give a second endothermic reaction between 500°–600°C, which is characteristic of the nonexpandable three-layer type of clay minerals. Neither of these samples gave a third endothermic reaction above 900°C. Such a third endotherm, when present, is generally attributed to the final destruction of the lattice that precedes the formation of a high temperature spinel phase (Grim and Rowland, 1942). Since the analyses do not show an exothermic peak, the formation of spinel may occur above the limit of the analysis—above 1000°C. Early formation of a glassy phase may have been facilitated by the presence of potassium.

The second endothermic reaction for Marblehead illite lies between 600°–
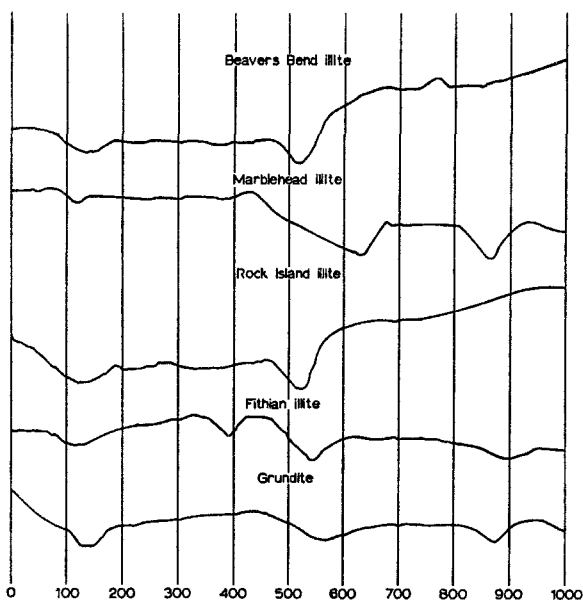
FIG. 8. Differential thermal analyses.

700°C, more indicative of expandable than nonexpandable clay minerals. However, since X-ray diffraction data indicate that the sample is relatively free of expandable material, this reaction may be attributed to the crystalline nature of the mineral. A third endotherm occurring between 800°–900°C combined with a slight exothermic reaction are indications of the development of a high temperature phase.

Fithian illite and "Grundite" show a normal curve for the three-layer, essentially nonexpandable clay minerals. Endothermic peaks occur between 100°–200°C, 500°–600°C, and 800°–900°C. The Fithian sample also shows an endothermic reaction around 400°C, most probably caused by ferric iron hydrates that may be present.

DISCUSSION

The chemical data for a series of illite samples containing from 0 to approximately 30 per cent mixed layering indicate that: (1) illite is deficient in interlayer potassium in comparison to well-crystallized dioctahedral muscovite, and (2) variability exists in the tetrahedral, octahedral, and interlayer structural positions among the illite samples investigated.

X-ray diffraction data indicate that most of the diffracting power is derived from a coherent silicate structural network of illitic nature in the mixed-layer

assemblages. One-dimensional structural projections derived from this diffraction data confirm this supposition and illustrate the nature of the illitic structure as predominantly dioctahedral with less potassium per unit cell than well-crystallized dioctahedral muscovite.

It is felt, therefore, that the term *illite* is valid as a group name for the 10Å nonexpanding clay material in argillaceous sediments as originally proposed, and that mixed-layer assemblages may then be best described as illite–montmorillonite, illite–vermiculite, etc, mixed-layer structures.

ACKNOWLEDGMENT

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